

Dioxirane Epoxidation of Alkenes

Waldemar Adam, Universität Würzburg, Würzburg, Germany

Chantu R. Saha-Möller, Universität Würzburg, Würzburg, Germany

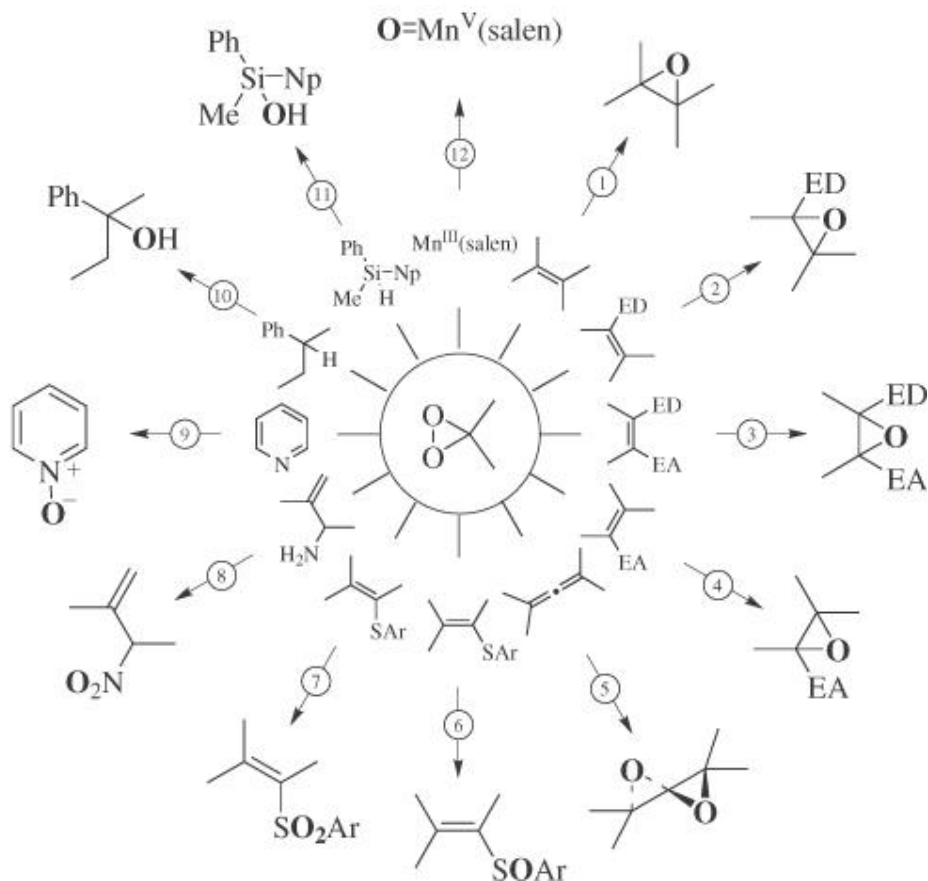
Cong-Gui Zhao, Universität Würzburg, Würzburg, Germany

1. Introduction

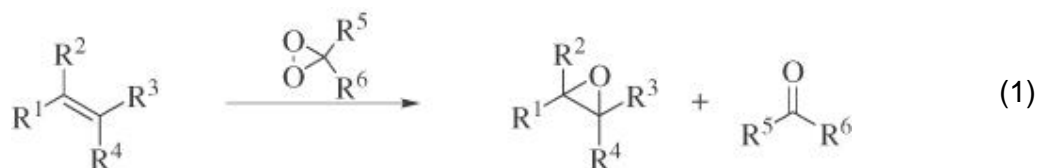
An ideal oxidant should be highly reactive, selective, and environmentally benign. It should transform a broad range of substrates with diverse functional groups, preferably under catalytic conditions, and be readily generated from commercially available and economical starting materials. Of course, such an ideal oxidant has not yet been invented; however, the dioxiranes, which have risen to prominence during the past few decades, appear to fulfill these requirements in many respects. These three membered ring cyclic peroxides are very efficient in oxygen transfer, yet very mild toward the substrate and product. They exhibit chemo-, regio-, diastereo-, and enantioselectivities, act catalytically, and can be readily prepared from a suitable ketone (for example, acetone) and potassium monoperoxysulfate ($2\text{KHSO}_5 \cdot \text{K}_2\text{SO}_4 \cdot \text{KHSO}_4$, Caroate[®], Oxone[®], or Curox[®]), which are low-cost commercial bulk chemicals. Throughout the text we shall use KHSO_5 to specify this oxygen source, rather than refer to one of the commercial trade names.

Isolated dioxiranes (as solutions in the parent ketones) perform oxidation under strictly neutral conditions so that many elusive oxyfunctionalized products have been successfully prepared in this way for the first time. Epoxidations, heteroatom oxidations, and X-H insertions constitute the most investigated oxidations by dioxiranes. An overview of these transformations is displayed in the rosette of Scheme 1. These preparatively useful oxidations have been extensively reviewed during the last decade in view of their importance in synthetic chemistry. (1-12)

Scheme 1. An Overview of Dioxirane Oxidations (Np = 1-Naphthyl, ED = Electron Donor, EA = Electron Acceptor)

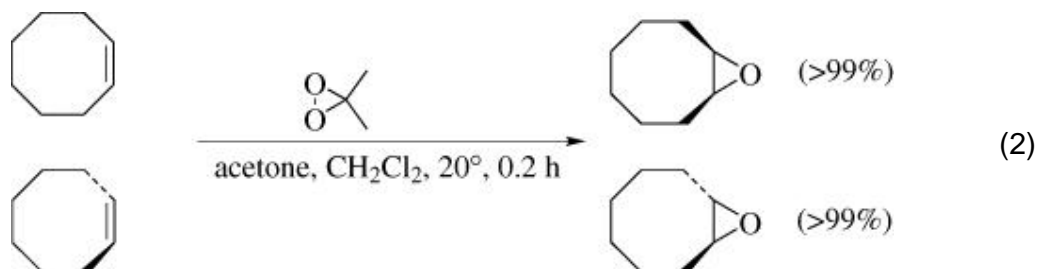


The present review deals mainly with the epoxidation of carbon-carbon double bonds [π bonds in simple alkenes and with these electron donors (ED), electron acceptors (EA), and with both ED and EA; examples 1–4 in the rosette] with either isolated or in situ generated dioxiranes (Eq. 1). In view of the vast amount of material on alkene oxidation (ca. 400 references), the epoxidation of the double bonds in cumulenes (allenes, acetylenes) and arenes is covered in a separate chapter, together with the oxidation of heteroatom functionalities (nonbonding electron pairs; examples 6–9 in the rosette), X-H insertions (σ bonds; examples 10–11 in the rosette), and transition-metal complexes (example 12 in the rosette).



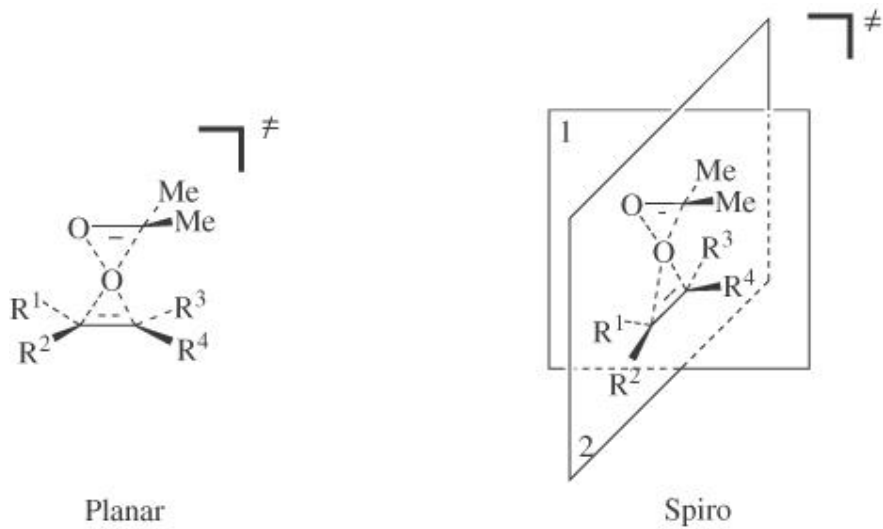
2. Mechanism

Dioxirane epoxidation proceeds strictly with retention of the initial alkene configuration. An impressive and mechanistically valuable example is the cis/trans pair of cyclooctenes (Eq. 2), of which the cis diastereomer leads exclusively to the cis epoxide and the trans congener to the trans epoxide in high yields. (13, 14)

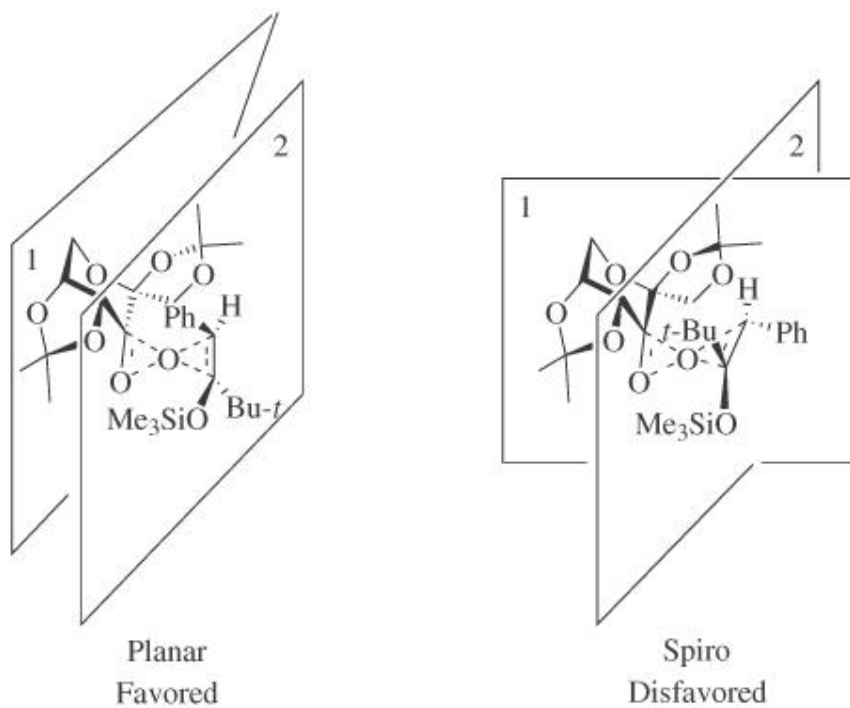
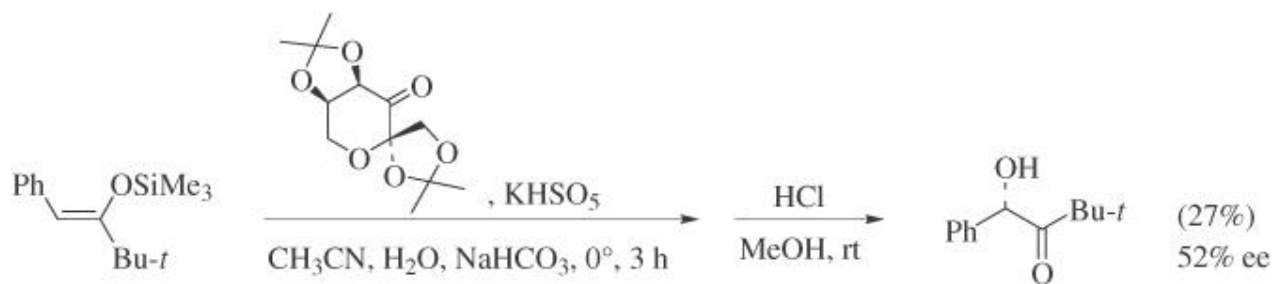


On the basis of the relative reaction rates of cis and trans open-chain alkenes (cis alkene faster than trans alkene by a factor of ten) in the dimethyldioxirane (DMD) oxidation, a spiro transition state was suggested, (15, 16) which is also supported by theoretical work. (17-23) In this oxygen transfer, the plane of the peroxide ring is oriented perpendicular to, and bisects the plane of the π system in the olefin substrate (Scheme 2, right). For this preferred geometry, DMD approaches the cis olefin from the unsubstituted side, which avoids steric interaction between the methyl groups and the alkyl substituents of the double bond. The concerted spiro transition-state structure also explains the results of enantioselective epoxidations by optically active dioxiranes. (24, 25) An exception is given in Scheme 3, for which the planar transition-state structure is favored over the spiro alternative. (26)

Scheme 2. Planar and Spiro Transition-State Structures for the DMD Epoxidation of Alkenes

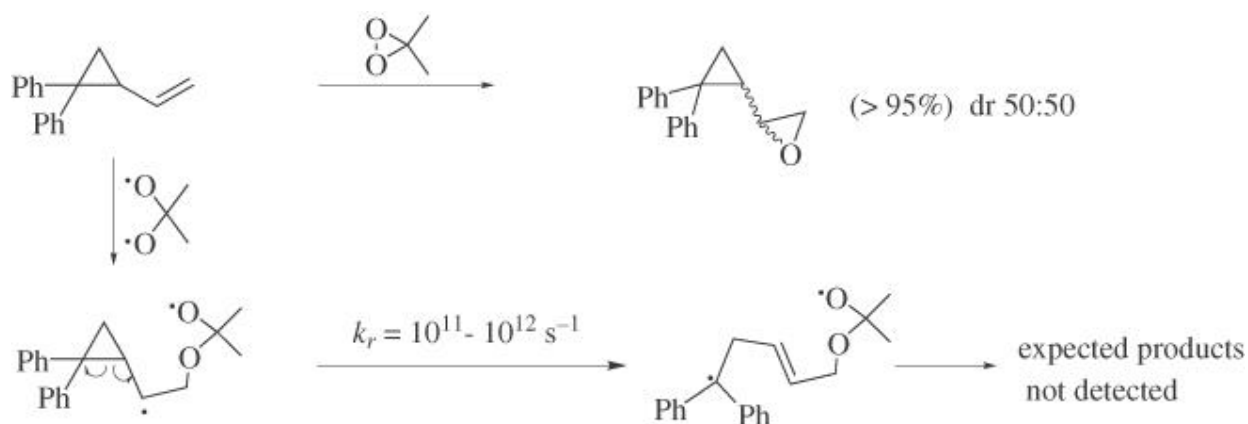


Scheme 3. Planar and Spiro Transition-State Structures



The fact that no cis/trans isomerization is observed in the oxygen transfer speaks against the earlier proposed diradical mechanism. (5, 27) Although the high stereoselectivity of DMD epoxidations may be accommodated by proposing much faster collapse of the resulting intermediary diradical than isomerization through bond rotation, it would be difficult to rationalize the established steric effects (i.e., cis olefins react faster than the trans isomers). (15, 16) For the diradical mechanism one would expect that the relative rates of cis alkenes and trans alkenes should be nearly the same for such an end-on attack. Moreover, as stated above, epoxidation of trans-cyclooctene with DMD yields solely the corresponding trans epoxide (Eq 2). (13, 14) In view of the high strain energy in trans-cyclooctene (23.2 kcal/mol), (28) cis/trans-isomerization would be expected, should the diradical intermediate intervene. (13) Furthermore, the lack of cyclopropylcarbinyl rearrangement in the epoxidation of 1-vinyl-2,2-diphenylcyclopropane by DMD (Scheme 4) as an ultra-fast radical clock ($k_r^{25} \gg 5 \times 10^{11} \text{ s}^{-1}$) clearly speaks against the involvement of radical intermediates in DMD epoxidations. (13)

Scheme 4. Radical-Clock Probe for the Mechanism of DMD Epoxidation



Despite this convincing experimental and theoretical evidence in favor of the concerted oxenoid mechanism for dioxirane epoxidations, the appreciable amount of allylic oxidation of α -methylstyrene to 2-phenylpropenal and 2-phenylpropenal by DMD has been interpreted in terms of a radical mechanism. (29, 30) However, when radical species are scrupulously avoided by operating in the presence of molecular oxygen (inhibitor), keeping the reaction temperature below 50° (no homolytic decomposition of the DMD), and avoiding radical-generating solvents such as BrCCl_3 , the DMD oxidation of α -methylstyrene gives exclusively the expected epoxide. (13)



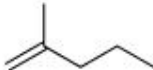

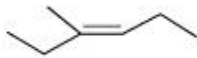
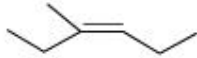
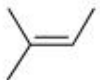
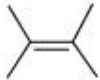
3. Scope and Limitations

With dioxiranes, either isolated or in situ generated, different types of alkenes [i.e., unfunctionalized, electron-rich (with electron donors) and electron-poor (with electron acceptors)] have been successfully epoxidized. As a solution in acetone, DMD (isol.) is the most often used dioxirane owing to its convenient preparation and low cost. While methyl(trifluoromethyl)dioxirane (TFD) is much more reactive than DMD, applications are limited because of the high cost and volatility of trifluoroacetone. With DMD (isol.), the scale of the reaction is usually limited to no more than 100 mmol, since the DMD solution in acetone is quite dilute (ca. 0.08 M). In the case of TFD (ca. 0.6 M), the prohibitive cost of trifluoroacetone precludes scales >10 mmol. When a large-scale preparation is desired, the in situ mode [DMD (in situ)] is recommended, for which both biphasic (31-34) and homogeneous (35, 36) media are available. Since the in situ oxidations are carried out in aqueous media, the substrate and the oxidized products must be resistant to hydrolysis and persist at temperatures above 0°. The in situ mode can also be carried out by applying a catalytic amount of ketone, (37-40) which is especially important for enantioselective epoxidations (see the Section on Enantioselectivity), since the optically active dioxiranes cannot be readily isolated.

3.1. Epoxidation of Unfunctionalized Alkenes

Some typical examples are collected in the rosette of Scheme 5. The epoxidation of unfunctionalized alkenes by dioxiranes, especially by DMD, has been mainly studied for elucidation of the reaction mechanism. The degree and pattern of alkyl substitution on the double bond control the reaction rate, with the more highly substituted alkenes being more reactive. The reactivity order is tetra > tri > di > mono (Table A), as is generally observed for electrophilic reagents. (15)

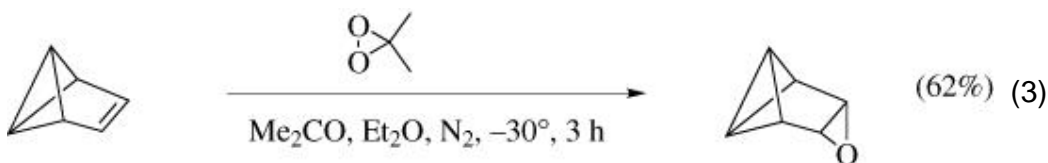
Scheme 5. Dioxirane Oxidation of Unfunctionalized Alkenes

Alkene	k_{rel}
	0.5
	1.0 ^a
	4.6
	8.5
	16.1
	24
	36
	106

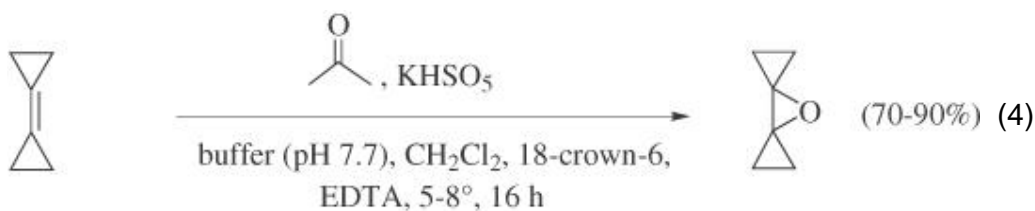
^a The absolute rate constant is $0.067 \pm 0.001 \text{ M}^{-1}\text{s}$

Steric factors also play an important role (e.g., cis alkenes are more reactive than the corresponding trans isomers). (15, 16) An important exception is the cis/trans-pair of the cyclooctenes (Eq. 2), for which the trans isomer reacts about 100 times faster than the cis isomer because of ring strain. (13, 14) Thus, quite generally, strained double bonds display the highest reactivity toward DMD. This fact is valuable for synthetic purposes since essentially quantitative yields of epoxides can be readily obtained with either isolated or in situ generated dioxiranes. In the latter reaction, the epoxide must resist hydrolysis. An excellent example is the epoxidation of benzvalene with DMD (isol.) at -30°

(Eq. 3), which affords a rather labile epoxide in good yield. (41) This constitutes the most important advantage of DMD (isol.) since the oxidation is performed under strictly neutral and nonhydrolytic conditions, at low temperatures, with acetone as the only byproduct.



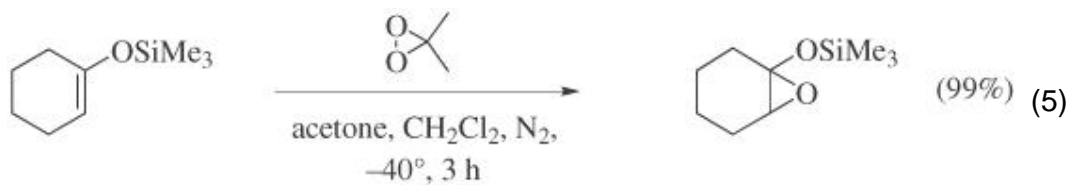
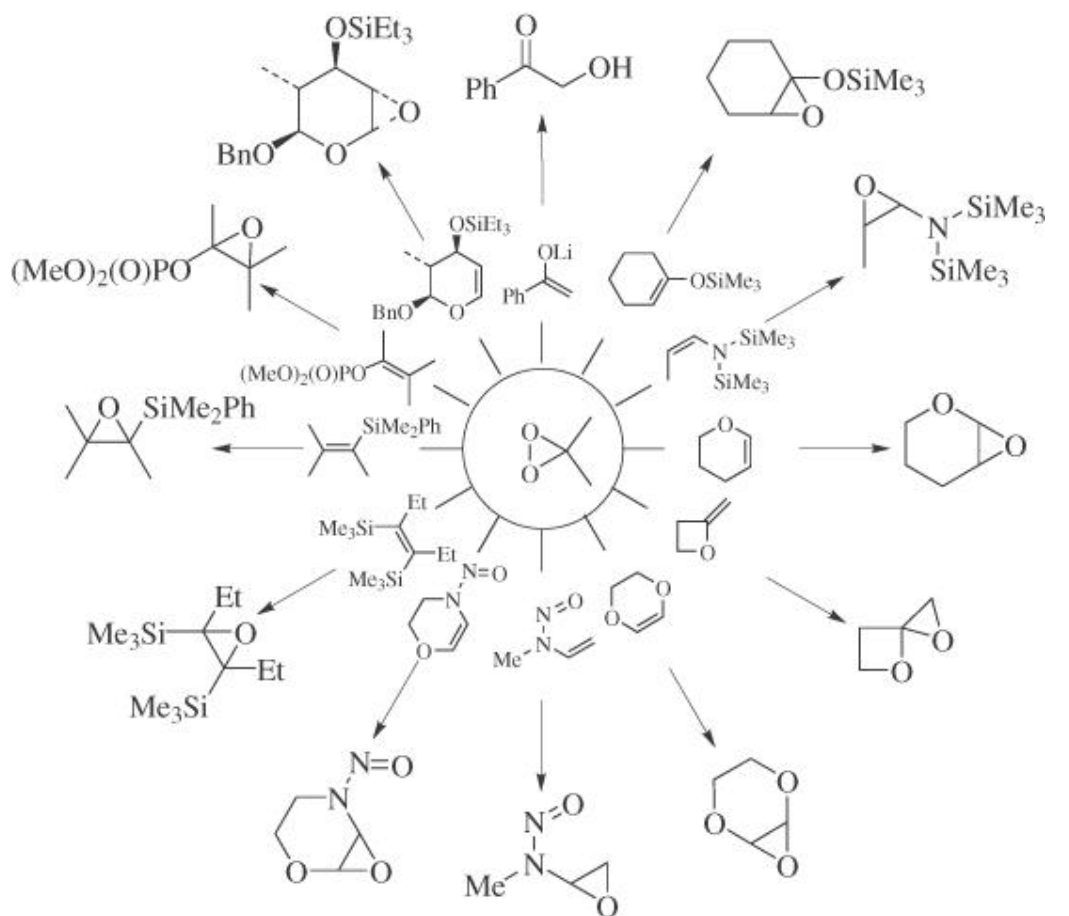
Acid-sensitive epoxides can also be prepared by applying the in situ mode, but the pH of the medium must be carefully controlled with buffers. For example, the oxaspiropropane is obtained by epoxidation of the corresponding cyclopropylidenecyclopropane (Eq. 4). (42) Usually such highly strained and hydrolytically labile oxaspiropropanes readily rearrange to the respective cyclobutanones. (42, 43)



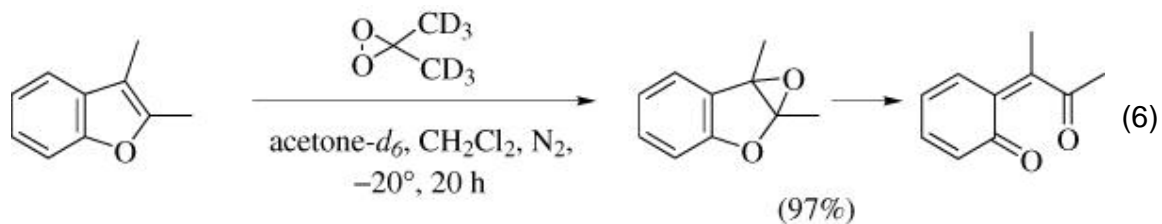
3.2. Epoxidation of Electron-Rich Alkenes

Electron-rich alkenes are usually more reactive toward oxidation than simple alkenes, and the corresponding epoxides are generally much more labile toward hydrolysis and thermolysis. With DMD (isol.), a broad variety of such epoxides has been prepared in essentially quantitative yields, and even excessively labile examples have been characterized spectroscopically (Scheme 6). For example, the DMD epoxidation of silyl enol ethers at subambient temperature affords the corresponding epoxides in quantitative yields (Eq. 5). (44, 45) These epoxides have been proposed as intermediates in the peracid oxidation of silyl enol ethers to α -hydroxy ketones (the Rubottom reaction). (46) Indeed, when the in situ mode is employed, the corresponding α -hydroxy ketones are obtained directly. (35)

Scheme 6. Dioxirane Oxidation of Electron-Rich Alkenes

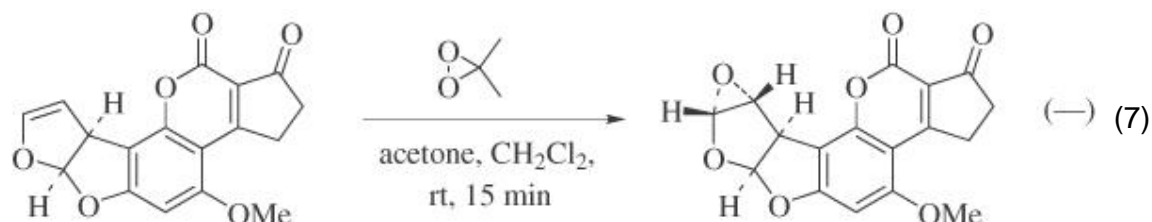


A labile epoxide is derived from 2,3-dimethylbenzofuran (Eq. 6), which even at -20° rearranges to the *o*-quinomethide. (47-49) To characterize this epoxide by ^1H NMR spectroscopy, the fully deuterated DMD- d_6 (isol.), prepared in acetone- d_6 , was employed for the oxidation, and the epoxide was detected at -78° . (47) This emphasizes the importance and convenience of the isolated dioxiranes for the



synthesis of exceedingly sensitive substances. Indeed, the epoxide of 2,3-dimethylfuran, prepared by the epoxidation of the furan with DMD- d_6 (isol.), could not be detected even at -100° , and only the rearrangement product hex-3-ene-2,5-dione was observed. (50)

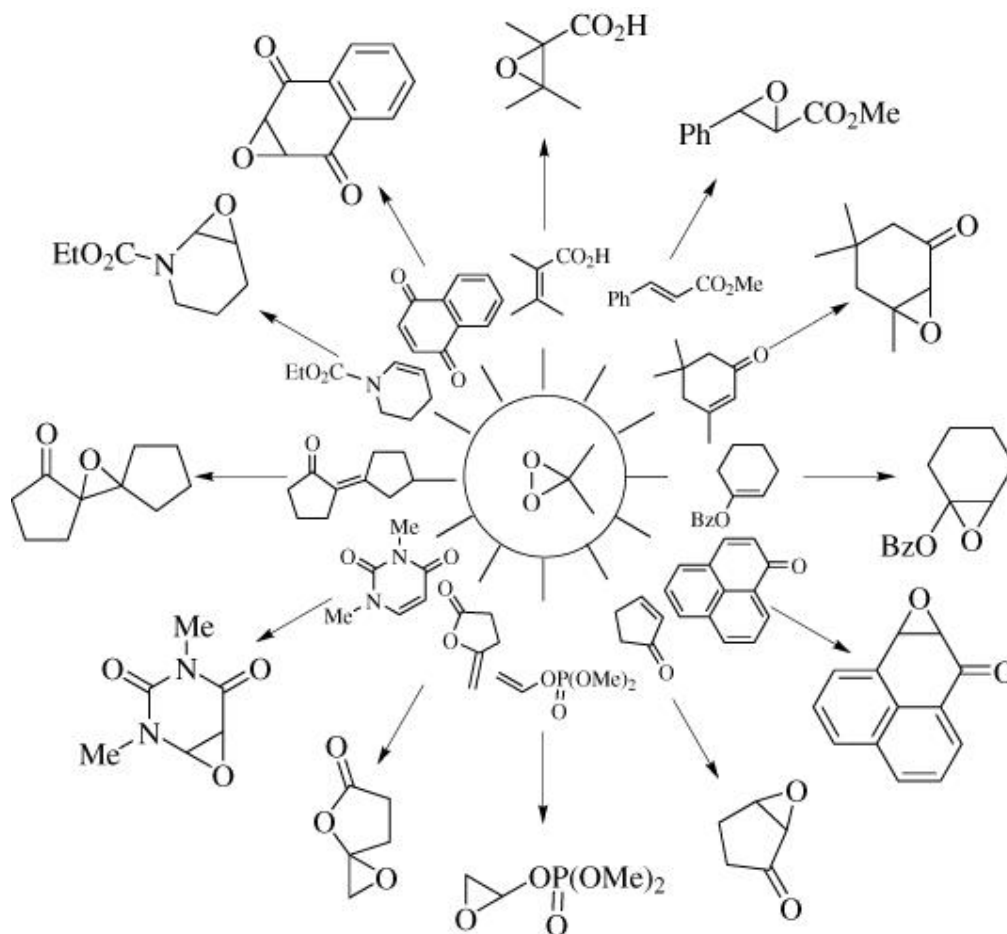
The 8,9-epoxide of aflatoxin B is a well-known carcinogen; however, because of its sensitivity toward hydrolysis, numerous efforts to prepare this epoxide failed. The synthesis is readily accomplished (no yield given) with DMD (isol.) at room temperature (Eq. 7). (51) Once this labile epoxide was available as a pure substance, the mutagenicity caused by its reaction with DNA was unequivocally confirmed.



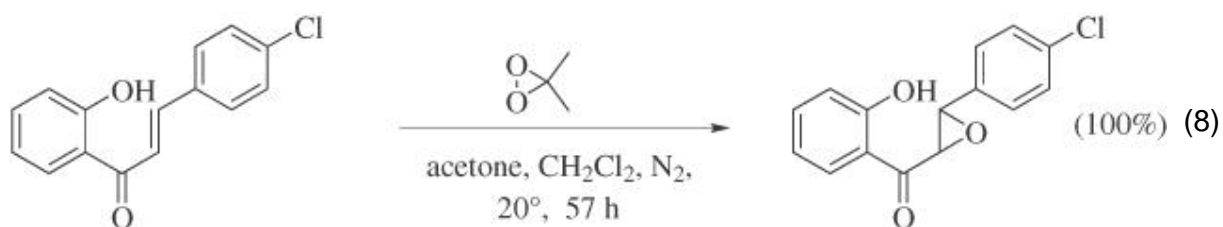
3.3. Epoxidation of Electron-Poor Alkenes

Dioxirane oxidation of electron-poor alkenes (Scheme 7) offers general access to the corresponding epoxides, which are usually difficult to prepare with peracids, or require the use of basic conditions as in the Weitz-Scheffer reaction. (52) Since the dioxirane is an electrophilic oxidant and these alkenes are electron-poor substrates, the reaction usually needs much longer time (up to several days) compared to that of electron-rich alkenes, which are oxidized usually within minutes. For very recalcitrant electron-poor substrates, a large excess of the dioxirane and elevated temperatures (heating at reflux in acetone, ca. 60°) may be needed to obtain good conversions. Nevertheless, the yields may be very high, since the product epoxides resist hydrolysis and thermolysis. For convenience, DMD (in situ) is employed; for very unreactive electron-poor alkenes, the much more reactive TFD (in situ) may have to be used.

Scheme 7. Dioxirane Oxidation of Electron-Poor Alkenes

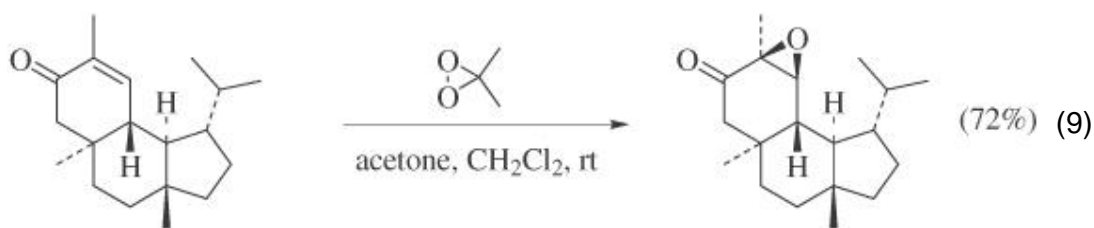


The epoxides of a number of α , β -unsaturated aryl ketones (chalcones) (53) have been prepared in excellent yields with DMD (isol.). An illustrative example is shown in Eq. 8. (53) This example is notable because the phenolic group does not require protection in this epoxidation, which hitherto had not been possible with other oxidants.

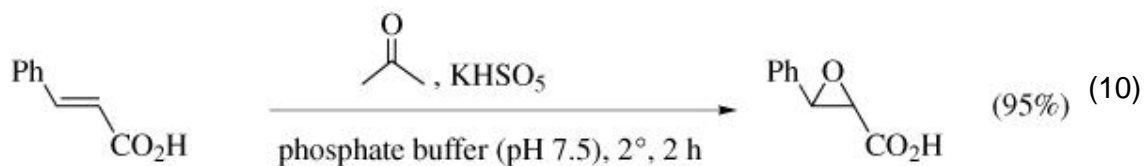


Numerous examples have been documented in the literature to show the usefulness of this method. For example, the dioxirane oxidation of an α , β

-unsaturated ketone in Eq. 9 is the key step in the total synthesis of verrucosan-2 β -ol and homoverrucosan-5 β -ol. (54)



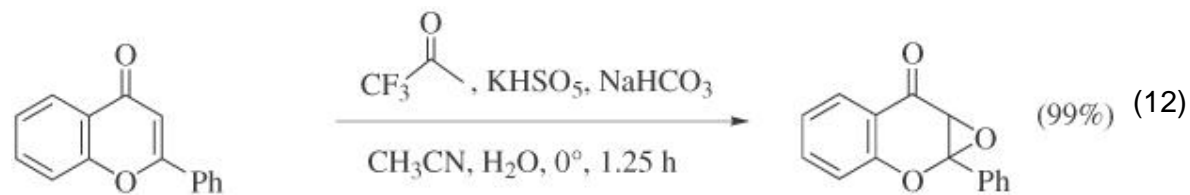
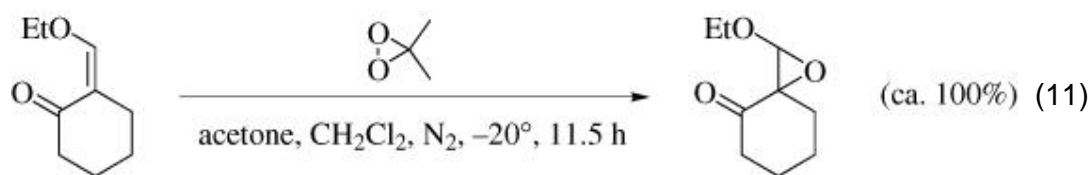
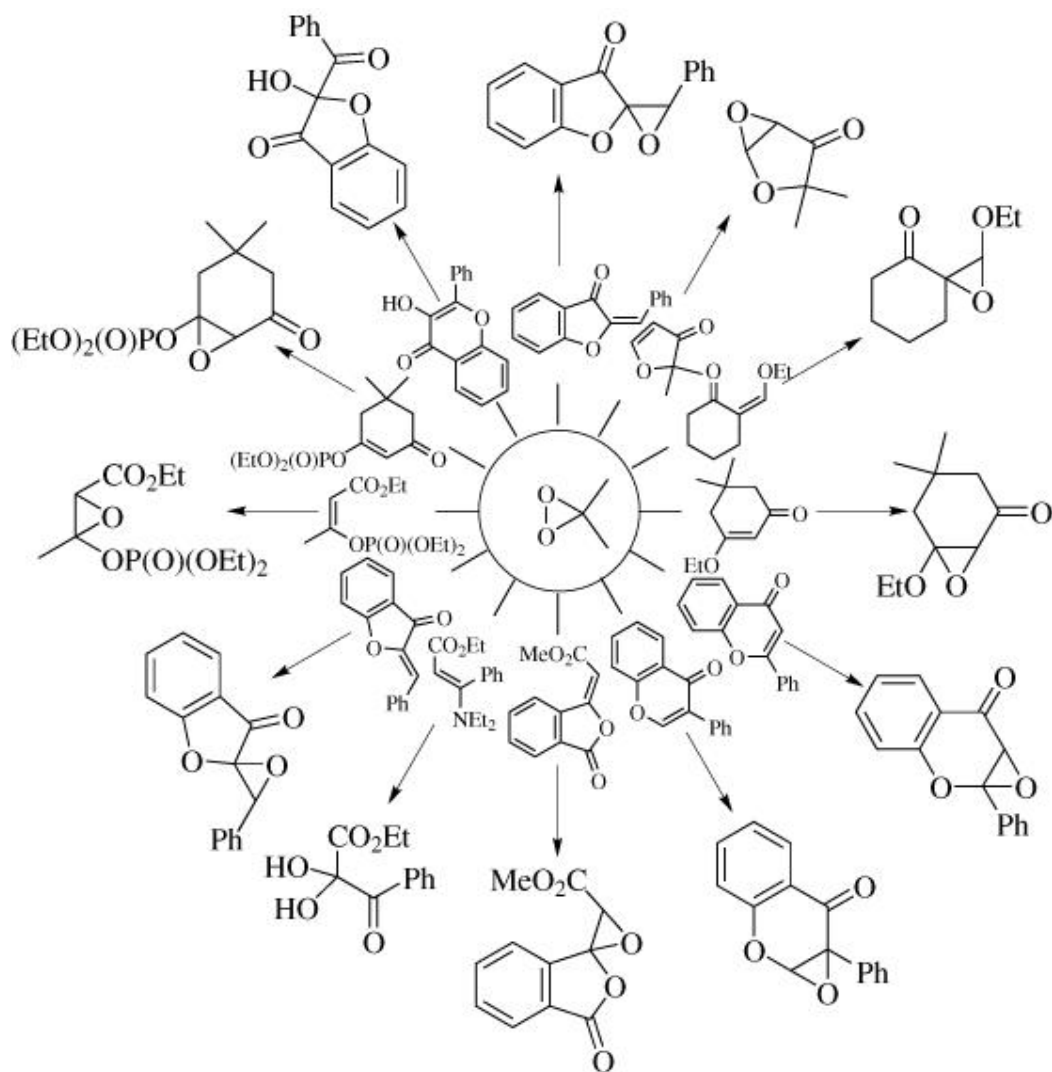
The in situ mode is quite suitable for such electron-poor substrates, since the epoxides usually survive the aqueous conditions, longer reaction times, and higher temperatures. (55) A good example is the oxidation of *trans*-cinnamic acid by DMD (in situ), which affords the epoxide in nearly quantitative yield (Eq. 10). (31)



3.4. Epoxidation of Alkenes with both Electron Donors and Electron Acceptors

The reactivity of the substrates in Scheme 8 depends on the nature of the substituents, but usually they behave more like the electron-poor substrates, so that longer reaction times, a large excess of DMD, and elevated temperatures ($<60^\circ$) may be required for complete conversion. β -Alkoxy-cyclohexenones (Eq. 11), (56) aurones, (57) flavones, (58, 59) and isoflavones (57, 60) are among the most studied substrates of this type. Some of these epoxides, which constitute valuable building blocks in natural product synthesis, have been made available for the first time by dioxirane oxidation. As an example of the in situ mode of oxidation, flavone has been epoxidized by TFD (in situ) in excellent yield (Eq. 12). (35)

Scheme 8. Dioxirane Oxidation of Alkenes with Both Electron Donors and Acceptors

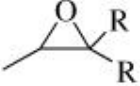


3.5. Chemoselectivity

Chemoselectivity is a crucial feature in planning a synthetic sequence, in which a key step may utilize an epoxidation by dioxiranes on a multifunctionalized substrate. Despite the vast number of oxidations (see Tables I–V) that have already been performed with dioxiranes over the last 20 years, no deliberate efforts to test functional-group compatibility have been made, even for difunctionalized substrates. The study of such chemoselectivities would require determination of quantitative rates [e.g., as was done for the alkyl-substituted alkenes (Table A)], but such data are not available.

Based on the data in Tables I–V and our personal experience, we have compiled a chart on the tolerance of the more common functional groups in dioxirane epoxidations (Table B). These trends are based merely on the conversion of the substrate and/or the yield of the oxidation product, rather than on hard kinetic data or competition experiments. Necessarily, the classification into “*compatible, moderately compatible, and incompatible*” categories of the functional groups (Table B) is approximate. Expectedly, exceptions must be reckoned with on account of possible electronic and steric effects in a particular substrate. Nevertheless, this compilation provides a useful qualitative guide on how to avoid undesirable misplannings in a synthetic application.

Table B. Functional-Group Tolerance to Epoxidation^a

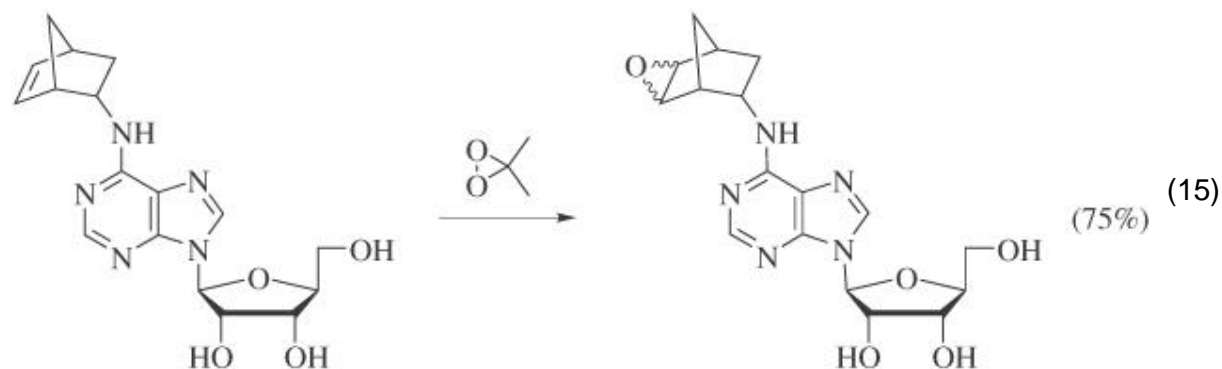
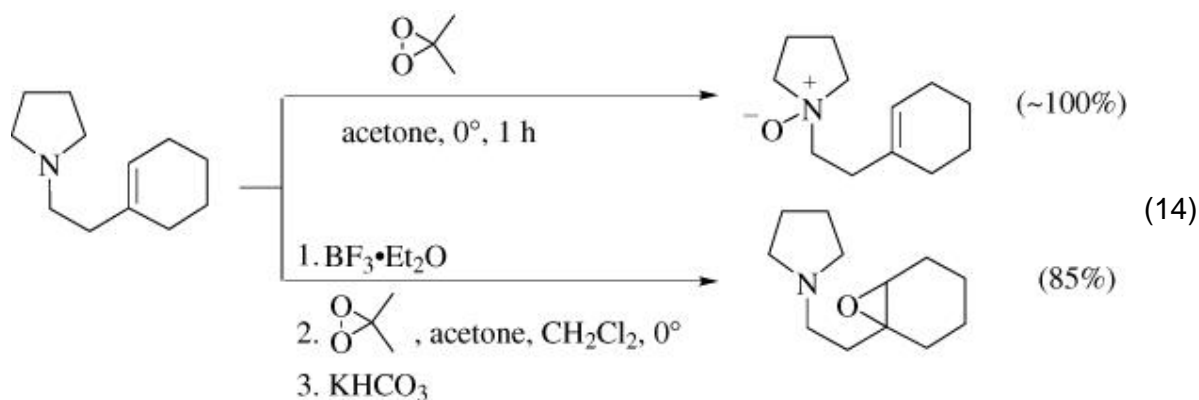
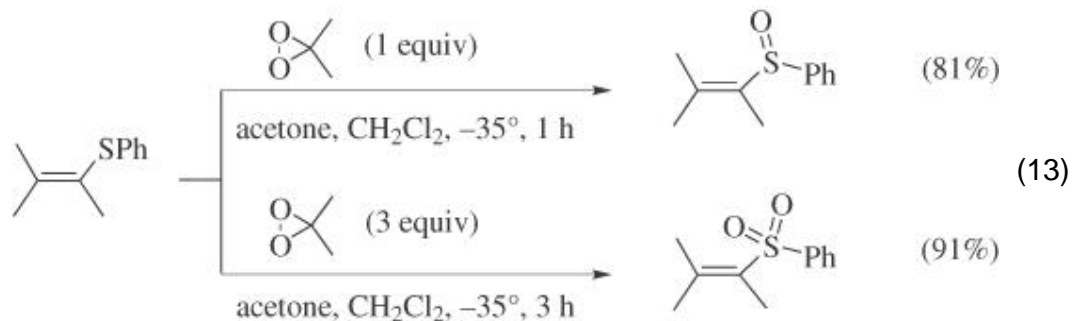
<i>compatible</i>	<i>moderately compatible</i>	<i>incompatible</i>
$-\text{CO}_2\text{H}; -\text{CO}_2\text{R}$	$\text{>C=NH}; \text{>C=NR}$	$-\text{PR}_2$
$-\text{CONH}_2; -\text{CONR}_2$	>C=N-NR_2	$-\text{SH}; -\text{SR}$
$-\text{COR}$	$\text{>C=N-OH}; \text{>C=N-OR}$	$-\text{SSR}$
$-\text{C}\equiv\text{N}$	$\text{>C}=\bullet=\text{NR}$	$-\text{NHNHR}$
$-\text{NH}_3^+; -\text{NR}_3^+$	$\text{>C}=\bullet=\text{O}$	$-\text{NH}_2; -\text{NHR}; -\text{NR}_2$
$-\text{SO}_2\text{R}$	$\text{>C}=\bullet=\text{CR}_2$	enolates
$-\text{SO}_3\text{H}; -\text{SO}_3\text{R}$	$-\text{N}=\text{C}=\text{S}; -\text{N}=\text{C}=\text{O}$	$\text{C}=\text{C}-\text{SR}$
$-\text{PO}(\text{OR})_2$	electron-rich arenes ^b	$\text{C}=\text{C}-\text{NR}_2$
$-\text{NO}_2$	polycyclic arenes ^c	$\text{C}=\text{C}-\text{OSiR}_3$
	heteroarenes ^d	$\text{C}=\text{C}-\text{OR}$
$-\text{O}_2\text{H}; -\text{O}_2\text{R}$	$-\text{C}\equiv\text{C}-\text{R}$	$\text{C}=\text{C}-\text{O}_2\text{CR}$
$-\text{X}$ (F, Cl, Br)	$-\text{CHO}$	$\text{>C}=\text{PR}_3$
$-\text{SiR}_3$	$-\text{CH}(\text{R})\text{OH}$	$\text{>C}=\text{S}$
$-\text{SnR}_3$	$-\text{CH}(\text{R})\text{OR}'$	$\text{>C}=\text{N}_2$
electron-poor arenes ^e	$-\text{CH}(\text{R})\text{OAc}$	$-\text{N}=\text{O}$
	<i>N</i> -oxides ^f	heteroarenes ^g

^a R can be an alkyl or aryl group; the latter are usually less reactive. ^b With electron donating substituents such as alkyl, hydroxy, and alkoxy groups. ^c Naphthalene, phenanthrene, anthracene. ^d Thiophenes. ^e With electron-withdrawing substituents such as nitro, cyano, and carboxy groups. ^f These induce dioxirane decomposition.^{60a} ^g Pyridines, pyrroles, furans.

Another point that needs clarification on the compatibility trends in Table B is the fact that this chapter is restricted to epoxidations. Unquestionably, an effective discussion of functional group compatibility requires knowledge of how competitive the epoxidations are with the oxidations of heteroatom substrates, arenes and heteroarenes, acetylenes and cumulenes (heterocumulenes), alkanes and silanes, and even organometallic functionalities; however, all of these are dealt with in a separate chapter. Unfortunately, few reliable reactivity data are accessible for such dioxirane oxidations; thus, only a qualitative assessment of trends is feasible.

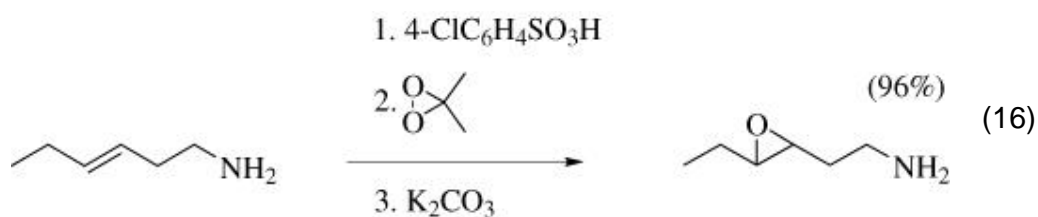
Provided we compare a set of substrates with similar electronic and steric features, the following reactivity order applies quite generally: heteroatom oxidation > epoxidation > CH insertion. Furthermore, among the heteroatoms, the general reactivity order P > S > N holds in their dioxirane oxidation [i.e., phosphines are more readily oxidized than sulfides (mercaptans), these in turn react faster than amines]. For epoxidations, the ease of oxidation follows the order alkenes > cumulenes > arenes > acetylenes. Arenes, particularly benzene derivatives, must be activated with hydroxy or alkoxy groups to achieve epoxidation, whereas *N*-heteroarenes undergo *N*-oxidation and thereafter are inert toward further reaction. For alkenes, the order is ED-C = C-ED>C = C-ED>C = C>EA-C = C-ED>C = C-EA>>EA-C = C-EA, in which the last substrate with two electron acceptors is unreactive (e.g., maleic and fumaric acids, esters, and nitriles are inert even toward the very reactive TFD). Finally, for CH insertions, the reactivity order is allylic > benzylic > tertiary > secondary > primary. These general directives should serve as a planning guide for synthesis; a few specific examples follow.

It should be evident from the preceding presentation of trends that certain functional group combinations are incompatible. For example, the epoxidation of a substrate with a double bond in the presence of a heteroatom functionality (sulfide or amine) is quite generally not feasible without protection. In the particular examples, the sulfide (Eq. 13) (61) is oxidized to the sulfoxide (even the sulfone is formed before the double bond is epoxidized), whereas a tertiary amine (Eq. 14), and

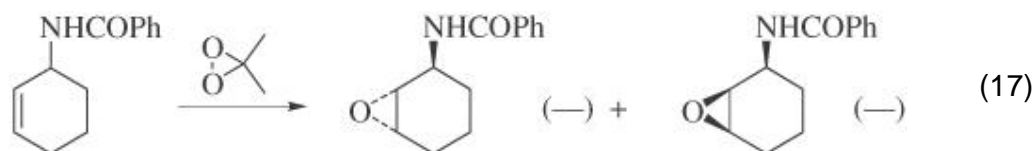


N-heteroarenes, e.g., pyridines, pyrimidines, etc., are transformed into their *N*-oxides. An exception is the adenosine-substituted norbornene displayed in Eq. 15, for which the purine functionality is sufficiently less prone toward *N*-oxidation that epoxidation dominates. (61a) This chemoselectivity also holds for enamines, which are preferentially oxidized to the corresponding *N*-oxides; (62, 63) exceptions are *N,N*-disilylenamides, which undergo epoxidation. (64) However, as illustrated for the pyrrolidine-substituted cyclohexene in Eq. 14, BF_3 complexation masks the amino functionality and the double bond is

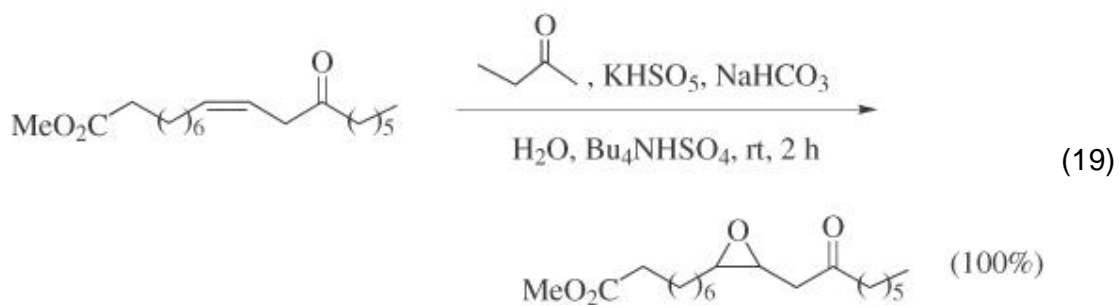
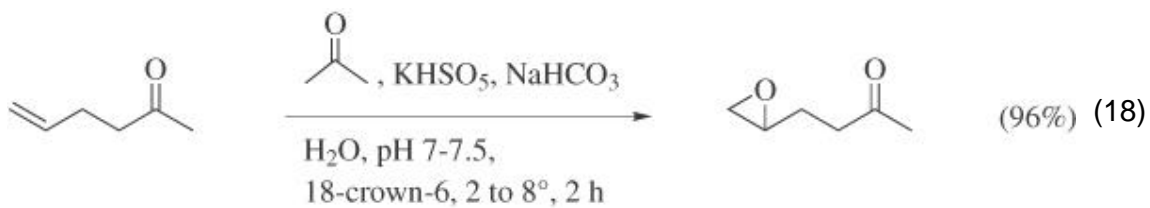
epoxidized without *N*-oxidation. (63) Alternatively, protonation may be employed for this purpose, since an ammonium ion also resists DMD oxidation, as demonstrated for an unsaturated amine (Eq. 16). (65) Such effective group-protected chemoselectivity still needs to be developed for the epoxidation of sulfide-functionalized alkenes, to avoid the inevitable sulfoxidation (Eq. 13). (66)



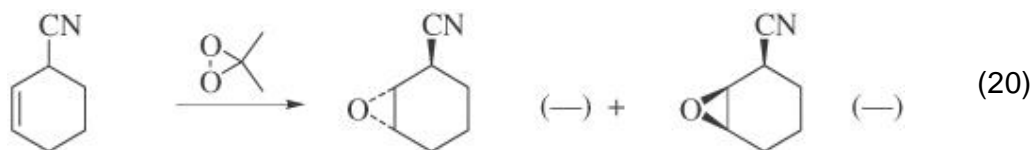
Acylation of the amino functionality also allows epoxidation, as demonstrated for the allylic amine in Eq. 17, (67) since the amide group resists DMD as well as TFD oxidation.



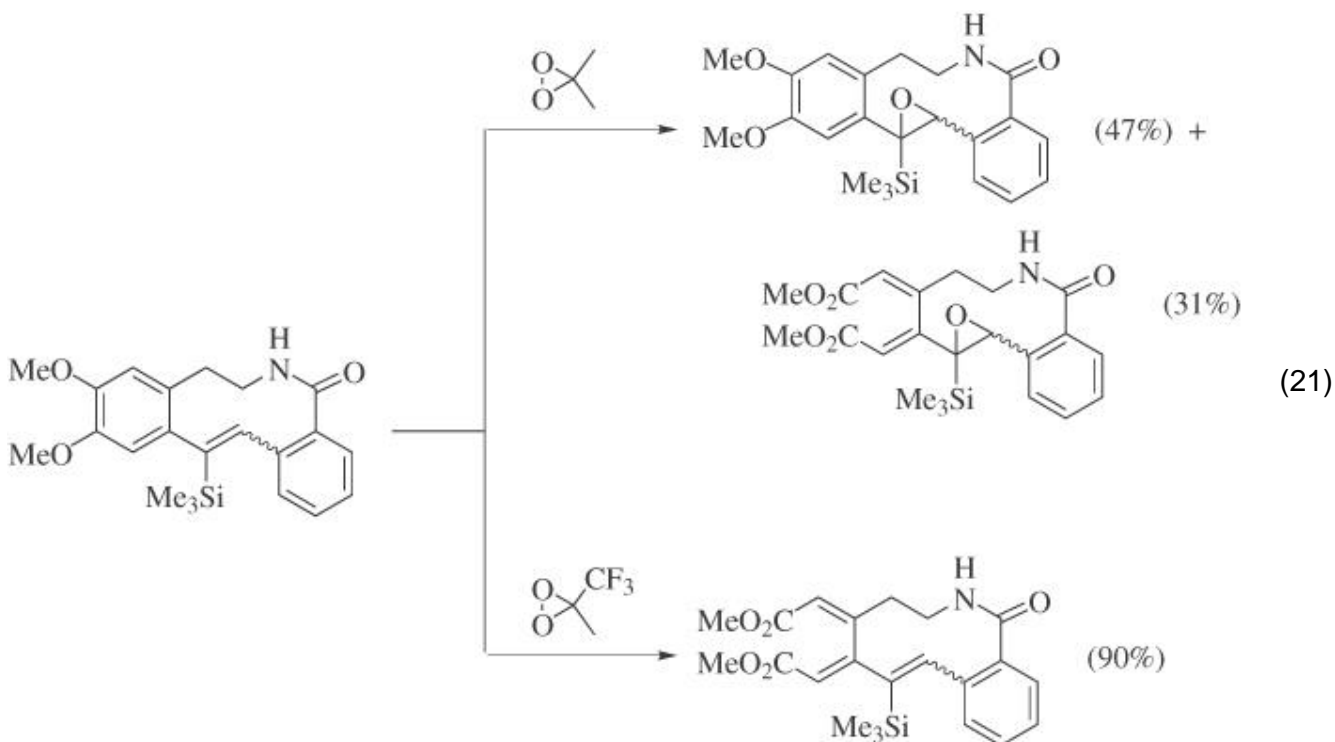
That ketone functionalities are compatible, since they are not themselves oxidized by isolated dioxirane, is illustrated for the unconjugated enone in Eq. 18. (32) This is not necessarily true for in situ generated dioxiranes, because ketones that are prone to undergo the Baeyer-Villiger reaction preferentially rearrange to esters with KHSO₅. Since intramolecular, ketone-mediated epoxidations have been documented, (68) it is uncertain whether in this in situ oxidation the inherent keto functionality of the substrate performs the oxygen transfer or whether it is DMD (in situ), or both. A more complex example is offered in Eq. 19, which demonstrates that an allylic keto group and the remote ester functionality do not interfere in this



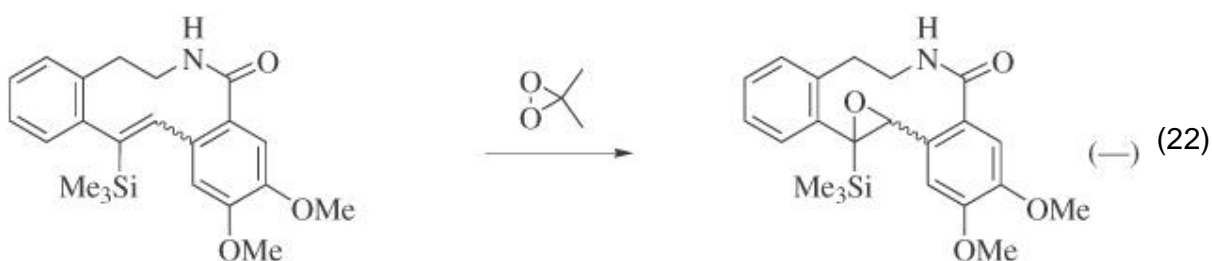
2-butanone-mediated, in situ epoxidation. (69) Expectedly, a cyano group is also inert toward dioxirane oxidation (DMD as well as TFD), as exemplified in Eq. 20. (67)



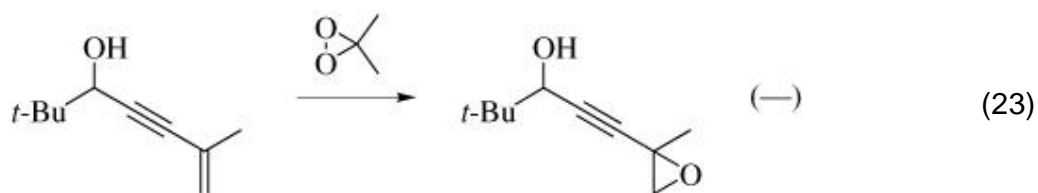
The oxidation (actually also an epoxidation) of electron-rich arenes in competition with alkene epoxidation is featured for the medium-sized ring vinylsilane substrate in Eq. 21. (70) Whereas DMD (isol.) affords a mixture of epoxidized and



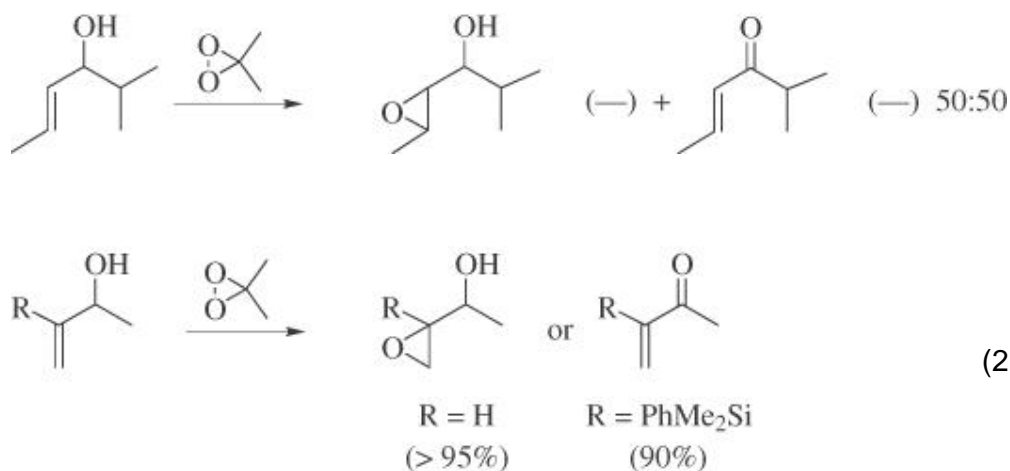
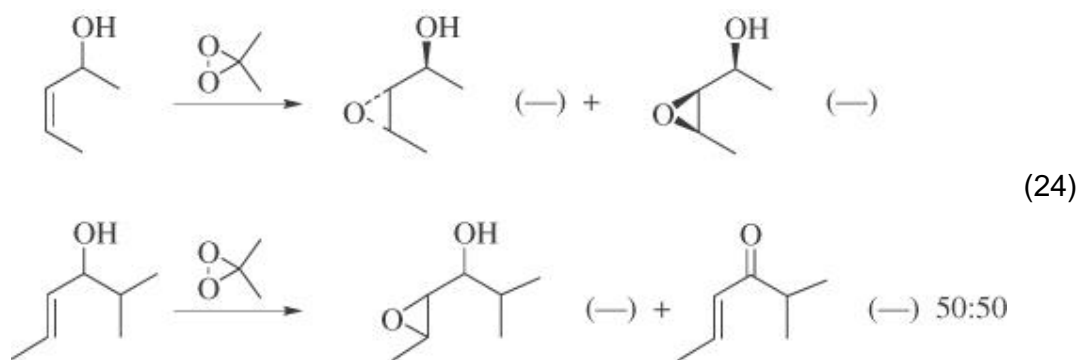
arene-oxidized products, the latter are formed exclusively with TFD (isol.). Presumably, steric effects are at play, which are more pronounced for the trifluoromethyl-substituted dioxirane. However, this chemoselectivity (arene oxidation versus epoxidation) depends on the arene functionality. Thus, the DMD oxidation of the cyclic vinylsilane substrate with two methoxy groups in the benzamide ring produces only the epoxide (Eq. 22). (70)



An example of double-bond versus triple-bond chemoselectivity is shown for the conjugated enyne in Eq. 23, which also bears an alcohol functionality. (71) Not only is the latter preserved (steric effect of the *tert*-butyl group), but also the double bond is exclusively epoxidized. This reaction displays the higher reactivity of C = C vs. C \equiv C bonds toward epoxidation by DMD.

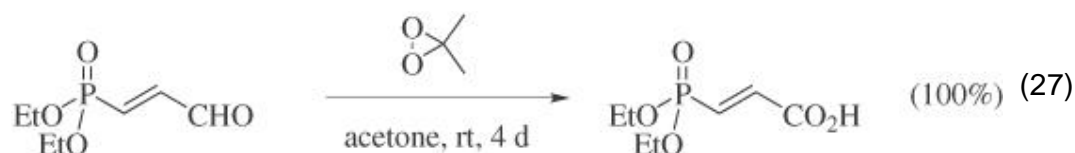
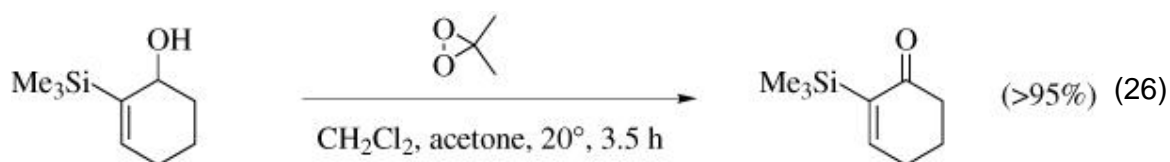


Competitive CH insertion vs. epoxidation is well documented for allylic alcohols. For example, whereas the *Z* isomer in Eq. 24 gives a diastereomeric mixture of threo- and erythro-epoxides with DMD (isol.), (72) equal amounts of epoxidation and allylic oxidation are formed from the *E* isomer. (73) Presumably, steric effects are again responsible since DMD is sensitive to such encumbrance. (6, 74, 75) A dramatic example is shown in Eq. 25, in which the introduction of an α -silyl substituent changes the exclusive epoxidation to predominant allylic oxidation; unquestionably, steric

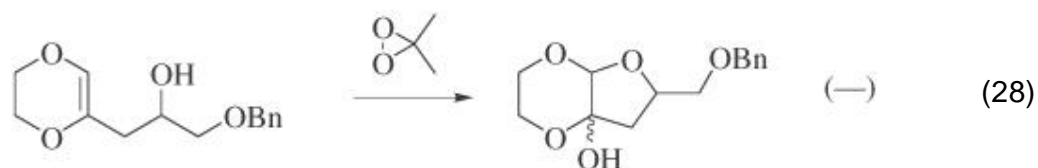


effects are at play here, because electronically, the silyl group should activate the double bond for epoxidation in view of its electron-releasing nature. In this context, an impressive example is given by the vinylsilyl-substituted cyclohexenol in Eq. 26, which yields only the corresponding enone. (74) An example of aldehyde oxidation to carboxylic acid (C-H insertion) rather than epoxidation is illustrated in Eq. 27 (76) for a phosphonate-substituted enal.

Here electronic effects come to bear, since the double bond is deactivated by the electron-withdrawing phosphonate ester.



Another type of incompatibility of a hydroxy functionality is exhibited in Eq. 28. (71) The labile epoxide functionality of the dioxene is attacked intramolecularly by the nucleophilic OH group to afford the bicyclic furan product through cyclization. Although the alcohol is not oxidized (this example is not a question of oxidative compatibility), it illustrates that remote nucleophilic functionalities may not be tolerated in view of further reaction with the epoxide ring.



These few examples of functional-group compatibility should be helpful for orientation, but more systematic studies (especially quantitative data on the reactivity of the common functionalities (toward dioxirane oxidation) would be desirable. Nonetheless, some combinations of compatible functional groups in Table B are straightforward to deduce: Any of the functionalities in the *compatible* category may be present in a substrate molecule equipped with groups of the *incompatible* and *moderately compatible* type, as long as the groups are chemically compatible toward each other (i.e., a silyl enol ether cannot bear a carboxylic or sulfonic acid group). Not simple to decide are combinations of functional groups from the *incompatible* and *moderately compatible* categories, nor within each of these categories. The general

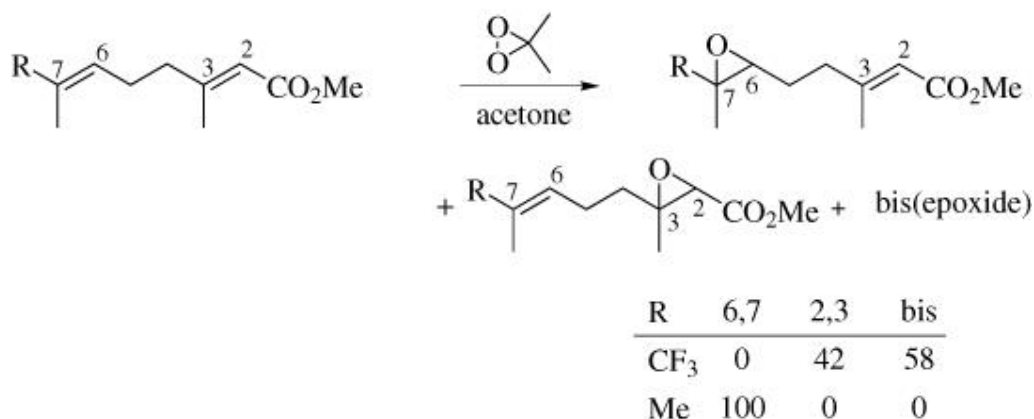
guidelines spelled out in the beginning of this section may be helpful, but are by no means foolproof.

3.6. Regioselectivity

By regioselective epoxidations we mean the preferential oxidation of one of the double bonds in a polyunsaturated substrate. Generally, oxidations by the electrophilic DMD take place at the site of higher electron density and lower steric demand. Good regioselectivities have been observed in heteroatom oxidations (8) and C-H insertions, (76a) but only the regioselectivity in epoxidations (77) is covered in this chapter.

The regioselectivity is mainly dictated by electronic effects in DMD epoxidations; a good example is shown in Scheme 9. Whereas the selectivity of epoxidation of the electron-rich 6,7-double bond over the electron-poor 2,3-double bond is very high in the methyl-substituted compound, the selectivity drops dramatically when the methyl group is replaced by the electron-withdrawing trifluoromethyl group. (78)

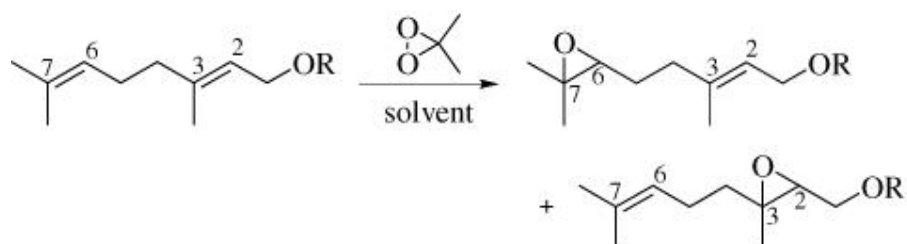
Scheme 9. Electronic Effects on the Regioselectivity in the DMD Epoxidations of Methyl 2,6-Octadienoate Derivatives



The influence of electronic substituents may be offset by the directing effect of a hydroxy group, which operates through the assistance of intramolecular hydrogen bonding. (8), (79) For instance, selectivity in the epoxidation of geraniol by DMD in protic versus aprotic solvent was shown to shift toward the 2,3-epoxide (from 88:12 in 9:1 MeOH/acetone to 51:49 in 9:1 CCl₄/acetone; Scheme 10). (72) In an aprotic medium (CCl₄/acetone), the allylic hydroxy group of geraniol stabilizes the transition-state structure through hydrogen bonding with the dioxirane and, consequently, the less nucleophilic 2,3-double

bond competes more effectively in the epoxidation. In the protic medium (9:1 methanol/acetone), methanol engages in hydrogen bonding with the dioxirane and the substrate, so that the allylic hydroxy group does not assist as effectively in the transition-state structure to control the selectivity. Thus, the electronic advantage of the more nucleophilic 6,7-double bond dictates the selectivity, so that the isomer ratio represents the relative nucleophilicities of the double bonds. In contrast, the methyl ether does not display this shift in the selectivity because assistance by hydrogen bonding is lacking in the transition-state structure for oxygen transfer and only electronic factors operate.

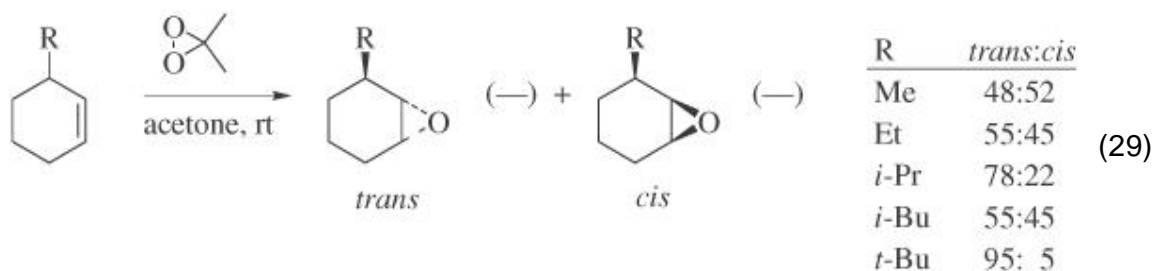
Scheme 10. Solvent Effects on the Regioselectivity in the DMD Epoxidation of Geraniol and its Methyl Ether (at 30% conversion)



R	Solvent	6,7	2,3
H	MeOH/acetone (9:1)	88	12
H	acetone	74	26
H	CCl ₄ /acetone (9:1)	51	49
Me	MeOH/acetone (9:1)	88	12
Me	acetone	88	12
Me	CCl ₄ /acetone (9:1)	87	13

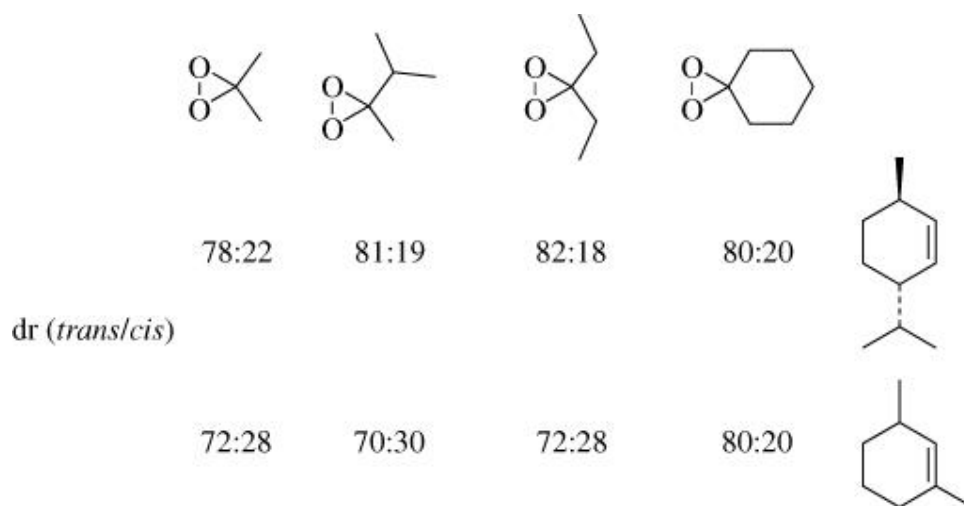
3.7. Diastereoselectivity

Dimethyldioxirane is responsive to the presence of substituents and functionalized groups in alkenes, which often leads to highly diastereoselective epoxidations. (8, 75, 80, 81) A comparative study on the diastereoselectivity of DMD versus *m*CPBA has revealed that DMD exhibits consistently higher diastereoselectivity than *m*CPBA as an epoxidizing reagent, (75, 82) although the difference is usually small. Results of the DMD epoxidation of some 3-alkyl-substituted cyclohexenes indicate that steric interactions between the substituents and DMD control the diastereo-selectivity (Eq. 29). (67, 83)

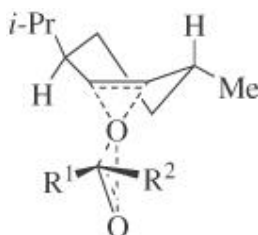


Epoxidation of 2-menthene and 1,3-dimethylcyclohexene (Scheme 11) by various dioxiranes demonstrates that the size of the dioxirane substituents has a minimal effect on diastereoselectivity. (75) This is because the alkyl groups of the dioxirane cannot interact effectively with substituents at the stereogenic center in the favored transition-state structures, as shown for 2-menthene (Scheme 12).

Scheme 11. Diastereoselective Epoxidation of 2-Menthene and 1,3-Dimethylcyclohexene by Various Dioxiranes

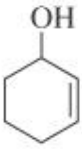
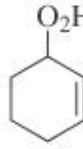


Scheme 12. Favored Transition-State Structure for the Dioxirane Epoxidation of 2-Menthene

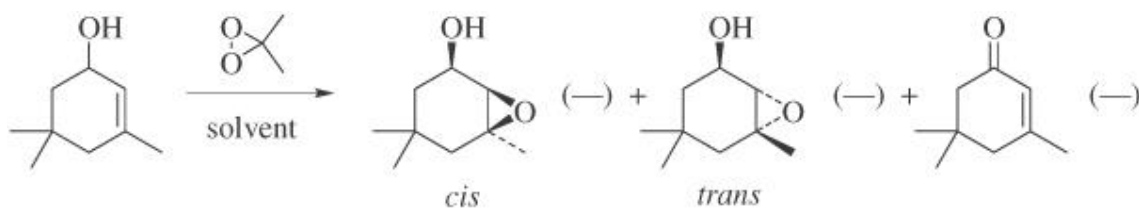


Hydrogen bonding plays an important role in the diastereoselective epoxidation of chiral allylic alcohols; an instructive example is shown in Scheme 13. (75) Whereas 3-hydroxycyclohexene displays a higher cis selectivity for both DMD and *m*CPBA, the 3-hydroperoxycyclohexene favors the trans diastereomer for DMD and is unselective for *m*CPBA. Evidently, the allylic hydroxy group in cyclohexenol directs the incoming oxidant through efficient hydrogen bonding to the cis face of the double bond, whereas the hydroperoxy group obstructs such an attack because of steric and, possibly, some electrostatic effects. (77, 84-86) Consequently, the trans epoxide is favored for DMD, which is more sensitive to steric repulsions with substrate substituents than *m*CPBA.

Scheme 13. Diastereoselective Epoxidation of Chiral Cyclohexenes by DMD vs. *m*CPBA

		
	<i>cis:trans</i>	<i>cis:trans</i>
DMD	53:47	9:91
<i>m</i> CPBA	95:5	57:43

An example of the importance of medium effects on hydrogen bonding is given for the chiral 2-cyclohexen-1-ol in Eq. 30. (87) The high cis selectivity (relative to the hydroxy substituent) in the nonpolar, aprotic medium (9:1 CCl₄/acetone) derives from intermolecular hydrogen bonding between the hydroxy group and the attacking dioxirane. This cis selectivity remains still high in acetone, but is considerably lower in the protic medium (9:1 MeOH/acetone). Methanol engages in intermolecular hydrogen bonding with DMD, which interferes with the interaction between the allylic hydroxy group and DMD.

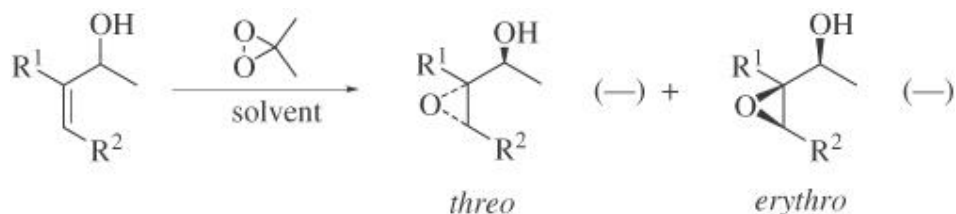


(30)

Solvent	<i>cis:trans</i>	epoxides:enone
MeOH/acetone (9:1)	62:38	92:8
acetone	83:17	77:23
CCl ₄ /acetone (9:1)	96:4	92:8

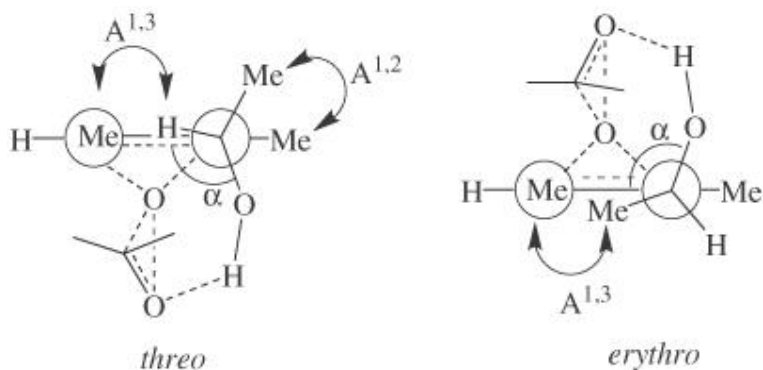
Similar effects are also observed in the epoxidation of acyclic allylic alcohols. (72) In these compounds, diastereoselectivity depends on the substitution pattern of the allylic alcohol, which controls the preferred conformation via steric interactions in the ground state and presumably also in the transition state. Appreciable π -facial selectivity is expected when hydrogen bonding of DMD by the allylic hydroxy functionality operates and allylic strain helps in aligning the appropriate conformation. As shown in Scheme 14, the allylic alcohol with minimal allylic strain ($R^1 = R^2 = H$) displays no diastereoselectivity in dioxirane epoxidation. In the substrate with only 1,2-allylic strain ($A^{1,2}$), the diastereoselectivity is quite low, but increases steadily with the use of increasingly nonpolar solvents. Evidently, 1,2-allylic strain is not effective enough to steer the π -facial attack. In contrast, for the substrate with only 1,3-allylic strain ($A^{1,3}$; $R^1 = H$, $R^2 = Me$), effective control of π -facial selectivity (85:15) is observed when CCl₄ is used as cosolvent. When both 1,2- and 1,3-allylic strain ($R^1 = R^2 = Me$) operate, expectedly, the π -facial diastereoselectivity is 91:9 in the nonprotic cosolvent CCl₄. These results provide useful mechanistic insight into the oxygen-transfer process. The two transition-state structures for the diastereomeric epoxides with both $A^{1,2}$ and $A^{1,3}$ strain are shown in Scheme 15 for DMD. The erythro transition-state structure is disfavored because of considerable 1,3-allylic strain. In the threo transition-state structure, however, 1,3-allylic strain is not significant since the steric interaction between H and Me is ineffective and, thus, high *threo* selectivity is obtained. The best conformational alignment (minimum 1,3-allylic strain) of the allylic hydroxy group for effective hydrogen bonding occurs at a dihedral angle (α) between 120–130°, as corroborated computationally. (23, 88, 89)

Scheme 14. Diastereoselectivity in the DMD Epoxidation of Chiral Acyclic Allylic Alcohols with Allylic Strain

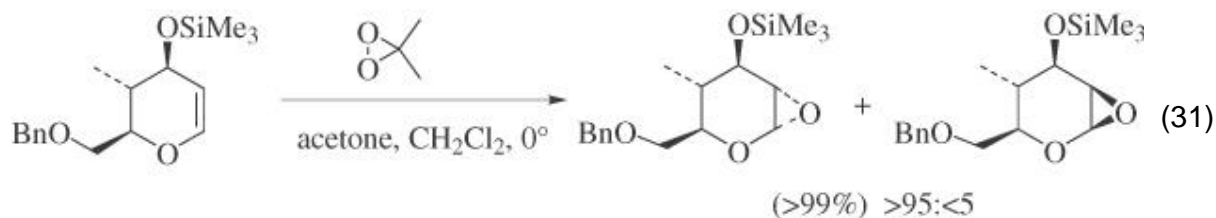


R ¹	R ²	Solvent	<i>threo</i> : <i>erythro</i>
H	H	acetone	50:50
Me	H	MeOH/acetone (9:1)	57:43
Me	H	acetone	60:40
Me	H	CCl ₄ /acetone (9:1)	70:30
H	Me	MeOH/acetone (9:1)	64:36
H	Me	acetone	67:33
H	Me	CCl ₄ /acetone (9:1)	85:5
Me	Me	MeOH/acetone (9:1)	82:18
Me	Me	acetone	87:13
Me	Me	CCl ₄ /acetone (9:1)	91 :9

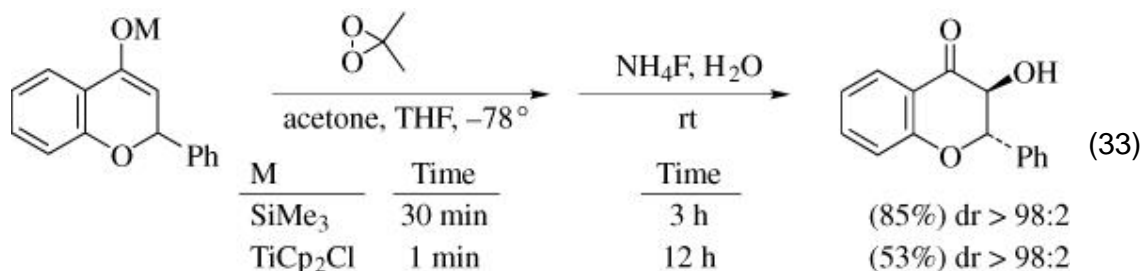
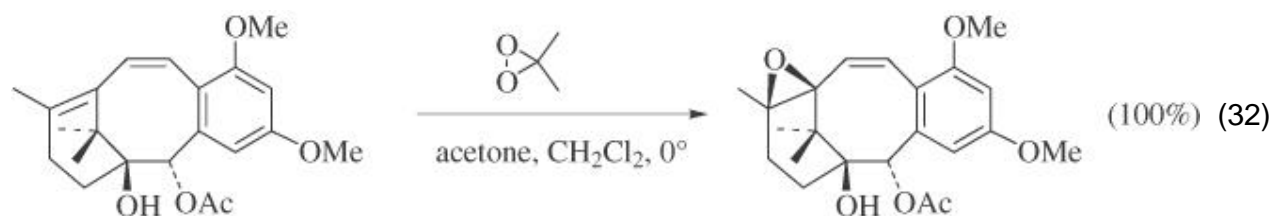
Scheme 15. Diastereomeric *threo* and *erythro* Transition-State Structures in the Hydroxy-Directed Epoxidation of a Chiral Allylic Substrate by DMD; A^{1,2} is 1,2-Allylic and A^{1,3} is 1,3-Allylic Strain



Highly diastereoselective epoxidations by dioxiranes have been widely employed in organic synthesis. For example, glycals have been epoxidized by DMD to afford high diastereoselectivities (Eq. 31); (90) this strategy has been successfully applied in



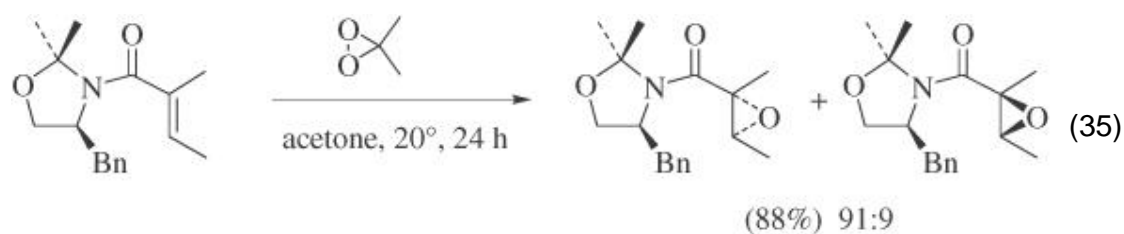
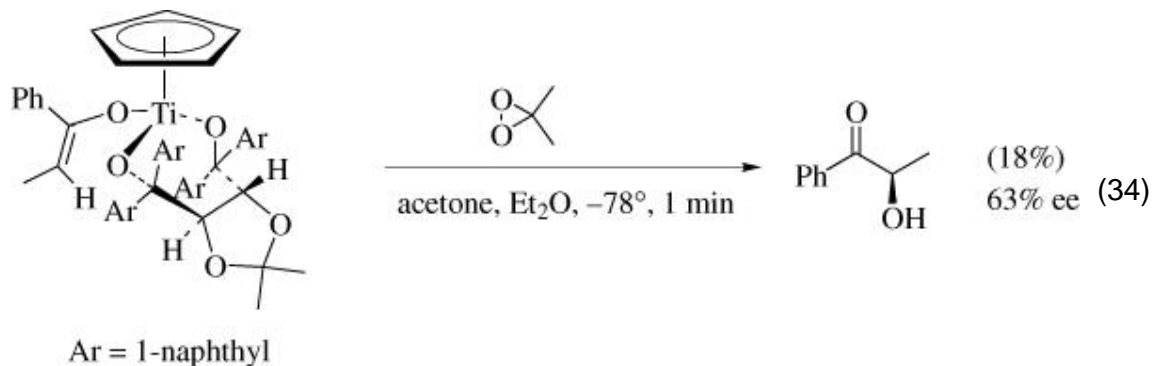
the synthesis of biologically important oligosaccharides. (91-95) Another example of diastereoselective DMD epoxidation in natural product synthesis is shown in Eq. 32. The epoxide that is potentially useful for the synthesis of taxol was obtained in quantitative yield by DMD epoxidation. (96) High diastereoselectivity is also achieved in the DMD epoxidation of the chiral silyl enol ether and titanium enolate in Eq. 33. (97)



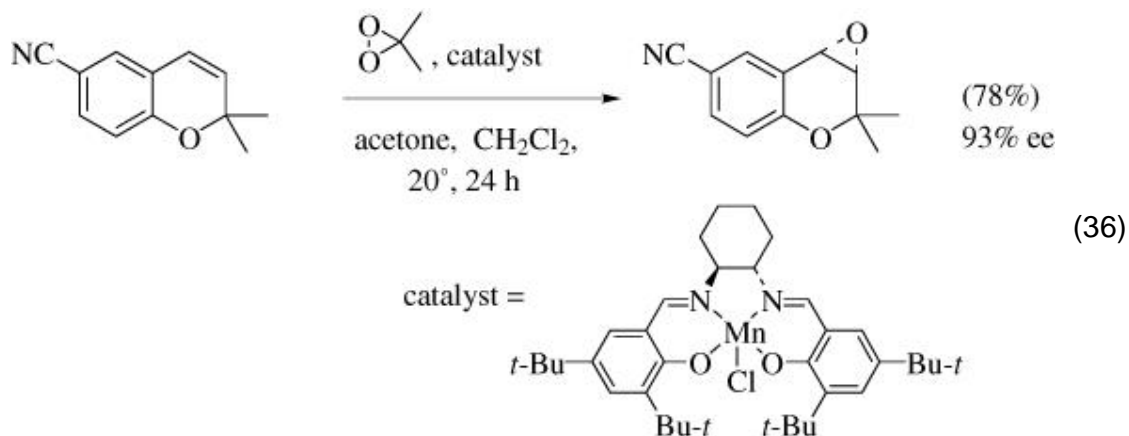
3.8. Enantioselectivity

There are several ways to obtain enantiomerically enriched epoxides with dioxiranes. One strategy is to use an achiral dioxirane, e.g., DMD, as stoichiometric oxidant and a prochiral olefin functionalized with an optically active auxiliary. The enantiomerically enriched final product is obtained after removal of the chiral auxiliary. For example, the DMD oxidation of titanium enolates with enantiomerically pure TADDOLs (α , α , α' , α' -tetraaryl-1,3-dioxolane-4,5-dimethanols) as chiral auxiliaries has been applied in the asymmetric synthesis of enantiomerically enriched α -hydroxy ketones. (98) (*R*)-2-hydroxy-1-phenylpropanone is obtained in up to 63% ee by DMD oxidation (Eq. 34), in which the initially formed epoxide rearranges to an

α -hydroxy ketone. (98) Asymmetric epoxidation by the achiral DMD is also achieved by employing 2,2-dimethyloxazolidines as chiral auxiliaries in tiglic amide derivatives (Eq. 35). (99)



An alternative approach is to employ DMD as the stoichiometric oxygen source for the preparation of an optically active oxidation catalyst. This is realized in the Jacobsen-Katsuki Mn-catalyzed (100, 101) enantioselective epoxidation of prochiral chromenes, in which DMD is used as oxygen source instead of NaOCl or iodosobenzene. (102) The advantage is that the use of DMD (isol.) allows one to operate in an organic medium (acetone, CH_2Cl_2 , etc.), whereas NaOCl requires a biphasic aqueous system and iodosobenzene a heterogeneous solid-liquid mixture. Since the DMD oxidation of manganese is faster than that of the olefinic substrate, the corresponding epoxides are obtained with high enantiomeric excess (Eq. 36). Similarly, isoflavone epoxides have also been obtained with good ee values by employing DMD together with the Jacobsen-Katsuki catalysts. (103, 104)

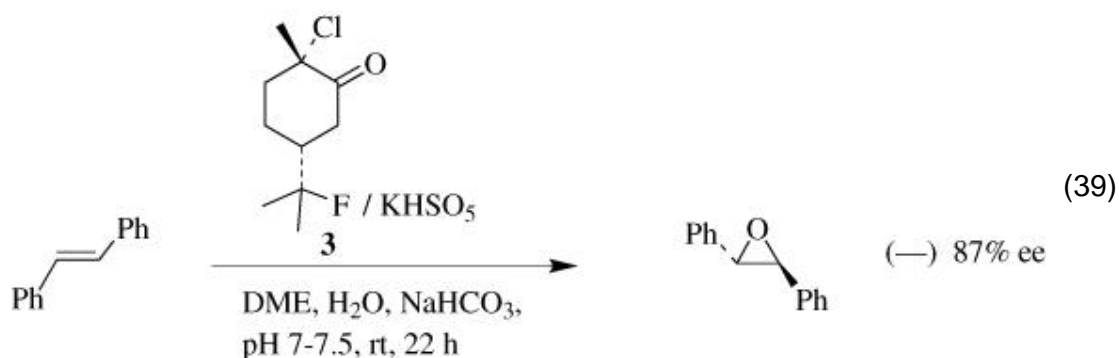
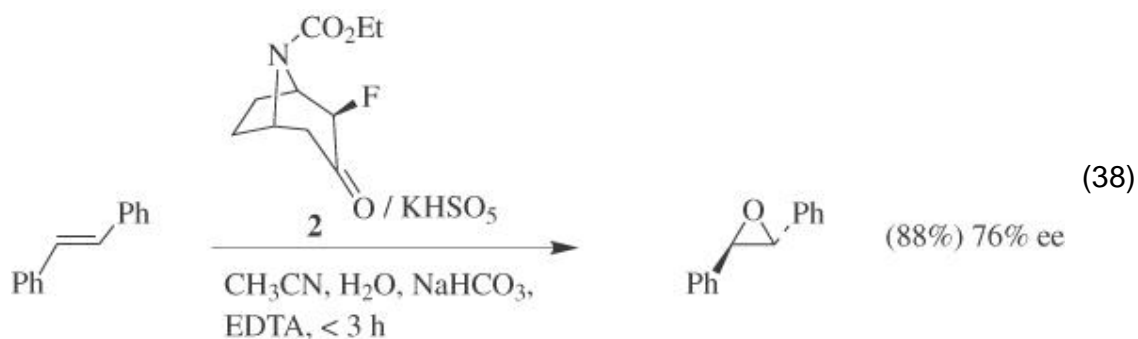
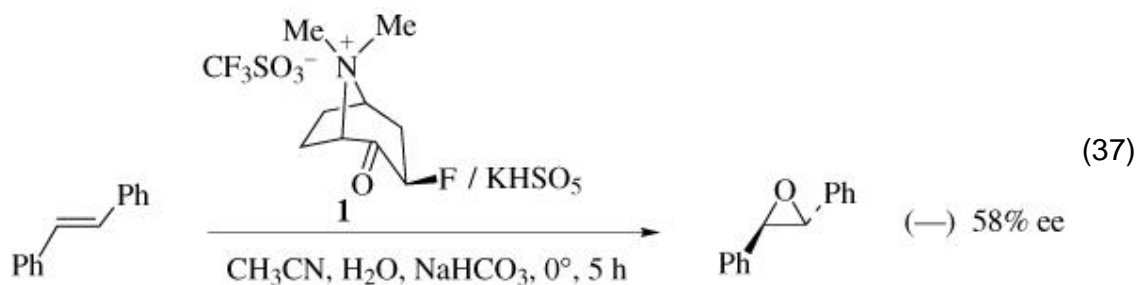


The most convenient and direct way to effect enantioselective epoxidation is to use enantiomerically enriched dioxiranes. Such dioxiranes can be generated in situ from the corresponding enantiomerically pure ketones. Thus, asymmetric oxidation may in principle be catalytic in the ketone. Indeed, the chiral ketones in Scheme 16 were employed for the asymmetric epoxidation of olefins at the very beginning of dioxirane chemistry. (105)

Scheme 16. Early Examples of Optically Active Ketone Catalysts for in situ Asymmetric Epoxidation of Prochiral Alkenes

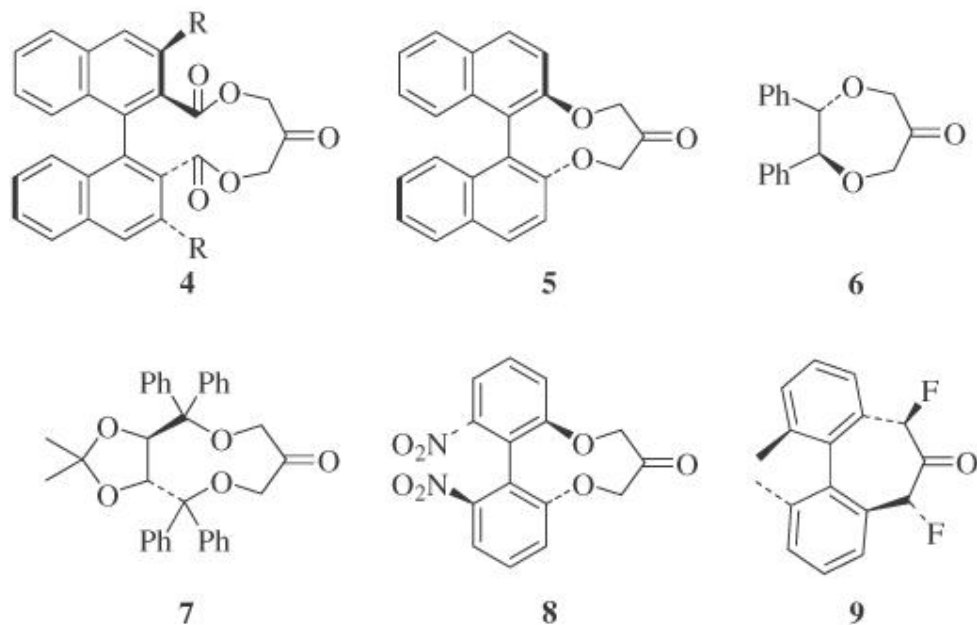


Unfortunately, enantioselectivity with these ketones is quite low (13% ee), (105) with the best ee value only up to 20%. (106) However, better enantioselectivities (up to 85% ee) have been realized with catalytic amounts of the α -hetero-substituted ketones **123** in Eqs. 37–39. (107-109)



Among the most selective catalysts for enantioselective epoxidation are the C_2 -symmetric ketones **4–9** in Scheme 17. The parent binaphthalene-derived catalyst **4** ($R = H$) epoxidizes *trans*-stilbene in 47% ee, whereas for *trans*-4,4'-diphenylstilbene epoxide, the ee is as high as 87%. (110) Enantioselectivity is enhanced by introducing substituents at the 2 and 2' positions of the binaphthalene moiety; thus, an ee of 84% ($R = 1,3$ -dioxan-2-yl) is obtained even for *trans*-stilbene epoxide. However, the substrate generality for this catalyst is quite limited. (24, 111)

Scheme 17. Optically Active C_2 -Symmetric Ketone Catalysts **4–9** for in situ Asymmetric Epoxidation



Several other C_2 -symmetric ketones **5-9** (Scheme 17) have been reported for asymmetric epoxidation. (11, 24, 112, 113) These ketones are readily available from the corresponding optically active diols. Although the C_2 -symmetric ketone **5** contains the same chiral binaphthalene scaffold as compound **4**, ketone **5** provides much inferior enantioselectivity. (24, 112, 113) The TADDOL-derived ketone **7** affords the highest enantioselectivity for the epoxidation of *trans*-stilbene (65% ee) among these diol-derived ketones. (113) Whereas the C_2 -symmetric dinitro-substituted biphenyl-derived ketone **8** performs poorly, (24) the difluoro-substituted ketone **9** acts catalytically under basic conditions (pH 10) and produces *trans*-stilbene epoxide in excellent enantioselectivity (94% ee); for *trans* alkenes without phenyl substituents, the enantioselectivity drops considerably. (11)

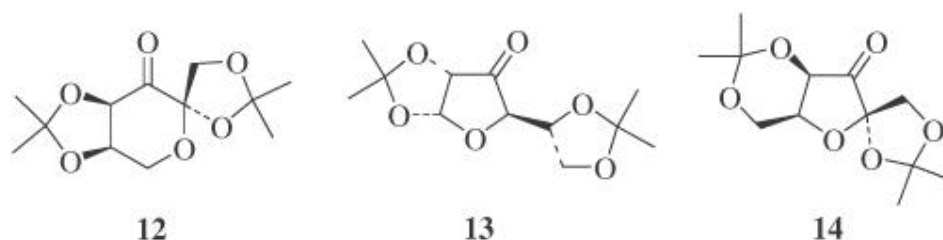
The chiral ketones **10** and **11** (Scheme 18), which are available from D-(–)-quinic acid, also serve as effective catalysts for asymmetric epoxidations. Whereas ketone **10** displays high enantioselectivity for *trans* olefins, the lengthy synthesis limits applications. (114, 115) Ketone **11** is more readily prepared from quinic acid and also provides good enantioselectivity, but an excess must be used since it does not persist under the reaction conditions. (116)

Scheme 18. Optically Active Ketone Catalysts **10** and **11** Derived from Quinic Acid for in situ Asymmetric Epoxidation



Ketone **12** (Scheme 19) represents one of the best catalysts for the asymmetric epoxidation of unfunctionalized as well as for functionalized *trans*-substituted and trisubstituted olefins. (25, 117) Under neutral conditions (pH ca. 8, NaHCO₃ as buffer), a stoichiometric amount of the ketone **12** is required to achieve good conversions, since this ketone undergoes oxidative degradation under the reaction conditions. (117) Nevertheless, ketone **12** can be employed in sub-stoichiometric amounts (ca. 0.3 equiv.) under basic conditions by adding K₂CO₃ (pH 10.5). (25, 118) The enantioselectivity is usually improved under such basic vs. neutral conditions, especially for allylic alcohols. The ease of preparation and generality of epoxidation make ketone **12** the best choice for asymmetric epoxidation. (119)

Scheme 19. Sugar-Derived Ketone Catalysts **12**, **13**, **14** for in situ Asymmetric Epoxidation



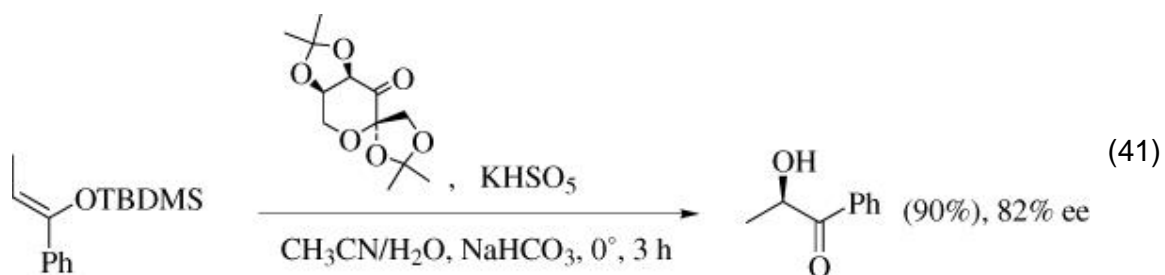
In contrast to ketone **12**, ketone **13**, prepared from glucose, is ineffective (e.g., no reaction with *trans*-stilbene was observed). (120) Presumably, this ketone suffers Baeyer-Villiger oxidation and is destroyed faster than it epoxidizes the substrate. A similar five membered ring ketone **14**, however, converts *trans*-stilbene to its epoxide in 75% ee. (119) For comparison, the ee values for the epoxidation of *trans*-stilbene by the ketones are collected in Table C. It is evident that the best ee values are obtained with ketone **12**. The corresponding in situ generated dioxiranes have been effectively applied for asymmetric epoxidation. For example, ketone **12** has been employed for the synthesis of enantiomerically enriched α -hydroxy ketones, which are versatile building blocks for natural products, through the epoxidation of silyl enol ethers by the in situ generated dioxirane (Eq. 41). (26) This protocol also has been used to epoxidize enol esters, (121) dienes, (112) and enynes (123, 124) in high enantioselectivity, as well as high chemo- and regioselectivity.

Table C. Comparison of Enantioselectivities in the Asymmetric Epoxidation of *trans*-Stilbene by Various in Situ Generated Dioxiranes

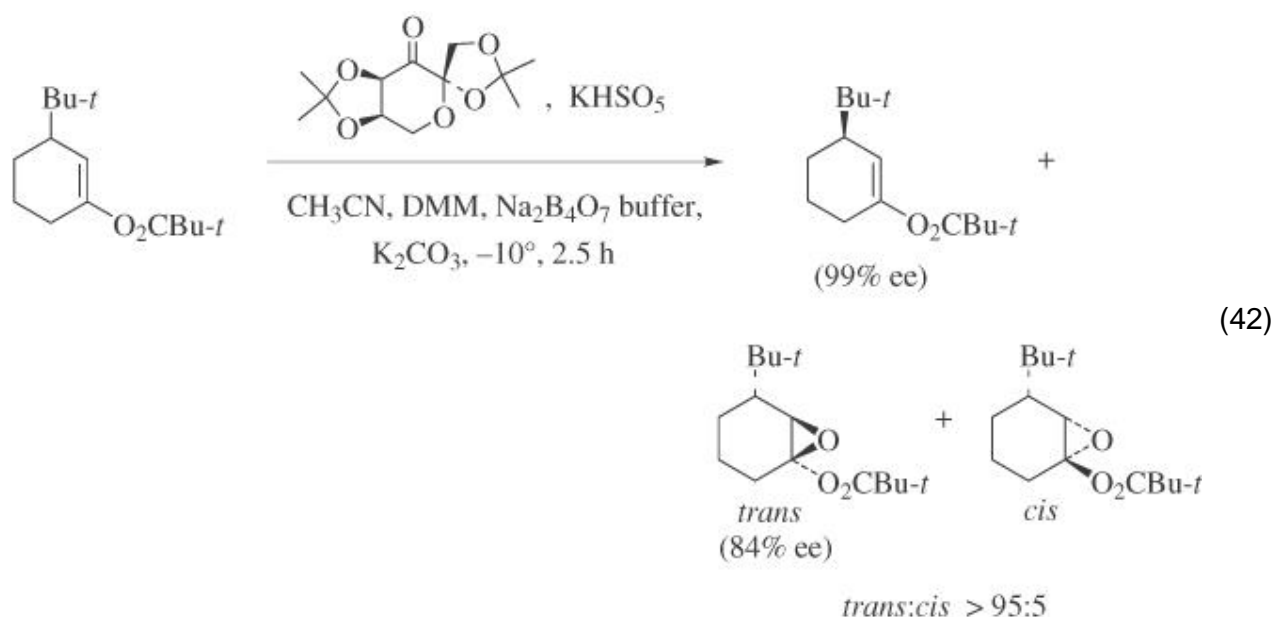


Ketone	pH of buffer	ee(%)	Configuration
1	8.0	58	<i>R,R</i>
2	8.0	76	<i>R,R</i>
3	8.0	87	<i>S,S</i>
4(R = H)	8.0	47	<i>S,S</i>
4(R = Br)	8.0	80	<i>S,S</i>
5	10.5	27	<i>R,R</i>
6	8.0	59	<i>S,S</i>
7	10.5	65	<i>R,R</i>
8	8.0	50	<i>S,S</i>
9	10.5	94	— ^a
10(R=H)	10.5	93	<i>R,R</i>
10(R=CMe₂OH)	10.5	96	<i>R,R</i>
11	8.0	85	<i>R,R</i>
12	10.5	97	<i>R,R</i>
14	10.5	75	<i>R,R</i>

^aThe absolute configuration was not given.

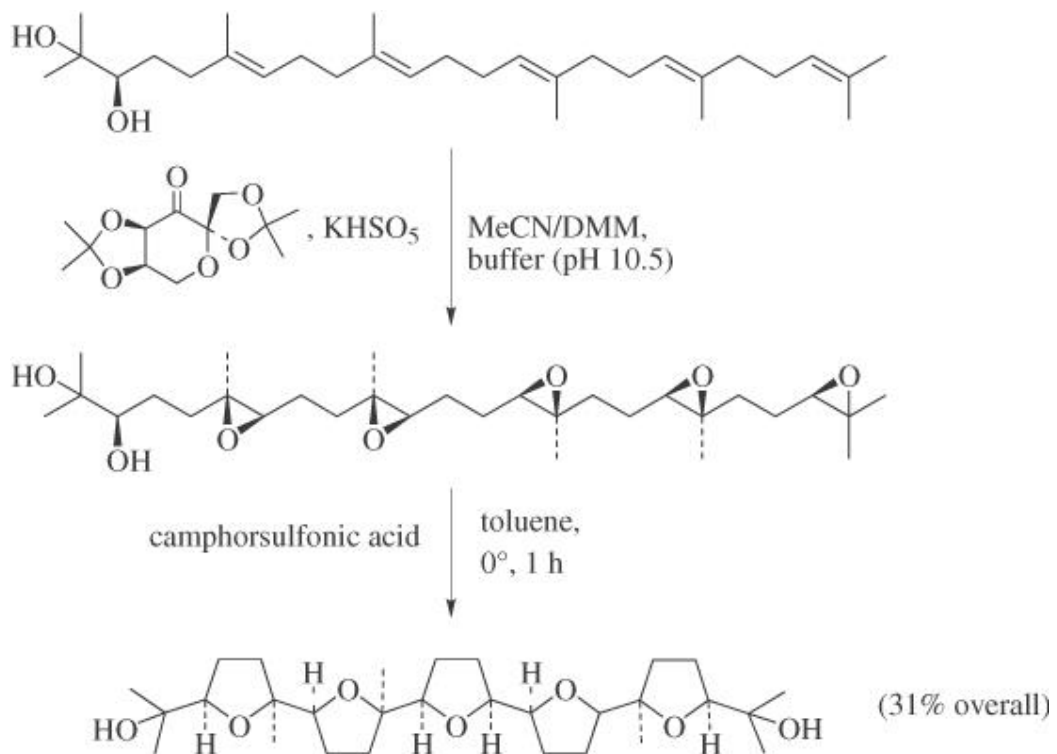


With the in situ generated dioxirane of ketone **12** the first kinetic resolution of racemic enol acetates has also been achieved through stereoselective epoxidation. (125) An illustrative example is shown in Eq. 42. The efficiency of this method is clearly demonstrated by the high ee values of the unreacted enol acetate and the major trans epoxide product, as well as by the high diastereoselectivity (trans:cis > 95:5).



A highlight of this epoxidation protocol is shown in Scheme 20. (126) The in situ generated dioxirane of ketone **12** has been used for constructing the pentaepoxide of desired configuration, so that the glabrescol analog was obtained in 31% overall yield in only two steps. The pentafuran has been used for revision of the glabrescol structure, a natural product with important biological activity. (126)

Scheme 20. Synthesis of a Glabrescol Analog

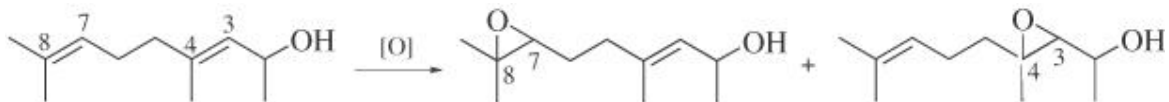


4. Comparison with Other Methods

Of the various reagents available for conducting epoxidations, none matches the versatility of dioxiranes. For the epoxidation of simple alkenes, peracids, (127, 128) especially *m*CPBA, are the most widely used reagents. Although the two oxidants are mechanistically quite similar, steric effects are more pronounced for dioxiranes than peracids. Thus, when the unsaturated substrate is sterically quite encumbered, e.g., vinylsilanes, C-H oxidation may occur instead of epoxidation, (74) which is almost never observed for peracids. The disadvantage of peracids is that they cannot be applied to acid-sensitive substrates and/or products. When an aqueous buffer is employed, the alkene and the resulting epoxide must be resistant toward hydrolysis. In contrast, as already stated above, isolated dioxiranes perform epoxidations under strictly neutral (pH ca. 7) and nonhydrolytic conditions so that labile substrates and products survive. Of course, in the catalytic mode, which necessarily must be conducted in aqueous media (pH ranges between 7.5 and 10.5) for the in situ generation of the dioxirane, the problems of hydrolysis apply. Thus, the catalytic method should be avoided for the preparation of hydrolytically sensitive epoxides.

Compared to other nonmetal-mediated epoxidations (129) [e.g., perhydrates (hexa-fluoroacetone/ H_2O_2 (130)) and $\text{CH}_3\text{CN} / \text{H}_2\text{O}_2/\text{HO}^-$ (Payne oxidation) (131)], the in situ method of dioxiranes offers advantages in terms of reactivity and selectivity. Thus, Weitz-Scheffer conditions (NaOCl , H_2O_2 / KOH , *t*- BuO_2H / KOH) are suited only for electron-poor olefins, (52) and *N*-sulfonyloxaziridines are limited to electron-rich enolates and enol ethers. (132) This reagent may be activated in the form of oxaziridinium salts, which are considerably more powerful oxidants and epoxidize even simple alkenes. (133, 134) In contrast, dioxiranes oxidize all types of electron-rich and electron-poor double bonds with good selectivities; moreover, the strongly basic conditions (pH > 10) used in the Weitz-Scheffer (52) and Payne (131) epoxidations, as well as the acidic conditions of perhydrates, (130) are avoided with isolated dioxiranes. A comparison of the regioselective and diastereoselective epoxidations of 1-methyl-geraniol by DMD (isol.) versus a few other oxidants is given in Table D.

Table D. Comparison of Regio- and Diastereoselectives for the Epoxidation of 1-Methylgeraniol by DMD (isol.) Vs Other Oxidants



Oxidant	Solvent	Epoxide Selectivity	
		regio 7,8:3,4	diastereo ^a threo:erythro
DMD (isol.) (134a)	CCl ₄	32:64	94:6
<i>m</i> CPBA (134a)	CCl ₄	51:49	90:10
HFAH/ H ₂ O ₂ ^b (135)	CH ₂ Cl ₂	52:48	96:4
VO(acac) ₂ /TBHP ^{a, c} (134a),	CH ₂ Cl ₂	< 5:95	89:11
Ti(OPr- <i>i</i>) ₄ /TBHP ^{a, c} (134a)	CH ₂ Cl ₂	< 5:95	98:2
Mn(salen)PF ₆ /PhIO (136)	CH ₂ Cl ₂	53:47	94:6
MTO/UHP ^{a, d} (134a),	CCl ₄	76:24	88:12

^aDiastereoselectivity of the 3, 4-epoxide regioisomer.

^bHexafluoroacetone hydrate.

^c*tert*-Butyl hydroperoxide.

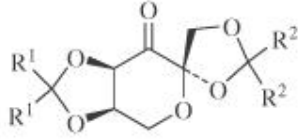

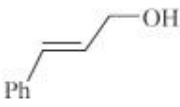
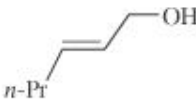
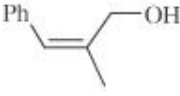
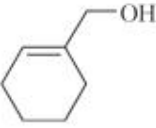


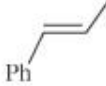
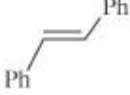
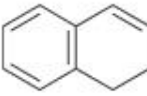
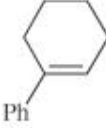
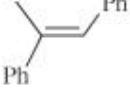
^dMethyltrioxorhenium/urea adduct of hydrogen peroxide.

Epoxides can also be prepared by treating alkenes with hydroperoxides, C1O⁻, PhIO or molecular oxygen as oxygen sources in the presence of transition-metal complexes, e.g., V, Mo, Ti, Mn, Cr, or Co. (137, 138) Hydrogen peroxide can be used as an oxygen donor in combination with catalysts such as tungstic acid and derivatives (139-142) as well as methyltrioxorhenium (MTO). (143-145) Representative examples are also listed in Table D. Evidently, the catalytic mode (in situ generation) of dioxiranes cannot compete in efficacy with metal-catalyzed epoxidations, but the toxicity of most transition metals must be kept in mind in view of environmental problems. Thus, in recent times, the search for nonmetal oxidants has been actively pursued, and dioxiranes can serve as an attractive alternative, especially since now a variety of dioxiranes and reaction conditions have become available. Dioxiranes are also superior to the F₂/ H₂O /MeCN system (146) in that dioxiranes are easier to handle and less toxic.

Furthermore, dioxiranes play a prominent role in asymmetric epoxidations.

High enantioselectivities have been achieved in the asymmetric epoxidation of unfunctionalized and functionalized trans and trisubstituted olefins by in situ generated optically active dioxiranes. Nevertheless, these enantioselective oxidations hardly surpass the efficiency of environmentally benign enzymatic processes (peroxidase/ H₂O₂ or RO₂H) (147) and the well-known Sharpless-Katsuki epoxidation. (148) The latter is limited to allylic alcohols, and the accessibility of large amounts of enzymes for preparative applications represents a major problem in biocatalytic reactions. Furthermore, the level of enantioselectivity in the epoxidation of cis olefins by enantiomerically enriched dioxiranes has yet to reach that of the Jacobsen-Katsuki Mn(salen)-catalyzed process. (100, 101, 149) Comparative examples are given in Table E for the Sharpless-Katsuki and the Jacobsen-Katsuki asymmetric epoxidations vs. that mediated by the dioxirane derived from ketone 12.

Table E. Comparison of Enantioselectivities in Epoxidations with Ketone 12 (R¹ = R² = Me) with the Sharpless-Katsuki and the Jacobsen-Katsuki Asymmetric Epoxidations

Substrate	 KHSO_5	$\text{Ti}(\text{OPr-}i\text{)}_4, t\text{-BuO}_2\text{H,}$ tartrate	$\text{Mn}(\text{salen}^*)$ PhIO or NaOCl
	(85%) 94% ee ^{149a}	(78%; 78% ee) ¹⁵⁰	—
	(70%) 90% ee ¹¹⁸	(89%; 98% ee) ¹⁵⁰	—
	(60%) 78% ee ¹¹⁷	(64%; 93% ee) ¹⁵⁰	—
	(75%) 74% ee ^{149a}	(79%; >98% ee) ¹⁵⁰	—
	(83%) 92% ee ^{123,124}	(77%; 93% ee) ¹⁵⁰	—
	(90%) 24% ee ²⁵	—	(88%; 86% ee) ¹⁵¹
	(81%) 28% ee ²⁵	—	(36%; 30% ee) ¹⁰⁰
	(99%) 96% ee ²⁵	—	(32%; 56% ee) ¹⁵¹
	(85%) 98% ee ²⁵	—	(17%; 81% ee) ¹⁵¹
	(85%) 32% ee ²⁵	—	(78%) 98% ee ¹⁵¹
	(94%) 98% ee ²⁵	—	(69%) 93% ee ¹⁵¹
	(89%) 96% ee ²⁵	—	(87%) 88% ee ¹⁵¹

Evidently, dioxirane chemistry is a fast-developing and growing field, and much progress is expected in the years to come. As the tabulated material (Tables 1–5) discloses, much has been achieved in the last 25 years and, unquestionably, dioxiranes have become established as important catalytic (in situ) and stoichiometric (isolated) epoxidants.

5. Experimental Conditions

5.1. Oxidations with Isolated Dioxiranes

5.1.1. General

Although no explosions have ever been documented, the preparation and reactions of isolated dioxiranes should be carried out in a hood with good ventilation, and all safety measures should be taken. Inhalation and direct exposure to skin must be avoided because dioxiranes are strong oxidants and can potentially damage biomolecules such as DNA. (152)

Solutions of isolated dioxiranes are prepared by treating the ketone precursor with KHSO_5 in buffered aqueous solutions. Isolation is achieved either through distillation of readily volatile dioxiranes such as DMD (isol.) (153) and TFD (isol.), (154, 155) or by salting out of the dioxirane derived from cyclohexanone (156, 157) (see Experimental Procedures). In view of the much higher electrophilicity of 1,1,1-trifluoro-2-propanone compared to acetone, TFD is generated much faster than DMD (about 1 minute for TFD vs. about 20 minutes for DMD). ketones that readily undergo Baeyer-Villiger rearrangement (cyclobutanone, cyclopentanone), that are not sufficiently electrophilic (benzophenone, acetophenone), or are sterically hindered (pinacolone, adamantanone) are not suitable precursors for the corresponding dioxiranes because either the dioxirane does not persist long enough (first category) or the dioxirane is not generated (last two categories).

The solution of the isolated dioxirane is usually dried over freshly activated molecular sieves (4 Å) or MgSO_4 . When rigorously dry solutions are required, further drying over P_2O_5 and subsequently over anhydrous K_2CO_3 is recommended, with only minor loss (<5%) of the dioxirane content. (158)

Magnetic stirring is usually sufficient for oxidation with the isolated dioxirane. For most oxidations, a properly sized, stoppered Erlenmeyer flask is used as reaction vessel. An inert gas atmosphere is not required unless the substrate or the product is air-sensitive or hydrolytically labile. Pipettes fitted with a bulb filler are routinely used for the transfer of dioxirane solutions. For low-boiling dioxiranes, such as methyl(trifluoromethyl)dioxirane [TFD (isol.)], the pipette must be precooled with liquid nitrogen to minimize loss through evaporation. When an excess of dioxirane is used, it is conveniently removed during solvent evaporation, but care should be taken to condense the evaporate and thereby avoid environmental hazards.

5.1.2. Solvents

Most common laboratory solvents are compatible with DMD (isol.) solutions. Acetone, CH_2Cl_2 , CHCl_3 , CCl_4 , and benzene are among the most frequently used cosolvents for epoxidations. With DMD (isol.), cosolvents such as

2-butanone, 1,4-dioxane, THF, *tert*-butyl methyl ether, dimethoxymethane, 1,2-dimethoxyethane, ethyl acetate, and acetonitrile can also be employed. Methanol, ethanol and 2-propanol should not be used since they react slowly with DMD (isol.) even at subambient temperature. (159) For TFD (isol.), ether solvents must be avoided because they are readily oxidized even at low temperature. (160)

5.1.3. Temperature

Epoxidation with DMD solutions [DMD (isol.)] is usually carried out at ambient temperature (ca. 20°). If labile substrates are used or labile products are expected, the reaction can be carried out at subambient or even at dry ice temperatures (−78°). In some cases, the reaction with slowly reacting substrates can be carried out at elevated temperature [e.g., with DMD (isol.) in boiling acetone]. Fortunately, dimethyldioxirane possesses a relatively high activation energy for decomposition (E_a ca. 24.9 kcal/mol), (161) which enables it to tolerate a temperature of 60°.

5.2. Oxidations with in Situ Generated Dioxiranes

If the substrate and product are hydrolytically robust, oxidation with in situ generated dioxiranes is the most convenient mode of operation. The advantages are that a large number of ketone catalysts are available, generation of the dioxirane is more efficient, and the reaction can be carried out on a large scale under catalytic conditions and with asymmetric induction. DMD (in situ) is by far the most frequently used dioxirane, but the more reactive TFD (in situ) is the choice for less reactive substrates such as electron-poor or sterically hindered alkenes.

5.3. Oxidations under Neutral Conditions

5.3.1. Biphasic Media

This is the original protocol for conducting dioxirane epoxidation with DMD (in situ). (31, 32) In this method, the substrate is dissolved in an organic solvent that is immiscible with water (for example, CH_2Cl_2 , benzene, etc.), and the oxygen source, monoperoxysulfate, is contained in the aqueous phase, in which the dioxirane is formed from the ketone catalyst (usually acetone). Vigorous stirring with a mechanical stirrer is recommended for efficient reaction. The action of phase-transfer catalysts (18-crown-6, Bu_4NHSO_4) may be helpful. The pH of the aqueous phase is maintained at 7 to 8 by adding a suitable buffer solution or solid NaHCO_3 ; for this purpose, use of a pH-stat is convenient and advantageous. If 2-butanone is employed as the dioxirane precursor, (34) no cosolvent is necessary because the aqueous medium and 2-butanone, which has good solubilizing properties, constitute a biphasic system.

5.3.2. Homogeneous Media

A water-miscible organic solvent is employed to bring the substrate and/or ketone catalyst into the aqueous phase. Whereas acetonitrile is most commonly used for this purpose, dioxane, dimethoxymethane (DMM), 1,2-dimethoxyethane (DME), or mixtures thereof, have also found application. The pH of the system is readily controlled by a pH-stat, or by adding the required amount of a powdered mixture of solid NaHCO_3 and solid monoperoxysulfate at the beginning of the reaction. Asymmetric epoxidations have all been carried out in homogeneous media; accordingly, this mode of operation has currently gained much importance.

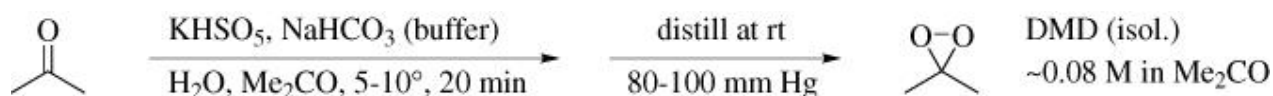
5.4. Oxidations under Basic Conditions in Homogeneous Media

This method is actually an extension of the above-mentioned homogeneous system in which a more basic buffer, such as 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ or $\text{K}_2\text{CO}_3/\text{AcOH}$ buffer (pH ca. 10.5), replaces the NaHCO_3 buffer. The advantage of this modification is that some ketone catalysts are more effective and more persistent under basic conditions, which is crucial for conducting catalytic asymmetric epoxidations (cf. Table C). The pH value of the reaction mixture can be conveniently maintained by adding a K_2CO_3 solution.

6. Experimental Procedures

Caution. Dioxiranes are usually volatile peroxides and thus should be handled with care, by observing all safety measures. The preparations and oxidations should be carried out in a hood with good ventilation. *Inhalation and direct exposure to skin must be avoided!*

6.1. Preparation of Isolated Dioxirane Solutions



6.1.1. Dimethyldioxirane [DMD (isol.)] (153)

(The procedure described here is a simplified version of a protocol originally reported by Murray et al.). (162, 163) A 4-L, three-necked, round-bottomed reaction flask was equipped with an efficient mechanical stirrer and an addition funnel for solids, connected by means of a U tube (i.d. 25 mm) to a 250-mL, two-necked receiving flask and the latter was cooled to -78° by means of a dry ice/ethanol bath. The reaction flask was charged with a mixture of water (254 mL), acetone (192 mL), and NaHCO₃ (58 g) and cooled to $5-10^\circ$ with the help of an ice/water bath. With vigorous stirring and cooling, solid potassium monoperoxysulfate (120 g, 0.195 mol) was added in five portions at 3-minute intervals. Three minutes after the last addition, a moderate vacuum (80–100 mmHg) was applied, the cooling bath ($5-10^\circ$) was removed from the reaction flask, and, while the mixture was stirred vigorously, the dimethyldioxirane/acetone solution was distilled (150 mL, 0.09–0.11 M, ca. 5% yield), and collected in the cooled (-78°) receiving flask. The concentration of the dimethyldioxirane solution was most conveniently determined by measuring the absorbance at λ_{max} 325 nm (ϵ $12.5 \pm 0.5 \text{ M}^{-1}\text{cm}^{-1}$). The acetone solution of dimethyldioxirane was dried over anhydrous K₂CO₃ and stored in the freezer (-20°) over molecular sieves (4 Å).

6.1.2. Dimethyldioxirane-*d*₆ in Acetone-*d*₆ [DMD-*d*₆ (isol.)]

Occasionally it is necessary to employ the deuterated dioxirane DMD-*d*₆ (isol.) to facilitate direct NMR spectroscopy of the oxidation mixture, without solvent removal. The following procedure is a modification of the procedure for the small-scale preparation of DMD (isol.) (34): A 250-mL, three-necked, round-bottomed flask, charged with water (20 mL), acetone-*d*₆ (10 mL), sodium bicarbonate (12 g), and a magnetic stirring bar, was equipped with an addition funnel for solids for the KHSO₅ (25 g, 0.041 mol), a gas-inlet tube, and

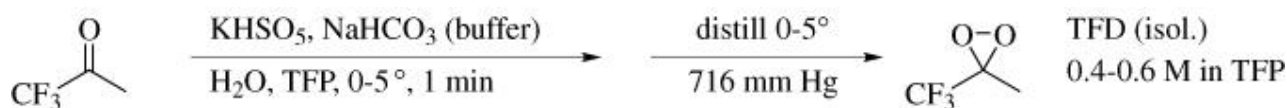
a 29-cm air condenser, loosely packed with glass wool. The exit of the air condenser was connected to the top entry of a high-efficiency, double-jacketted, spiral condenser, supplied with methanol coolant (-85 to -78°) from a Colora Ultra Cryostat (Model KT 290 S). The bottom exit of the high-efficiency condenser was attached to a 25-mL receiving flask, kept at dry ice/acetone temperature (-78°). A slow stream of argon gas was passed through the reaction flask, while the solid KHSO_5 was added in one portion under vigorous agitation at $<15^\circ$ and application of water-aspirator pressure (15 mmHg). The effluent was collected as a pale yellow solution (6 mL) of DMD- d_6 in acetone (0.08 M), as determined by UV spectroscopy (cf. procedure for DMD (isol.)).

6.1.3. Dimethyldioxirane in Carbon Tetrachloride (164)

“Acetone-free” (actually not **all** of the acetone is removable!) solutions of DMD in the appropriate solvent may be prepared as reported. (164) Here the protocol is given for the preparation of DMD in CCl_4 .

The freshly distilled DMD (isol.) solution (60 mL, 0.08 M in acetone), as prepared above, was diluted with 60 mL of cold water and extracted at 5° in a chilled separately funnel with cold CCl_4 (4×3 mL), to afford a total volume of 36 mL of extract as a pale yellow solution. The concentration of the DMD solution was determined by iodometry [see procedure for TFD (isol.)], and of the remaining acetone by $^1\text{H-NMR}$ spectroscopy.

To concentrate this DMD solution still further, the combined CCl_4 extracts were washed three times with 1.5 volumes of 0.01 M phosphate buffer (pH 7, prepared by dissolving 3.9 mmol of NaH_2PO_4 and 6.1 mmol of Na_2HPO_4 in 1 L of H_2O) in a cold separatory funnel at 5° . The resulting CCl_4 solution was 0.268 ± 0.082 M in DMD (by iodometry) and 0.155 ± 0.082 M in acetone (by $^1\text{H-NMR}$ spectroscopy). Further washing led only to a greater loss of DMD without higher concentrations of DMD. The recovery of DMD from the initial



distillate was $41 \pm 7.0\%$

6.1.4. Methyl(trifluoromethyl)dioxirane in 1,1,1-Trifluoro-2-propanone [TFD (isol.)] (154, 155)

A 250-mL, four-necked, round-bottomed flask was equipped with an efficient mechanical stirrer, an addition funnel for low-boiling liquids [1,1,1-trifluoro-2-propanone (TFP boils at 21°; it is important to use ether-free TFP doubly distilled over P₂O₅ (165))], an addition funnel for solids, and a gas-inlet tube. The exit of the gas-inlet tube was connected to the top entry of a high-efficiency, double-jacketed, spiral condenser, supplied with ethanol coolant (−80°) from a Lauda RLS 6-D cryostat (2.1 kW). The bottom exit of the high-efficiency condenser was attached to a 50-mL, pear-shaped receiving flask, cooled to −60 to −50° by an ethanol bath with liquid nitrogen. A sidearm at the condenser allowed application of a slightly reduced pressure by means of a water aspirator, which controlled the desired pressure automatically.

The 250-mL, four-necked, round-bottomed flask was charged with a slurry of NaHCO₃ (13.0 g, 155 mmol) in water (13 mL) while being cooled in an ice bath. Potassium monoperoxysulfate (24.0 g, 39.1 mmol) was added through the addition funnel to the vigorously stirred slurry of NaHCO₃, while much CO₂ gas evolved. The precooled (0°) addition funnel for liquids was quickly charged with TFP (12.0 mL, 134 mmol) after 80 seconds of CO₂ evolution, and the TFP was added to the reaction mixture within 1 minute. After a further 20 seconds the water aspirator was adjusted to a slight vacuum (650 mmHg) and the pale yellow solution of the TFD in TFP was collected in the cooled (−60 to −50°) receiving flask. After 8 minutes a new batch of potassium monoperoxysulfate (8.0 g, 13 mmol) was added, and the reaction mixture was stirred for an additional 8 minutes. The water aspirator was disconnected and the receiving flask was allowed to warm to −25° (to allow the frozen CO₂ to evolve). The flask was removed after 5 minutes from the high-efficiency condenser, tightly closed with a plastic stopper, and wrapped with aluminum foil to protect the TFD from light. IR (vapor): 1259, 1189, 971 cm^{−1}; (155) ¹H NMR (200 MHz, −20°) δ 1.97 (s); (155) ¹³C NMR (100 MHz, −20°) δ 14.5 (q), 97.3 (q, J_{C-F} = 40.2 Hz), 122.2 (q, J_{C-F} = 280.7 Hz); (155) ¹⁷O NMR (54 MHz, −20°) δ 297 (s); (155) ¹⁹F NMR (188 MHz, −20°) δ −81.5 (s); (155) UV: λ_{max} 347 nm (ε » 9 M^{−1}cm^{−1} at 0°). (155) The TFD yield was 2.0 ± 0.5% (relative to TFP) and was determined iodometrically (1 mL H₂O, 3 mL glacial acetic acid, 0.5 mL saturated KI solution; addition of 0.200 mL of the TFD solution at 0°; titration with a freshly standardized 0.05 N Na₂S₂O₃ solution). The concentration of TFD in TFP ranged from 0.4 to 0.6 M, the volume of the distillate from 4 to 6 mL (determined gravimetrically by assuming a density of that of TFP, i.e., 1.252 g/mL).

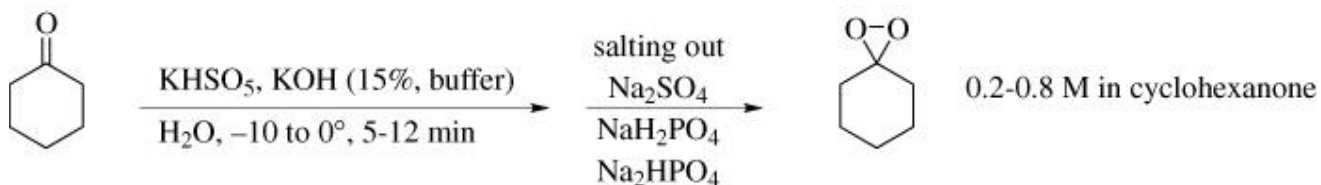
The solution can be stored for several months at −20° with only minor loss of peroxide titer (ca. 5% loss per month). A calibrated pipette, which was cooled briefly with liquid nitrogen, was used to administer conveniently amounts of the oxidant (titer ± 5% error).

6.1.5. Methyl(trifluoromethyl)dioxirane in Carbon Tetrachloride (27)

Ketone-free solutions of TFD in the appropriate solvent can be prepared as reported. (27) Here the protocol for TFD in CCl_4 is given.

A 50-mL, jacketed separatory funnel was charged with 4–6 mL of the yellow TFD (isol.) solution (0.5–0.6 M) in TFP, as prepared above, and 4–6 mL CCl_4 . The solution was washed with 8–12 mL of cold, doubly distilled water (over KMnO_4) at 0° . The TFP went quickly into the aqueous phase while the “ketone-free” TFD was contained in the organic layer. The latter was dried briefly over MgSO_4 , quickly filtered, and its TFD content was determined by iodometry [cf. procedure for TFD (isol.)]. The TFD solution in CCl_4 was stored over 4 Å molecular sieves in the freezer (-20°), and protected from exposure to light.

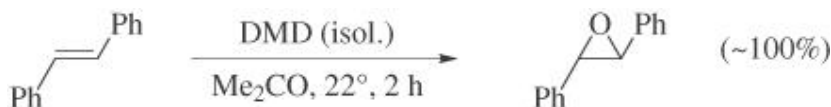
The TFD solution in CCl_4 was further concentrated by slow evaporation of a frozen (liquid N_2) sample under high vacuum (>0.01 mmHg). The effluent was condensed in a cold trap kept at liquid nitrogen temperature. Typically, 2 mL of an 0.85 M solution of TFD in CCl_4 was obtained from 3 mL of a 0.6 M solution.



6.1.6. 1,2-Dioxaspiro[2.5]octane (Cyclohexanone Dioxirane) (156, 157)

All materials used in the preparation, including drying agents, were cooled in an ice-salt bath before use. Cyclohexanone (50 mL) and crushed ice (10–15 g) were stirred well with a mechanical stirrer. A cold slurry of potassium monoperoxysulfate (35 g) in water (100 mL) was added to the reaction vessel over a period of 5–10 minutes while the pH was maintained between 7.5 and 8.5 by addition of cold 15% KOH , followed by additional stirring for 1–2 minutes. At this point, the reaction mixture was dark yellow. The reaction mixture was then poured into a cold mixture of 70 g of sodium sulfate, sodium dihydrogen phosphate, and sodium monohydrogen phosphate (4:2:1). This mixture was stirred vigorously for a few seconds and then poured into a cold separatory funnel; care was taken to minimize the transfer of undissolved salts to the separatory funnel. The yellow organic layer was then separated and dried (Na_2SO_4). The separated liquid was then decanted, dried over molecular sieves, and stored in the freezer. The concentration of the dioxirane obtained in this manner was in the range 0.2–0.8 M, as determined by iodometric titration [see the TFD (isol.) procedure above.]

6.2. Epoxidations

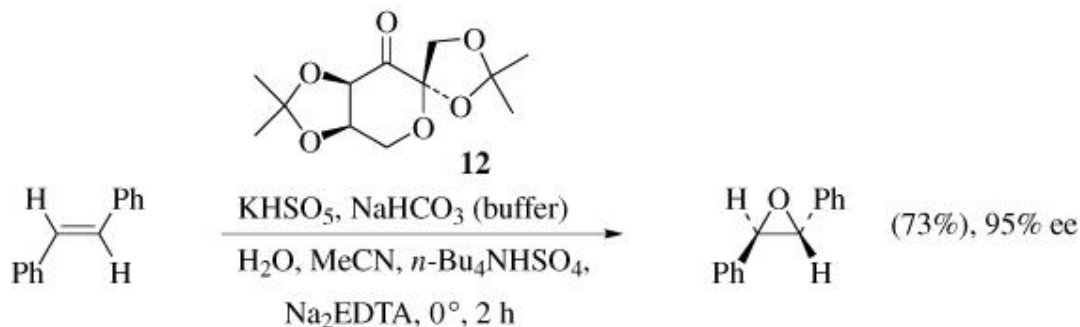


6.2.1. Racemic *trans*-1,2-Diphenyloxirane Method A [with DMD (isol.)] (163)

To a magnetically stirred solution of *trans*-stilbene (0.724 g, 4.02 mmol) in 5 mL of acetone, contained in a 125-mL stoppered Erlenmeyer flask, was added a solution of DMD in acetone (0.062 M, 66 mL, 4.09 mmol) at room temperature (ca. 20°). The progress of the reaction was followed by GLC analysis, which indicated that *trans*-stilbene was converted into the oxide in 6 hours. Removal of the excess acetone on a rotary evaporator (20°, 15 mmHg) afforded a white crystalline solid. The solid was dissolved in CH₂Cl₂ (30 mL) and dried over anhydrous Na₂SO₄. The drying agent was removed by filtration and washed with CH₂Cl₂. The solution was concentrated on a rotary evaporator, and the remaining solvent was removed (20°, 15 mmHg) to give an analytically pure sample of the oxide (0.788 g, 100%). Crystallization from aqueous EtOH gave white plates, mp 69–70°; IR (CHCl₃) 3076, 3036, 2989, 1603, 1497, 1457, 870 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 3.86 (s, 2 H), 7.26–7.45 (m, 10 H); ¹³C NMR (75 MHz, CDCl₃): δ 62.8 (d), 125.4 (d), 128.2 (d), 128.4 (d), 137.0 (s).

6.2.2. Method B [with DMD (in Situ)] (36)

To a 5-L, three-necked flask, equipped with a mechanical stirrer, was added *trans*-stilbene (18.0 g, 100 mmol), a mixture of CH₃CN and dimethoxymethane (1.17 L, 2:1 v/v) as solvent, 0.1 M aqueous K₂CO₃ (330 mL), acetone (220 mL, 3 mol), and tetrabutylammonium hydrogen sulfate (1.5 g). Potassium monoperoxysulfate (92.2 g, 150 mmol) in 330 mL of aqueous 4 × 10⁻⁴ M EDTA and K₂CO₃ (92.2 g, 667 mmol) in 330 mL of H₂O were added separately by means of addition funnels over a period of 2 hours, while the pH was adjusted to 10.5 by administering glacial acetic acid dropwise. Subsequently, the reaction mixture was extracted with hexane (3 × 1.5 L), the extracts were washed with brine (1 × 1 L), dried (Na₂SO₄), concentrated (20°, 15 mmHg), and the residue was purified by flash chromatography on silica gel (deactivated with 1% Et₃N in hexane) to yield *trans*-1,2-diphenyloxirane as a white solid (17.0 g, 87%).



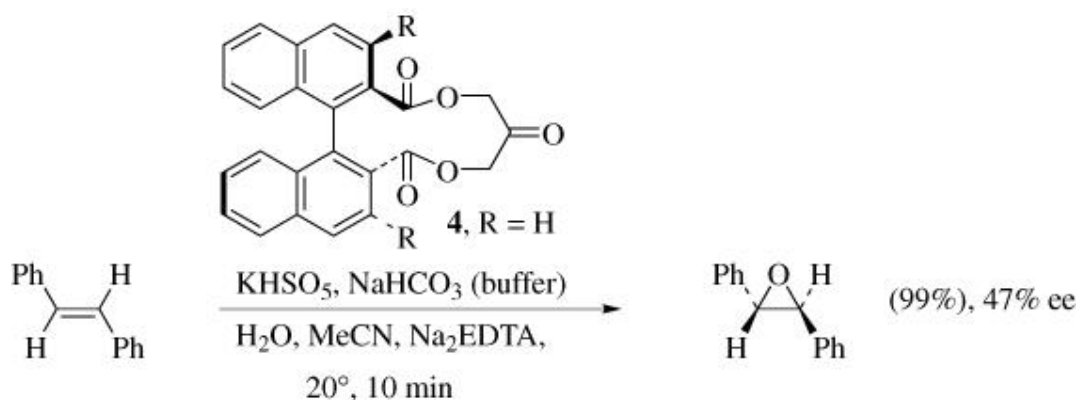
6.2.3. (*R, R*)-1,2-Diphenyloxirane with Ketone **12** Method A (Neutral, in Situ Non-Catalytic Conditions) (25, 117)

An aqueous solution of Na₂EDTA (1×10^{-4} M, 10 mL) and a catalytic amount of tetrabutylammonium hydrogen sulfate (15 mg) were added under vigorous magnetic stirring at 0° to a solution of *trans*-stilbene (0.18 g, 1.00 mmol) in acetonitrile (15 mL), contained in a stoppered 100-mL Erlenmeyer flask. A mixture of potassium monoperoxysulfate (3.07 g, 5.00 mmol) and sodium bicarbonate (1.3 g, 15.5 mmol) was pulverized and a small portion of this solid mixture was added to the reaction mixture to bring the pH to above 7. After 5 minutes, 0.77 g (3.0 mmol) of ketone **12** was added in equal portions over a period of one hour. Simultaneously, the rest of the pulverized solid mixture of KHSO₅ and sodium bicarbonate was added in equal portions within 50 minutes to maintain the pH at 7. After completion of the addition, the reaction mixture was magnetically stirred for another hour at 0°, diluted with water (30 mL), and extracted with hexane (4 × 40 mL). The combined extracts were washed with brine, dried (Na₂SO₄), filtered, and concentrated (20°, 15 mmHg). The product was purified by flash chromatography on silica gel (deactivated with 1% Et₃N in hexane), first eluted with hexane and subsequently with a 50:1 mixture of hexane/Et₂O to afford (*R,R*)-1,2-diphenyloxirane as a white solid (0.149 g, 73%, 95.2% ee). The ee value was determined by ¹H-NMR spectroscopy with Eu(hfc)₃ as the shift reagent.

6.2.4. Method B (Basic, in Situ Catalytic Conditions) (25)

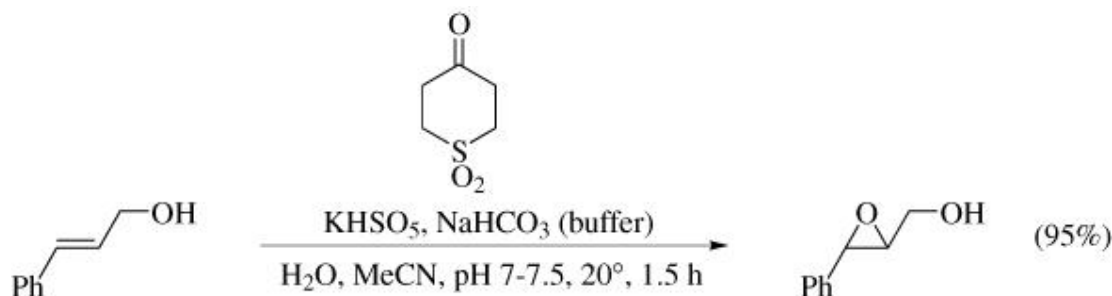
To a solution of *trans*-stilbene (0.181 g, 1.00 mmol) in CH₃CN /DMM mixture (15 mL, 1:2 v/v), contained in a stoppered, 100-mL Erlenmeyer flask, was added an aqueous solution (10 mL) of 0.05 M Na₂B₄O₇ · 10H₂O, which contained 4×10^{-4} M Na₂EDTA, tetrabutylammonium hydrogen sulfate (15 mg, 0.04 mmol), and 0.0774 g (0.30 mmol) of ketone **12**. An aqueous solution (6.5 mL) of potassium monoperoxysulfate (1.00 g, 1.60 mmol) contained in 4×10^{-4} M Na₂EDTA and an aqueous solution (6.5 mL) of K₂CO₃ (0.93 g, 6.74 mmol) were added dropwise with vigorous magnetic stirring at 0° over a period of 30 minutes through two separate addition funnels. The reaction

mixture was then diluted with water (30 mL) and extracted with hexane (4 × 40 mL). The combined extracts were washed with brine, dried (Na₂SO₄), filtered, and concentrated (20°, 15 mmHg). The product was purified by flash chromatography on silica gel (deactivated with 1% Et₃N in hexane), by first eluting with hexane and subsequently with a mixture of 50:1 hexane/Et₂O, to afford (*R,R*)-1,2-diphenyloxirane as a white solid (0.166 g, 85%, 97.9% ee), mp 68–70° (hexane); [α]_D²⁵ +356.1° (c 0.95, benzene). The ee value was determined by ¹H-NMR spectroscopy with Eu(hfc)₃ as the shift reagent.



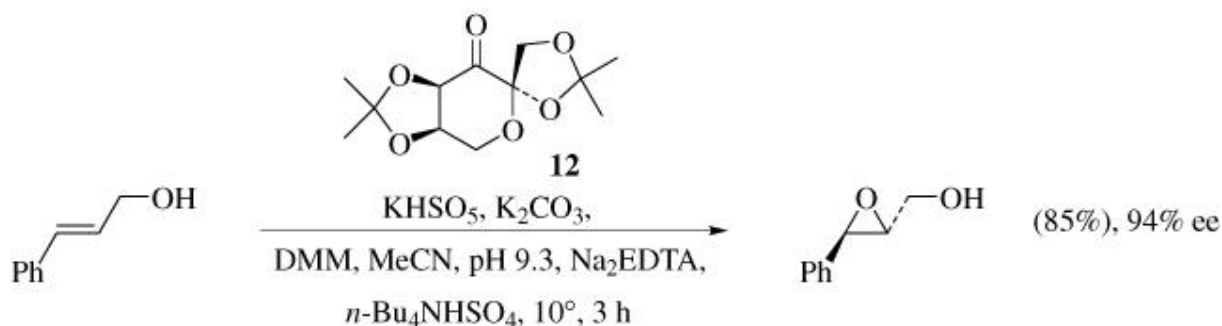
6.2.5. (*S,S*)-1,2-Diphenyloxirane with Ketone **4** (in Situ Catalytic Conditions) (24)

To a solution of *trans*-stilbene (18.0 mg, 0.10 mmol) and ketone **4** (R = H) (29.6 mg, 0.10 mmol) in CH₃CN (1.5 mL) contained in a stoppered, 25-mL Erlenmeyer flask at room temperature (ca. 20°) was added a 4 × 10⁻⁴ M aqueous Na₂EDTA solution (1 mL). To this solution was added in portions a solid mixture of pulverized sodium bicarbonate (130 mg, 1.55 mmol) and potassium monoperoxysulfate (614 mg, 1.00 mmol), while vigorously stirring magnetically. After 7 minutes, the reaction mixture was poured into water (20 mL), extracted with CH₂Cl₂ (3 × 20 mL), and dried (Na₂SO₄). Upon removal of the solvent (20°, 15 mmHg), the residue was purified by flash chromatography on silica gel (deactivated with 2% Et₃N in hexane), by first eluting with hexane (50 mL), followed by a 1:19 mixture of EtOAc/hexane (100 mL), which gave (*S,S*)-1,2-diphenyloxirane [19.4 mg, 99%, 47% ee]. Subsequent elution with a 2:3 mixture of EtOAc/hexane afforded 27.6 mg (93% recovery) of ketone **4**. The ee was determined by ¹H-NMR spectroscopy with Eu(hfc)₃ as chiral shift reagent.



6.2.6. Racemic 2,3-Epoxy-3-phenyl-1-propanol with 1,1-Dioxotetrahydrothiopyran-4-one as Ketone Catalyst (38)

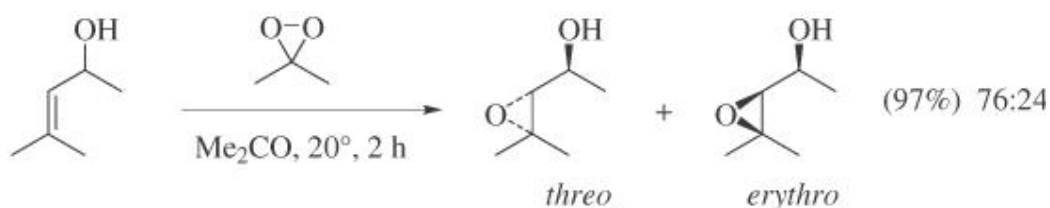
A 50-mL stoppered Erlenmeyer flask was charged with a CH₃CN solution (9 mL) of cinnamyl alcohol (2.0 mmol), ketone catalyst (5 mol%), and an aqueous Na₂EDTA solution (6 mL, 4 × 10⁻⁴ M). At room temperature was added, with vigorous magnetic stirring, a pulverized solid mixture of KHSO₅ (1.84 g, 3.0 mmol) and NaHCO₃ (0.78 g, 9.3 mmol) within 1.5 hours. The reaction progress was monitored by TLC (silica gel) and after complete consumption of the substrate, the reaction mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were dried (MgSO₄) and concentrated (20°, 15 mmHg). The residue was purified by flash chromatography on silica gel to afford the epoxide (95% yield) and ketone catalyst (80% recovery).



6.2.7. (R,R)-2,3-Epoxy-3-phenyl-1-propanol with Ketone 12 (in Situ Catalytic Conditions) (149a)

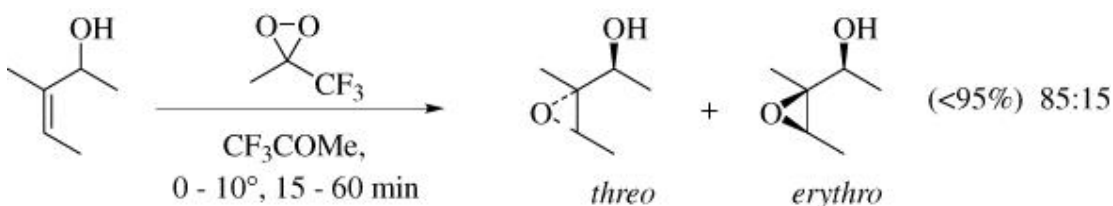
A 100-mL, two-necked, round-bottomed flask, equipped with a magnetic stirrer, was charged with cinnamyl alcohol (136 mg, 1.0 mmol), ketone **12** (77.4 mg, 0.30 mmol), and tetrabutylammonium hydrogen sulfate (15.0 mg, 0.016 mmol) in 10 mL of DMM/ CH₃CN (2:1 v/v). An aqueous solution (7 mL) of

K_2CO_3 /HOAc [prepared by mixing 100 mL of 0.1 M aqueous K_2CO_3 and 0.5 mL HOAc (pH 9.3)] was added with stirring and cooling in a NaCl/ice bath (-10°). This was followed by the dropwise addition of an aqueous solution (5 mL) of $KHSO_5$ (0.85 g, 1.38 mmol) in 4×10^{-4} M Na_2EDTA and an aqueous solution (5 mL) of K_2CO_3 (0.80 g, 5.8 mmol), separately by means of syringe pumps, over a period of 3 hours. After CH_2Cl_2 (20 mL) and water were added, the aqueous layer was extracted with CH_2Cl_2 (3×20 mL), and the combined organic phases were washed with brine, dried (Na_2SO_4), and concentrated (20° , 15 mmHg). The residue was purified by flash chromatography on silica gel [deactivated with 1% Et_3N in hexane/ Et_2O (2:1 v/v)] by elution with a hexane/ Et_2O mixture [first 2:1 (v/v) and subsequently 1:1 (v/v)], to afford 0.128 g (85% yield) of the epoxide (94% ee, by chiral HPLC on a Chiracel OD column).



6.2.8. *threo*- and *erythro*- α ,3,3-Trimethyloxiranemethanol [with DMD (isol.)] (72)

A stoppered 25-mL Erlenmeyer flask was charged at 20° with 72 mg (0.72 mmol) of 4-methylpent-3-en-2-ol and a 0.069 M solution (10 mL, 0.73 mmol) of DMD (isol.). The mixture was stored at 20° in the dark until the peroxide test (KI /HOAc) was negative. The solvent was removed (20° , 20 mmHg) and 81 mg (97% yield) of a 76:24 mixture of *threo*/*erythro* epoxides (by 1H -NMR analysis) were obtained as a colorless oil.



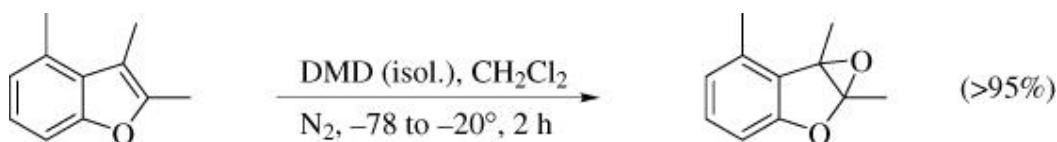
6.2.9. *threo*- and *erythro*- α ,2,3-Trimethyloxiranemethanol [with TFD (isol.)] (80)

stirring at 0° an aqueous solution (4×10^{-4} M) of Na₂EDTA (1.0 mL). A mixture of KHSO₅ (307 mg, 0.500 mmol) and NaHCO₃ (130 mg, 1.55 mmol) as a pulverized solid was added in small portions over 50 minutes. Ketone **12** (77.5 mg, 0.300 mmol) was added in portions simultaneously. The mixture was stirred magnetically for 18 hours at 0°, and was then diluted with water and extracted with hexane. The hexane extracts were combined and concentrated (40°, 250 mmHg). Methanol (5 mL) was added to the residue and the solution was stirred for 2 hours for complete desilylation. After removal of the methanol (20°, 15 mmHg), the crude product was purified by silica gel chromatography (1:2 Et₂O/ petroleum ether as eluent) to give the title compound as a colorless oil (10.4 mg, 69%, 82% ee). The ee value was determined by HPLC analysis on a Chiralcel OD column, 9:1 hexane/2-propanol, flow 0.6 mL/min. IR (film): 3700–3100 (br), 3063, 2981, 2933, 1682, 1597, 1578, 1451, 1271 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ 1.42 (d, *J* = 7.0 Hz, 3 H), 3.81 (s, 1 H, OH), 5.14 (q, *J* = 7.0 Hz, 1 H), 7.44–7.59 (m, 3 H), 7.87–7.95 (m, 2 H). ¹³C NMR (63 MHz, CDCl₃): δ 22.5 (q), 69.6 (d), 128.9 (d), 129.1 (d), 133.6 (s), 134.2 (d), 202.6 (s).



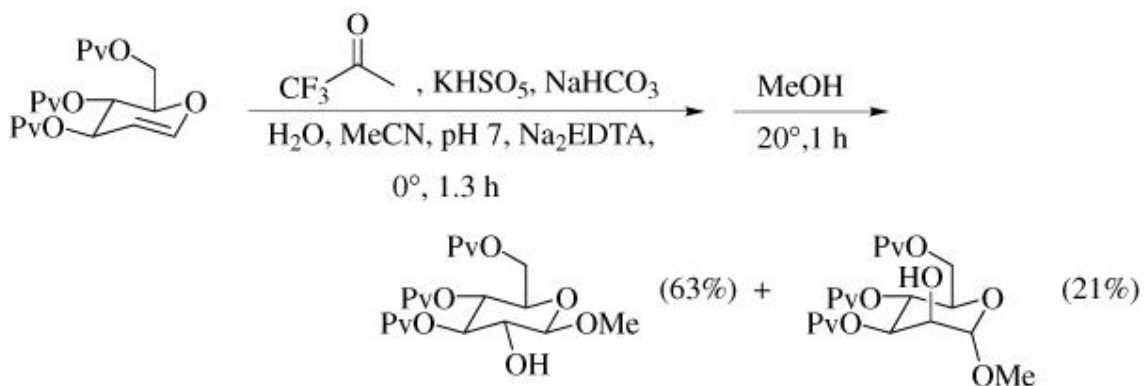
6.2.12. *trans*-(2-Methyloxiranyl)Benzamide [with DMD-*d*₆ (isol.)] (**167**)

A 5-mm NMR tube was charged at -78° under a N₂ atmosphere with 9.0 mg (55.8 μmol) of the enamide in 50 μL of CDCl₃. By means of a syringe, 750 μL (55.9 μmol) of a well-dried (over 4 Å molecular sieves) 0.074 M solution of DMD-*d*₆ (isol.) in acetone-*d*₆ was added rapidly at -78°. After 1 hour, the NMR tube was submitted to low-temperature (-50°) ¹H-NMR and ¹³C-NMR spectroscopy, which showed that the epoxide was obtained quantitatively. At temperatures higher than -50°, the epoxy enamide deteriorated into an intractable, undefined product mixture. ¹H NMR (acetone-*d*₆, 200 MHz, -50°): δ 1.37 (d, *J* = 6.8 Hz, 3 H, CH₃), 3.36 (m, 1 H, CH), 4.82 (m, 1 H, CH), 7.49–7.59 (m, 3 H), 7.86–7.99 (m, 2 H), 8.14 (br s, 1 H; NH); ¹³C NMR (acetone-*d*₆, 50 MHz, -50°): δ 16.8 (q, CH₃), 53.3 (d, CH), 61.6 (d, CH), 127.8 (2xd), 129.1 (2xd), 132.6 (d), 134.2 (s), 168.8 (s, CO).



6.2.13. 2,3-Epoxy-2,3-Dihydro-2,3,4-Trimethylbenzo[b]furan [with DMD (isol.)] (48)

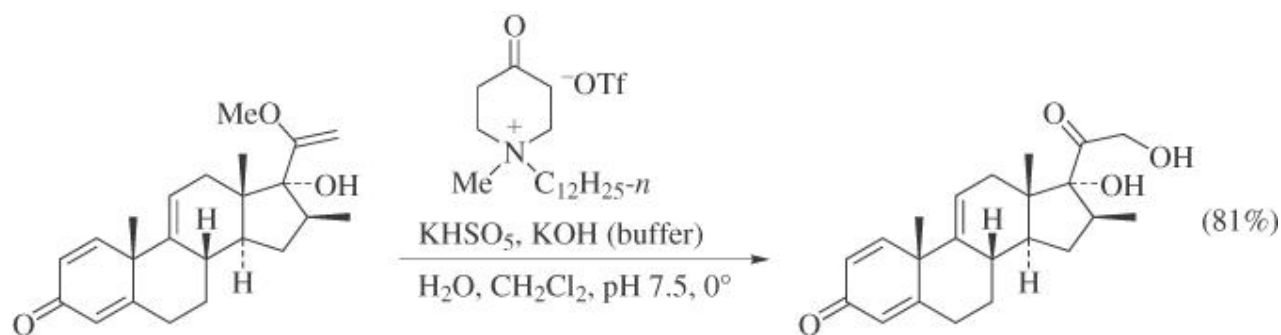
A cooled (-78° , 0.086 M) solution of dimethyldioxirane in acetone (15 mL, 1.30 mmol), dried over 4 Å molecular sieves, was rapidly added to a cooled (-78°), magnetically vigorously stirred solution of 2,3,4-trimethylbenzofuran (160 mg, 1.00 mmol) in dry CH_2Cl_2 (2 mL) under a N_2 atmosphere. Stirring was continued for 3 hours at -78 to -20° . The solvent was removed (-20° , 0.001 mmHg) to afford the benzofuran epoxide essentially quantitatively, as confirmed by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis at -20° . $^1\text{H NMR}$ (200 MHz, acetone- d_6 , -20°): δ 1.82 (s, 3 H), 1.84 (s, 3 H), 2.46 (s, 3 H), 6.74–6.78 (m, 2 H), 7.12–7.70 (m, 1 H). $^{13}\text{C NMR}$ (50 MHz, acetone- d_6 , -20°): δ 13.9 (q), 14.7 (q), 18.8 (q), 67.2 (s), 94.8 (s), 109.2 (d), 123.7 (d), 128.4 (s), 129.6 (d), 136.6 (s), 160.4 (s).



6.2.14. Methyl 3,4,6-Tri-O-Pivaloyl- β -D-Glucopyranoside and Methyl 3,4,6-Tri-O-Pivaloyl- α -D-mannopyranoside [with TFD (in Situ)] (35)

A stoppered 10-mL Erlenmeyer flask, equipped with a magnetic stirring bar, was charged with a CH_3CN solution (1 mL) of 3,4,6-tri-O-pivaloyl-D-glucal (40 mg, 0.1 mmol) and an aqueous solution of Na_2EDTA (0.4 mL, 4×10^{-4} M). After cooling to 8° by means of an ice bath, TFP (0.2 mL) was added by means of a precooled syringe. A powdered mixture of solid KHSO_5 (0.307 g, 1.00 mmol) and solid NaHCO_3 (0.130 g, 155 mmol) was added to the vigorously stirred mixture. The reaction was complete within 15 minutes, as

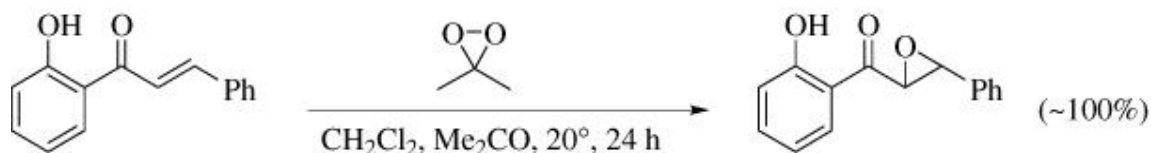
assessed by TLC (silica gel) monitoring. Anhydrous Na_2SO_4 (3.0 g) was added at 20° followed by dry MeOH (10 mL). TLC (silica gel) monitoring indicated that ring-opening of the epoxide was complete within 1 hour. After the addition of water (20 mL), the reaction mixture was extracted with CH_2Cl_2 (3×20 mL), and the combined extracts were dried (Na_2SO_4) and concentrated (20° , 15 mmHg). The residue was purified by flash column chromatography on silica gel, with a 23:77 mixture of EtOAc and hexane as eluent, to afford 28.2 mg (63% yield) of glucopyranoside as a colorless solid and 9.5 mg (21% yield) of mannopyranoside as a colorless oil.



6.2.15. 17α -hydroxy-21-Hydroxypregna-4,9(11)-diene-3,20-dione with 1-Dodecyl-1-Methyl-4-Oxopiperidinium Trifluoromethanesulfonate as Ketone Catalyst (168)

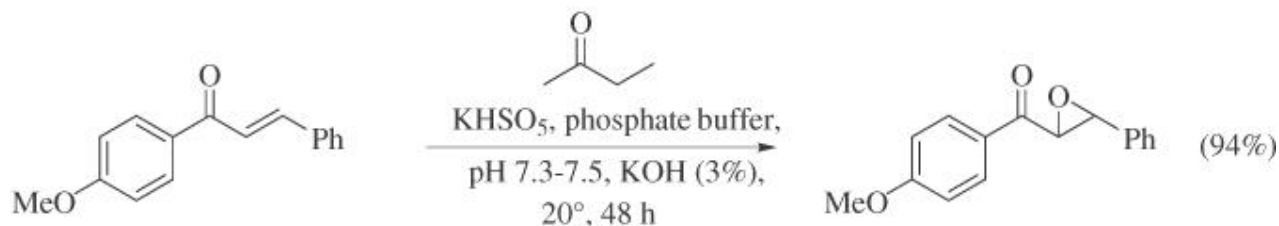
A 250-mL, three-necked, round-bottomed flask was equipped with a Brinkmann-Heidolph overhead stirrer (Model No. 2050). The glass stirring shaft was fitted with an elliptically shaped Teflon stirring paddle (40-mm long \times 18-mm high \times 3-mm wide). A glass pH probe/electrode (Broadley-James Model No. C1207A-121-A03BC), connected to a Brinkmann pH-stat (Brinkmann Models: E512 pH meter, Impulsomat No. 473, and Dosimat No. E412), was inserted into the flask at one of the side necks of the flask and clamped such that the bottom of the probe was 0.5–1.0 cm from the bottom of the flask. The third neck was fitted with two separate Teflon tubes, one that delivered KOH (2 N) (the rate of addition was controlled by the pH-stat) and the other that delivered aqueous KHSO_5 [(0.45 M, stabilized by 0.43 mM Na_2EDTA), its rate of addition controlled by a syringe pump (Sage Instruments Model 355)]. The 250-mL flask was charged with phosphate buffer (23 mL, pH 7.8), CH_2Cl_2 (20 mL), the steroid (75 mg, 0.21 mmol), and the ketone catalyst (9 mg, 0.021 mmol). The contents were cooled to 0° by means of an ice bath, and with vigorous stirring (800–1000 rpm), the aqueous KHSO_5 solution (4.6 mL, 1.98 mol) was added by means of the syringe pump at such a rate that the pH of the reaction mixture was kept constant at $7.5 (\pm 0.1)$ by

automated simultaneous addition of the 2 N aqueous KOH solution (ca. 80 minutes). The temperature was kept at 0° by cooling with an ice bath. The reaction progress was monitored by TLC (silica gel), and after complete consumption of the steroid, the organic layer was removed. To the aqueous layer was added brine (60 mL) and the solution was extracted with CH₂Cl₂ (4 × 10 mL). The combined organic layers were dried (NaSO₄) and concentrated (20°, 15 mmHg). The residue was purified by silica gel chromatography with a 1:1 mixture of EtOAc/hexane as eluent to afford 61 mg (81% yield) of the colorless product; mp 208–209° after recrystallization from CH₂Cl₂/hexane.



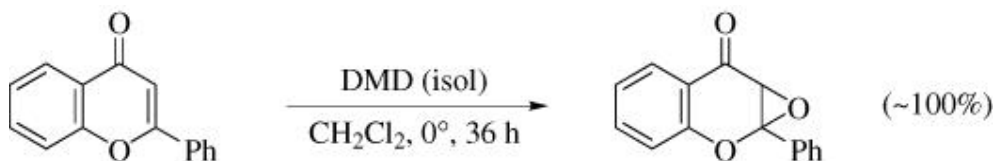
6.2.16. 2,3-Epoxy-1-(2-Hydroxyphenyl)-3-Phenyl-1-Propanone [with DMD (isol.)] (34)

A stoppered 100-mL Erlenmeyer flask equipped with a magnetic stirring bar was charged with chalcone (205 mg, 0.92 mmol) in CH₂Cl₂ (10 mL), and 17.5 mL of a 0.060 M (1.05 mmol) acetone solution of DMD (isol.) was added rapidly with stirring at 20°. After 12 hours of stirring, a fresh batch of 17.5 mL of a 0.060 M (1.05 mmol) acetone solution of DMD (isol.) was added rapidly and stirring was continued for another 12 hours at 20°. The reaction progress was monitored by TLC (silica gel). After complete consumption of the chalcone, the solvent was removed (20°, 15 mmHg) and 220 mg (~100%) of pure epoxide were obtained as a colorless powder, mp 73–74° (from CHCl₃/petroleum ether).



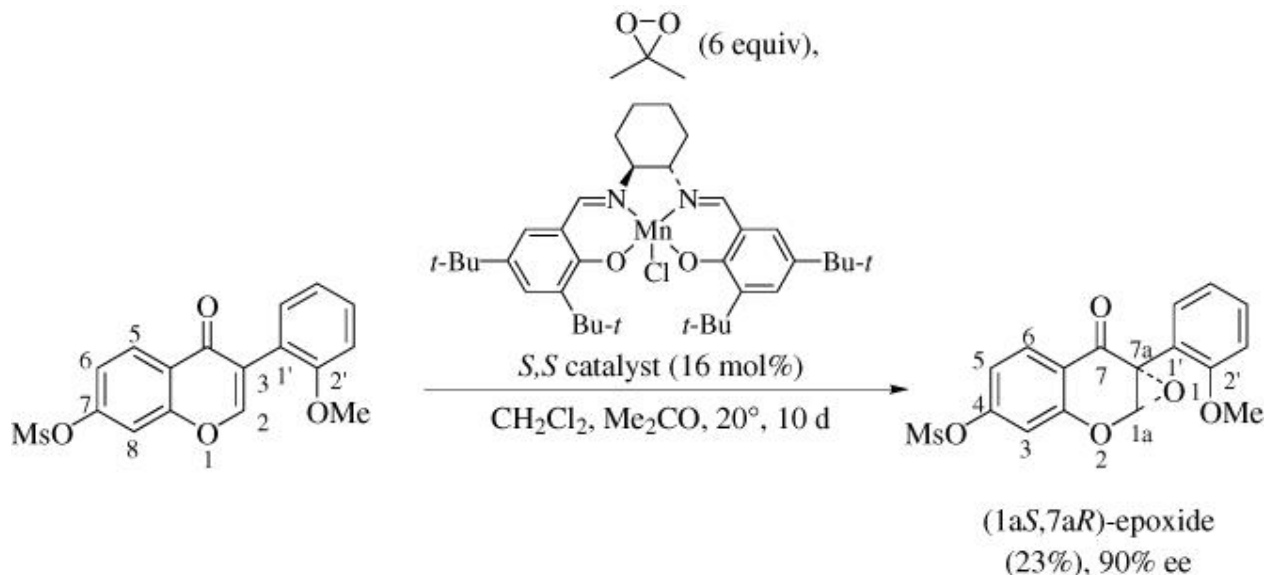
6.2.17. 1-(4-Anisyl)-2,3-Epoxy-3-Phenyl-1-Propanone with 2-Butanone as Ketone Catalyst [in Situ Catalytic Conditions] (34)

To a vigorously stirred (mechanical agitation) mixture of the chalcone (3.57 g, 15.0 mmol), 2-butanone (150 mL), and phosphate buffer, prepared by dissolving 0.177 g of KH_2PO_4 and 0.648 g of Na_2HPO_4 in 150 mL of water, contained in a 1-L, 3-necked, round-bottomed flask, was slowly added (6 hours) at room temperature a saturated aqueous solution (200 mL) of KHSO_5 (45 g, 0.073 mol). The pH of the mixture was kept at 7.3–7.5 by continuously administering an aqueous KOH (3%) solution. After 18 hours of additional stirring, a new batch of a saturated, aqueous solution (200 mL) of KHSO_5 (45 g, 0.073 mol) was added slowly (6 hours) and the mixture was stirred for an additional 18 hours. The reaction progress was monitored by TLC (silica gel). After complete consumption of the chalcone, solid NaCl was added to the cloudy reaction mixture until saturation, the organic phase was separated by decantation, and the aqueous phase was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were dried (MgSO_4), filtered, and the solvent was evaporated (20°, 15 mmHg) to afford 3.60 g (94%) of the epoxide in high purity (by $^1\text{H-NMR}$ spectroscopy) as colorless plates, mp 75–76°.



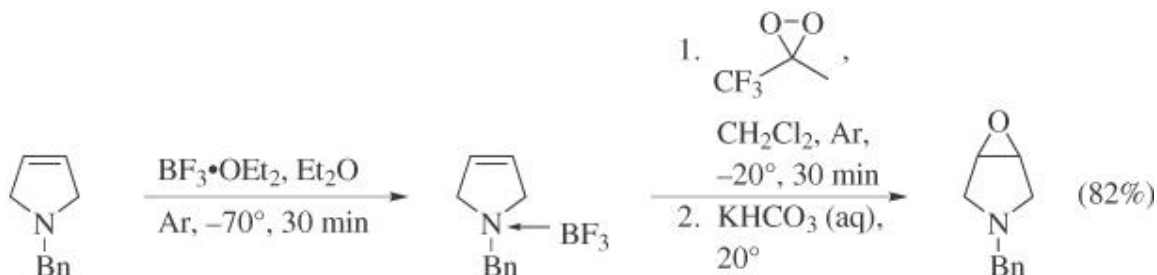
6.2.18. 1a,7a-Dihydro-1a-Phenyl-7H-Oxireno[b][1]Benzopyran-7-One (Flavone Epoxide) [with DMD (isol.)] (59)

A stoppered 125-mL Erlenmeyer flask was charged with 187 mg (0.840 mmol) of flavone in 10 mL CH_2Cl_2 . While stirring magnetically, a total of 61.5 mL of a 0.084 M (5.14 mmol) DMD solution in acetone was added at 20° in equal portions at three 12-hour intervals. After 36 hours, the conversion of the flavone was complete, as confirmed by TLC (silica gel), and the solvent was removed (20° at 15 mmHg) to yield 200 mg (~100%) of the epoxide as colorless needles, mp 99–100° (from CHCl_3 /petroleum ether).



6.2.19. (1*aS*,7*a**R*)-1*a*,7*a*-Dihydro-4-Mesyloxy-7*a*-(2-Methoxyphenyl)-7*H*-oxireno[*b*][1]Benzopyran-7-One with Jacobsen's (*S,S*)-Catalyst [with DMD (isol.)] (103, 104)**

A stoppered 250-mL Erlenmeyer flask equipped with a magnetic stirring bar was charged with the isoflavone (346 mg, 1.00 mmol) and the *S,S*-configured Jacobsen's Mn(III)salen complex (101 mg, 0.16 mmol, 16 mol %) in dry CH₂Cl₂ (10 mL). While stirring magnetically, 12.0 mL of a 0.05 M (0.6 mmol) acetone solution of DMD (isol.) was added at 20°. The reaction progress was monitored by TLC (silica gel), and new batches (as above) were added in 24-hour intervals until the consumption of the isoflavone halted [40% conversion after 10 days reaction time, during which a total of 120 mL (6.0 mmol) of DMD (isol.) in acetone was administered]. The solvent was evaporated (25, 15 mmHg) and the product was purified by silica gel chromatography, with toluene/EtOAc (4:1 v/v) as eluent, to afford 83.3 mg (23% yield) of the epoxide; colorless plates (methanol), mp 145–146°; 90% ee, determined by chiral HPLC analysis (Chiracel OD column), with hexane/2-propanol (9:1) as eluent (flow rate 0.6 mL/minute).



6.2.20. *N*-Benzyl-3,4-Epoxyrrolidine [with TFD (isol.)] (63)

A 10-mL, two-necked, round-bottomed flask with gas-inlet and gas-outlet tubes and magnetic stirring bar was charged with a solution of *N*-benzyl-3-pyrrolidine (159 mg, 1.0 mmol) in Et₂O (2 mL). To this solution was added with stirring under argon 135 μ L (1.05 mmol) of freshly distilled BF₃ · Et₂O at -70°. The mixture was stirred for 30 minutes under these conditions, and a white solid precipitated. The solvent was removed (-20°, 1 mmHg), to afford the BF₃ adduct of the amine quantitatively. ¹H-NMR analysis confirmed that all of the ether had been rigorously removed. ¹H NMR (300 MHz) δ 3.89 (d, *J* = 14 Hz, 2 H), 4.13 (s, 2 H), 4.26 (d, 2 H), 5.48 (s, 2 H), 7.30–7.60 (m, 5 H). ¹³C NMR (75 MHz) δ 59.9 (2 × t), 60.4 (2 × t), 124.7 (2 × d), 128.6 (2 × d), 129.4 (d), 131.7 (2 × d).

The BF₃ adduct was dissolved in dry CH₂Cl₂ (3 mL) at -70°, and the solution was added at this temperature with stirring to 1.9 mL of a 0.60 M solution (1.1 mmol) of TFD (isol.). The reaction mixture was allowed to warm to -20° and stirred for 30 minutes for complete consumption of the TFD, as confirmed by the negative peroxide test (KI/HOAc). The reaction mixture was poured into 100 mL of a 0.1 M aqueous KHCO₃ solution at 20°, and extracted with *tert*-butyl methyl ether (2 × 50 mL). The combined organic phases were dried (MgSO₄) and concentrated (20°, 15 mmHg). The residue was purified by alumina (grade V) chromatography, first with hexane as eluent and subsequently with a 1:1 mixture of hexane and *tert*-butyl methyl ether to afford the pure epoxide (143 mg, 82% yield) as a colorless oil. IR (film): 3028, 2933, 2894, 2846, 2800, 1454, 1377, 1153, 844 cm⁻¹. ¹H NMR (200 MHz): δ 2.67 (d, *J* = 12 Hz, 2 H), 3.24 (d, *J* = 12 Hz, 1 H), 3.64 (s, 2 H), 3.80 (s, 2 H), 7.12–7.50 (m, 5 H). ¹³C NMR (50 MHz): δ 53.2(2 × t), 55.6 (2 × d), 59.8 (t), 127.3 (s), 128.3 (2 × d), 129.0 (2 × d), 137.2 (s). Anal. Calcd. for C₁₁H₁₃NO: C, 75.40, H, 7.48, N, 7.99. Found C, 75.43, H, 7.51, N, 8.06.

7. Tabular Survey

The epoxidation of alkenes by dioxiranes is presented in the appended tables. The literature survey was conducted by computer search of *Chemical Abstracts* (CAS-on-line), and the references cover work inclusive of the first quarter of 2000.

The tables are arranged in the order of the discussion in the section on Scope and Limitations. Thus, the data on epoxidation of simple alkenes, alkenes with electron donors, with electron acceptors, and with both electron donors and acceptors by isolated dioxiranes (mainly DMD) are presented in Tables IA–ID. Epoxidations with in situ generated achiral dioxiranes are shown in Table IE. Chemo- and regioselective epoxidations are collected in Tables II and III, while the diastereoselective epoxidations of chiral alkenes by isolated and in situ generated dioxiranes are shown in Table IV. Enantioselective reactions, for which the catalytic in situ method has been applied exclusively, are compiled in Table V.

The entries within each table are arranged in order of increasing carbon number of the alkene substrate. The carbon count is based on the total number of carbon atoms. In Table V, the structures of the chiral ketone catalysts are given in a separate column, left of the column on reaction conditions. Yields of products are given in parentheses, and a dash (—) indicates that no yield was reported in the original reference. If reported in the original reference, the data on conversion (% convn) are mentioned in the product column, preferentially in subtables. Ratios of different products or diastereomers are normalized to 100, and given without parentheses. In Table V, the enantiomeric excess (% ee) for the major isomer is listed in the product column without parentheses.

The following abbreviations are used in the tables:

Ac	acetyl
Bn	benzyl
CBZ	benzyloxycarbonyl
Cp	cyclopentadienyl
DMAP	4-(dimethylamino)pyridine
DMD	dimethyldioxirane
DMD (in situ)	in situ generated dimethyldioxirane
DMD (isol.)	isolated dimethyldioxirane in acetone

DMD- d_6	isolated hexadeuterated dimethyldioxirane in acetone- d_6 (isol.)
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMM	dimethoxymethane
EDTA	ethylenediaminetetraacetic acid
Na ₂ EDTA	disodium salt of ethylenediaminetetraacetic acid
ee	enantiomeric excess
HMPA	hexamethylphosphoric triamide
LDA	lithium diisopropylamide
Ms	methanesulfonyl (mesyl)
Oxone	potassium monoperoxysulfate
TBS	<i>tert</i> -butyldimethylsilyl
TDMPP	dianion of 5,10,15,20-tetrakis(2,6-dimethoxyphenyl)porphyrin
C18	dianion of 5,10,15,20-tetrakis(3,5-dichloro-2,6-dimethoxyphenyl)porphyrin
TDMPP	
C116	dianion of
TDMPP	2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(3,5-dichloro-2,6-dimethoxyphenyl)porphyrin
Tf	trifluoromethylsulfonyl (triflyl)
TFD	methyl(trifluoromethyl)dioxirane
TFD (in situ)	in situ generated methyl(trifluoromethyl)dioxirane
TFD (isol.)	isolated methyl(trifluoromethyl)dioxirane in TFP
TFP	1,1,1-trifluoro-2-propanone
THF	tetrahydrofuran
THP	tetrahydropyranyl
TMS	trimethylsilyl
Tr	trityl (triphenylmethyl)
Ts	<i>p</i> -toluenesulfonyl

Table 1A. Epoxidation of Unfunctionalized Olefins by Isolated Dioxiranes

[View PDF](#)

Table 1B. Epoxidation of Olefinic Substrates with Electron Donors by Isolated Dioxiranes

[View PDF](#)

Table 1C. Epoxidation of Olefins with Electron Acceptors by Isolated Dioxiranes

[View PDF](#)

Table 1D. Epoxidation of Olefins with Electron Donors and Acceptors by Isolated Dioxiranes

[View PDF](#)

Table 1E. Epoxidation of Olefins by In-situ-generated Dioxiranes

[View PDF](#)

Table 2. Chemoselective Oxidations by Isolated Dioxiranes

[View PDF](#)

Table 3. Regioselective Epoxidations by Dioxiranes

[View PDF](#)

Table 4. Diastereoselective Epoxidations of Alkenes by Dioxiranes

[View PDF](#)

Table 5. Enantioselective Epoxidation of Olefins by Enantiomerically Enriched Dioxiranes

[View PDF](#)

TABLE 1A. EPOXIDATION OF UNFUNCTIONALIZED OLEFINS BY ISOLATED DIOXIRANES



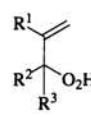
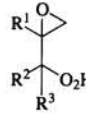
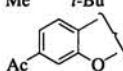






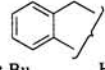
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																
C_2 	Difluorodioxirane, CF ₄ , O ₂ , 77 K	 (—) <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </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>Me</td> <td>Me</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Me</td> </tr> </tbody> </table>	R ¹	R ²	R ³	H	H	H	Me	H	H	Me	Me	H	Me	H	Me	169																																																																	
R ¹	R ²	R ³																																																																																	
H	H	H																																																																																	
Me	H	H																																																																																	
Me	Me	H																																																																																	
Me	H	Me																																																																																	
C_{4-11} 	DMD, acetone/CH ₂ Cl ₂	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Temp</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>0°</td> <td>3 h (>98)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Me</td> <td>20°</td> <td>8 h (82)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>20°</td> <td>1 h (71)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>20°</td> <td>1 h (96)</td> </tr> <tr> <td>Me</td> <td><i>i</i>-Pr</td> <td>H</td> <td>20°</td> <td>3 h (98)</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>H</td> <td>H</td> <td>20°</td> <td>0.5 h (98)</td> </tr> <tr> <td>Me</td> <td><i>t</i>-Bu</td> <td>H</td> <td>20°</td> <td>1.5 h (>98)</td> </tr> <tr> <td></td> <td></td> <td></td> <td>20°</td> <td>3 h (>98)</td> </tr> </tbody> </table> 	R ¹	R ²	R ³	Temp	Time	Me	H	H	0°	3 h (>98)	H	Me	Me	20°	8 h (82)	Me	Me	H	20°	1 h (71)	Me	Me	Me	20°	1 h (96)	Me	<i>i</i> -Pr	H	20°	3 h (98)	<i>t</i> -Bu	H	H	20°	0.5 h (98)	Me	<i>t</i> -Bu	H	20°	1.5 h (>98)				20°	3 h (>98)	170																																			
R ¹	R ²	R ³	Temp	Time																																																																															
Me	H	H	0°	3 h (>98)																																																																															
H	Me	Me	20°	8 h (82)																																																																															
Me	Me	H	20°	1 h (71)																																																																															
Me	Me	Me	20°	1 h (96)																																																																															
Me	<i>i</i> -Pr	H	20°	3 h (98)																																																																															
<i>t</i> -Bu	H	H	20°	0.5 h (98)																																																																															
Me	<i>t</i> -Bu	H	20°	1.5 h (>98)																																																																															
			20°	3 h (>98)																																																																															
C_5 	DMD, acetone, under N ₂ or air, -20 to 0°, 30 min	 (>98)	18																																																																																
	DMD, acetone, 25°	 (—) <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>k₂ (M⁻¹s⁻¹)</th> </tr> </thead> <tbody> <tr> <td>—(CH₂)₃—</td> <td>H</td> <td>H</td> <td>H</td> <td>0.62 ± 0.01</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>H</td> <td>2.4 ± 0.1</td> </tr> <tr> <td>Me</td> <td><i>n</i>-Pr</td> <td>H</td> <td>H</td> <td>0.61 ± 0.01</td> </tr> <tr> <td>Me</td> <td>H</td> <td><i>n</i>-Pr</td> <td>H</td> <td>0.084 ± 0.002</td> </tr> </tbody> </table> <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>k₂ (M⁻¹s⁻¹)</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>Et</td> <td>H</td> <td>H</td> <td>0.57 ± 0.02</td> </tr> <tr> <td>Et</td> <td>H</td> <td>Et</td> <td>H</td> <td>0.067 ± 0.001</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td><i>n</i>-Pr</td> <td>0.31 ± 0.01</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>Me</td> <td>7.1 ± 0.6</td> </tr> <tr> <td></td> <td>—(CH₂)₄—</td> <td>H</td> <td>Me</td> <td>1.59 ± 0.06</td> </tr> <tr> <td>Et</td> <td>Et</td> <td>Me</td> <td>H</td> <td>1.61 ± 0.06</td> </tr> <tr> <td>Et</td> <td>Me</td> <td>Et</td> <td>H</td> <td>1.08 ± 0.04</td> </tr> <tr> <td></td> <td>—(CH₂)₄—</td> <td>Me</td> <td>Me</td> <td>2.0 ± 0.1</td> </tr> <tr> <td><i>n</i>-C₈H₁₇</td> <td>H</td> <td>H</td> <td>H</td> <td>0.35 ± 0.005</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	k ₂ (M ⁻¹ s ⁻¹)	—(CH ₂) ₃ —	H	H	H	0.62 ± 0.01	Me	Me	Me	H	2.4 ± 0.1	Me	<i>n</i> -Pr	H	H	0.61 ± 0.01	Me	H	<i>n</i> -Pr	H	0.084 ± 0.002	R ¹	R ²	R ³	R ⁴	k ₂ (M ⁻¹ s ⁻¹)	Et	Et	H	H	0.57 ± 0.02	Et	H	Et	H	0.067 ± 0.001	Me	H	H	<i>n</i> -Pr	0.31 ± 0.01	Me	Me	Me	Me	7.1 ± 0.6		—(CH ₂) ₄ —	H	Me	1.59 ± 0.06	Et	Et	Me	H	1.61 ± 0.06	Et	Me	Et	H	1.08 ± 0.04		—(CH ₂) ₄ —	Me	Me	2.0 ± 0.1	<i>n</i> -C ₈ H ₁₇	H	H	H	0.35 ± 0.005	15					
R ¹	R ²	R ³	R ⁴	k ₂ (M ⁻¹ s ⁻¹)																																																																															
—(CH ₂) ₃ —	H	H	H	0.62 ± 0.01																																																																															
Me	Me	Me	H	2.4 ± 0.1																																																																															
Me	<i>n</i> -Pr	H	H	0.61 ± 0.01																																																																															
Me	H	<i>n</i> -Pr	H	0.084 ± 0.002																																																																															
R ¹	R ²	R ³	R ⁴	k ₂ (M ⁻¹ s ⁻¹)																																																																															
Et	Et	H	H	0.57 ± 0.02																																																																															
Et	H	Et	H	0.067 ± 0.001																																																																															
Me	H	H	<i>n</i> -Pr	0.31 ± 0.01																																																																															
Me	Me	Me	Me	7.1 ± 0.6																																																																															
	—(CH ₂) ₄ —	H	Me	1.59 ± 0.06																																																																															
Et	Et	Me	H	1.61 ± 0.06																																																																															
Et	Me	Et	H	1.08 ± 0.04																																																																															
	—(CH ₂) ₄ —	Me	Me	2.0 ± 0.1																																																																															
<i>n</i> -C ₈ H ₁₇	H	H	H	0.35 ± 0.005																																																																															
C_{5-14} 	DMD, acetone, 23°	 (—) <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>k₂ (M⁻¹s⁻¹)</th> </tr> </thead> <tbody> <tr> <td>Me₂(HO)C</td> <td>H</td> <td>H</td> <td>0.016 ± 0.002</td> </tr> <tr> <td>—(CH₂)₄—</td> <td>H</td> <td>H</td> <td>0.48 ± 0.02</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>H</td> <td>H</td> <td>0.033 ± 0.001</td> </tr> <tr> <td>Et</td> <td>Et</td> <td>H</td> <td>0.47 ± 0.03</td> </tr> <tr> <td>Et</td> <td>H</td> <td>Et</td> <td>0.057 ± 0.004</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>Me</td> <td>H</td> <td>0.33 ± 0.02</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>H</td> <td>Me</td> <td>0.02 ± 0.01</td> </tr> <tr> <td>4-BrC₆H₄</td> <td>H</td> <td>H</td> <td>0.089 ± 0.003</td> </tr> <tr> <td>3-O₂NC₆H₄</td> <td>H</td> <td>H</td> <td>0.030 ± 0.003</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>0.13 ± 0.01</td> </tr> <tr> <td><i>i</i>-Pr</td> <td><i>i</i>-Pr</td> <td>H</td> <td>0.39 ± 0.02</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>H</td> <td><i>i</i>-Pr</td> <td>0.02 ± 0.01</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>H</td> <td>H</td> <td>0.25 ± 0.01</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>H</td> <td>0.18 ± 0.01</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>0.29 ± 0.02</td> </tr> <tr> <td></td> <td></td> <td></td> <td>0.22 ± 0.01</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>H</td> <td><i>t</i>-Bu</td> <td>0.00024 ± 0.00004</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>H</td> <td>0.040 ± 0.001</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Ph</td> <td>0.043 ± 0.002</td> </tr> </tbody> </table> 	R ¹	R ²	R ³	k ₂ (M ⁻¹ s ⁻¹)	Me ₂ (HO)C	H	H	0.016 ± 0.002	—(CH ₂) ₄ —	H	H	0.48 ± 0.02	<i>t</i> -Bu	H	H	0.033 ± 0.001	Et	Et	H	0.47 ± 0.03	Et	H	Et	0.057 ± 0.004	<i>t</i> -Bu	Me	H	0.33 ± 0.02	<i>t</i> -Bu	H	Me	0.02 ± 0.01	4-BrC ₆ H ₄	H	H	0.089 ± 0.003	3-O ₂ NC ₆ H ₄	H	H	0.030 ± 0.003	Ph	H	H	0.13 ± 0.01	<i>i</i> -Pr	<i>i</i> -Pr	H	0.39 ± 0.02	<i>i</i> -Pr	H	<i>i</i> -Pr	0.02 ± 0.01	4-MeC ₆ H ₄	H	H	0.25 ± 0.01	Ph	Me	H	0.18 ± 0.01	Ph	H	Me	0.29 ± 0.02				0.22 ± 0.01	<i>t</i> -Bu	H	<i>t</i> -Bu	0.00024 ± 0.00004	Ph	Ph	H	0.040 ± 0.001	Ph	H	Ph	0.043 ± 0.002	16
R ¹	R ²	R ³	k ₂ (M ⁻¹ s ⁻¹)																																																																																
Me ₂ (HO)C	H	H	0.016 ± 0.002																																																																																
—(CH ₂) ₄ —	H	H	0.48 ± 0.02																																																																																
<i>t</i> -Bu	H	H	0.033 ± 0.001																																																																																
Et	Et	H	0.47 ± 0.03																																																																																
Et	H	Et	0.057 ± 0.004																																																																																
<i>t</i> -Bu	Me	H	0.33 ± 0.02																																																																																
<i>t</i> -Bu	H	Me	0.02 ± 0.01																																																																																
4-BrC ₆ H ₄	H	H	0.089 ± 0.003																																																																																
3-O ₂ NC ₆ H ₄	H	H	0.030 ± 0.003																																																																																
Ph	H	H	0.13 ± 0.01																																																																																
<i>i</i> -Pr	<i>i</i> -Pr	H	0.39 ± 0.02																																																																																
<i>i</i> -Pr	H	<i>i</i> -Pr	0.02 ± 0.01																																																																																
4-MeC ₆ H ₄	H	H	0.25 ± 0.01																																																																																
Ph	Me	H	0.18 ± 0.01																																																																																
Ph	H	Me	0.29 ± 0.02																																																																																
			0.22 ± 0.01																																																																																
<i>t</i> -Bu	H	<i>t</i> -Bu	0.00024 ± 0.00004																																																																																
Ph	Ph	H	0.040 ± 0.001																																																																																
Ph	H	Ph	0.043 ± 0.002																																																																																

TABLE 1A. EPOXIDATION OF UNFUNCTIONALIZED OLEFINS BY ISOLATED DIOXIRANES (Continued)



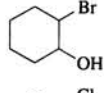
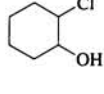
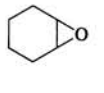
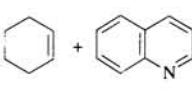

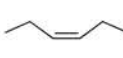
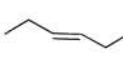
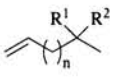

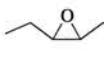
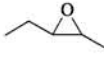
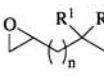

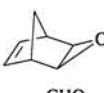

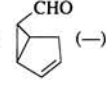
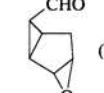
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																		
C ₆ 	1. DMD, acetone/Et ₂ O, N ₂ , -30° 2. -25°, 3 h	 (62)	41																		
	1. DMD, acetone, dark, rt, 8 h 2. NaBr or LiBr, Amberlyst 15, rt, 12 h	 (85)	171																		
	1. DMD, acetone, dark, rt, 8 h 2. NaCl or LiCl, Amberlyst 15, rt, 12 h	 (76)	171																		
	Cyclohexanone dioxirane, cyclohexanone, -20°, 10 min	 I (100)	156																		
	DMD, CDCl ₃ , minutes	I (—)	172, 173																		
	DMD, acetone/solvent (v/v = 1:1), 25°	I (—)	<table border="1"> <thead> <tr> <th>Solvent</th> <th>k₂ (M⁻¹s⁻¹)</th> </tr> </thead> <tbody> <tr><td>AcOH</td><td>3.48 ± 0.39</td></tr> <tr><td>MeOH</td><td>2.26 ± 0.19</td></tr> <tr><td>CHCl₃</td><td>1.663 ± 0.025</td></tr> <tr><td>CDCl₃</td><td>1.447 ± 0.026</td></tr> <tr><td>CH₂Cl₂</td><td>1.03 ± 0.04</td></tr> <tr><td><i>t</i>-BuOH</td><td>0.942 ± 0.010</td></tr> <tr><td>Cl(CH₂)₂Cl</td><td>0.920 ± 0.029</td></tr> <tr><td>PhCl</td><td>0.641 ± 0.018</td></tr> </tbody> </table>	Solvent	k ₂ (M ⁻¹ s ⁻¹)	AcOH	3.48 ± 0.39	MeOH	2.26 ± 0.19	CHCl ₃	1.663 ± 0.025	CDCl ₃	1.447 ± 0.026	CH ₂ Cl ₂	1.03 ± 0.04	<i>t</i> -BuOH	0.942 ± 0.010	Cl(CH ₂) ₂ Cl	0.920 ± 0.029	PhCl	0.641 ± 0.018
Solvent	k ₂ (M ⁻¹ s ⁻¹)																				
AcOH	3.48 ± 0.39																				
MeOH	2.26 ± 0.19																				
CHCl ₃	1.663 ± 0.025																				
CDCl ₃	1.447 ± 0.026																				
CH ₂ Cl ₂	1.03 ± 0.04																				
<i>t</i> -BuOH	0.942 ± 0.010																				
Cl(CH ₂) ₂ Cl	0.920 ± 0.029																				
PhCl	0.641 ± 0.018																				
    	DMD, acetone, 18°, 4 h	I (—)	30																		
	DMD, acetone, rt, 1 h	 (—)	175																		
	DMD, acetone, rt, 2 h	 (—)	175																		
	DMD, acetone, rt, 2 h	 (—)	175																		
	DMD, acetone, 15 min	 (—)	<table border="1"> <thead> <tr> <th>n</th> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr><td>0</td><td>Et</td><td>H</td></tr> <tr><td>0</td><td>Et</td><td>OH</td></tr> <tr><td>1</td><td>Et</td><td>OH</td></tr> <tr><td>2</td><td>Me</td><td>OH</td></tr> </tbody> </table>	n	R ¹	R ²	0	Et	H	0	Et	OH	1	Et	OH	2	Me	OH	176		
	n	R ¹	R ²																		
0	Et	H																			
0	Et	OH																			
1	Et	OH																			
2	Me	OH																			
C ₇ 	DMD, acetone/CH ₂ Cl ₂ , 20°, 0.2 h	 (—) +  (—) +  (—) +  (—)	177, 178																		

TABLE 1A. EPOXIDATION OF UNFUNCTIONALIZED OLEFINS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																												
	DMD, acetone/CH ₂ Cl ₂ , 20°, 0.2 h	(>98)	14																												
C _{8,9} 	Phenyl(trifluoromethyl)dioxirane, CH ₃ CN, 20°, 30 min	(—) R = H, 2-Cl, 4-Me, 4-MeO	179																												
C ₈ 	DMD (1.1 equiv), acetone, CH ₂ Cl ₂ , N ₂ , -10°, 3 h	(70) + I (30)	180																												
	DMD (2.5 equiv), acetone, CH ₂ Cl ₂ , N ₂ , 0°, 3 h	I (91)	180																												
	DMD, acetone/CH ₂ Cl ₂ , 20°, 0.2 h	I (>98)	14																												
	DMD, acetone, rt, 20 min	I (97)	181																												
	DMD, acetone/CH ₂ Cl ₂ , 20°, 0.2 h	(>98)	14, 13																												
	Cyclohexanone dioxirane, cyclohexanone, -20°, 1 h	I (100)	156																												
	DMD, acetone, rt, 3 h	I (74)	181																												
	Cyclohexanone dioxirane, cyclohexanone, -20°, 10 min	I (100)	156																												
	DMD, acetone, rt, 1 h	I (81)	181																												
	TFD, TFP, -20°, 1 min	C ₅ H ₁₁ (90)	155																												
C ₉ 	DMD	I (>98)	13																												
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>Time</th> <th>% Convn</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>20°</td> <td>1.0 h</td> <td>96</td> </tr> <tr> <td>acetone/N₂</td> <td>20°</td> <td>0.6 h</td> <td>88</td> </tr> <tr> <td>acetone</td> <td>56°</td> <td>0.3 h</td> <td>85</td> </tr> <tr> <td>acetone</td> <td>-78°</td> <td>12 h</td> <td>>95</td> </tr> <tr> <td>acetone/CCl₄</td> <td>-20°</td> <td>9 h</td> <td>>95</td> </tr> <tr> <td>acetone/CBrCl₃</td> <td>0°</td> <td>12 h</td> <td>>95</td> </tr> </tbody> </table>	Solvent	Temp	Time	% Convn	acetone	20°	1.0 h	96	acetone/N ₂	20°	0.6 h	88	acetone	56°	0.3 h	85	acetone	-78°	12 h	>95	acetone/CCl ₄	-20°	9 h	>95	acetone/CBrCl ₃	0°	12 h	>95	
Solvent	Temp	Time	% Convn																												
acetone	20°	1.0 h	96																												
acetone/N ₂	20°	0.6 h	88																												
acetone	56°	0.3 h	85																												
acetone	-78°	12 h	>95																												
acetone/CCl ₄	-20°	9 h	>95																												
acetone/CBrCl ₃	0°	12 h	>95																												
	DMD, acetone, under N ₂ or air, -20 to 0°, 30 min	I (—)	18																												
	DMD, acetone		29																												
	DMD, acetone, 20°, N ₂ , 6 h	I (86) + II (6) + III (5)	30																												

TABLE 1A. EPOXIDATION OF UNFUNCTIONALIZED OLEFINS BY ISOLATED DIOXIRANES (Continued)





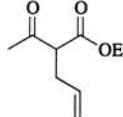
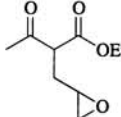
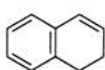
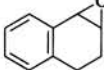


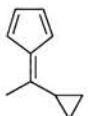
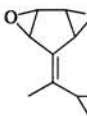
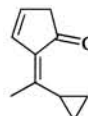
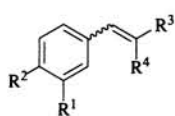
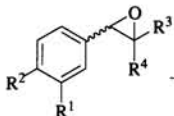
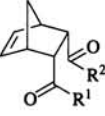
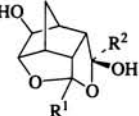
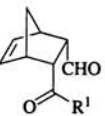
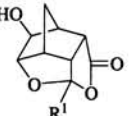
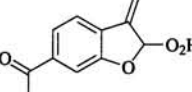
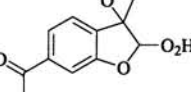
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																						
	DMD, acetone, rt, 1 h	 I (98)	181																																																						
	TFD, TFP, -20°, 1 min	I (90)	155																																																						
	DMD, acetone, 20°, N ₂ , 6 h	 (>98)	30																																																						
	DMD, acetone, -20°, 4.5 h	 (>95)	182																																																						
	DMD, acetone, Ni(acac) ₂ , -20°	mixture	182																																																						
C₁₀ 	DMD, acetone, 20°, 1 h	 (100)	183																																																						
	DMD, acetone, rt, 1 h	 (99)	181																																																						
	DMD (1.0 equiv), acetone, CH ₂ Cl ₂ , N ₂ , -10°, 3 h	 I (13) +  (72)	180																																																						
	DMD (2.5 equiv), acetone, CH ₂ Cl ₂ , N ₂ , 0°, 3 h	I (85)	180																																																						
C₁₀₋₁₅ 	DMD, acetone, rt	 <table border="1" data-bbox="1085 1297 1432 1549"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>MeO</td> <td>H</td> <td>Me</td> <td>40 min</td> <td>(98)</td> </tr> <tr> <td>MeO</td> <td>MeO</td> <td>H</td> <td>H</td> <td>40 min</td> <td>(96)</td> </tr> <tr> <td>MeO</td> <td>MeO</td> <td>H</td> <td>Me</td> <td>40 min</td> <td>(100)</td> </tr> <tr> <td>MeO</td> <td>MeO</td> <td>Me</td> <td>Me</td> <td>40 min</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>Cl</td> <td>H</td> <td>Ph</td> <td>3 h</td> <td>(87)</td> </tr> <tr> <td>H</td> <td>NO₂</td> <td>H</td> <td>Ph</td> <td>24 h</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>Ph</td> <td>40 min</td> <td>(95)</td> </tr> <tr> <td>H</td> <td>MeO</td> <td>H</td> <td>Ph</td> <td>40 min</td> <td>(100)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Time		H	MeO	H	Me	40 min	(98)	MeO	MeO	H	H	40 min	(96)	MeO	MeO	H	Me	40 min	(100)	MeO	MeO	Me	Me	40 min	(100)	H	Cl	H	Ph	3 h	(87)	H	NO ₂	H	Ph	24 h	(100)	H	H	H	Ph	40 min	(95)	H	MeO	H	Ph	40 min	(100)	184
R ¹	R ²	R ³	R ⁴	Time																																																					
H	MeO	H	Me	40 min	(98)																																																				
MeO	MeO	H	H	40 min	(96)																																																				
MeO	MeO	H	Me	40 min	(100)																																																				
MeO	MeO	Me	Me	40 min	(100)																																																				
H	Cl	H	Ph	3 h	(87)																																																				
H	NO ₂	H	Ph	24 h	(100)																																																				
H	H	H	Ph	40 min	(95)																																																				
H	MeO	H	Ph	40 min	(100)																																																				
C₁₀₋₁₇ 	1. DMD (1 equiv), acetone, -78° 2. rt, 30 min 3. HCl (1 M), 25°, 10 min	 <table border="1" data-bbox="1137 1561 1345 1733"> <thead> <tr> <th>R¹</th> <th>R²</th> <th></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>(75)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(86)</td> </tr> <tr> <td>n-Bu</td> <td>H</td> <td>(78)</td> </tr> <tr> <td>n-Bu</td> <td>n-Bu</td> <td>(84)</td> </tr> <tr> <td>n-C₈H₁₇</td> <td>H</td> <td>(80)</td> </tr> </tbody> </table>	R ¹	R ²		Me	H	(75)	Me	Me	(86)	n-Bu	H	(78)	n-Bu	n-Bu	(84)	n-C ₈ H ₁₇	H	(80)	185																																				
R ¹	R ²																																																								
Me	H	(75)																																																							
Me	Me	(86)																																																							
n-Bu	H	(78)																																																							
n-Bu	n-Bu	(84)																																																							
n-C ₈ H ₁₇	H	(80)																																																							
	1. DMD (3 equiv), acetone, -78° 2. rt, 30 min 3. HCl (1 M), rt, 10 min	 <table border="1" data-bbox="1137 1756 1275 1871"> <thead> <tr> <th>R¹</th> <th></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(80)</td> </tr> <tr> <td>n-Bu</td> <td>(84)</td> </tr> <tr> <td>n-C₈H₁₇</td> <td>(83)</td> </tr> </tbody> </table>	R ¹		Me	(80)	n-Bu	(84)	n-C ₈ H ₁₇	(83)	185																																														
R ¹																																																									
Me	(80)																																																								
n-Bu	(84)																																																								
n-C ₈ H ₁₇	(83)																																																								
C₁₁ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 20°, 3 h	 (>98)	170																																																						

TABLE 1A. EPOXIDATION OF UNFUNCTIONALIZED OLEFINS BY ISOLATED DIOXIRANES (Continued)

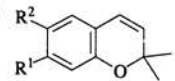
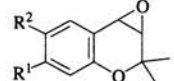
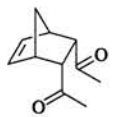
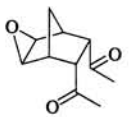
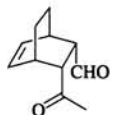
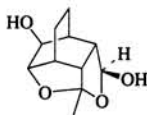

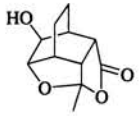
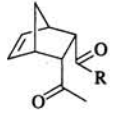
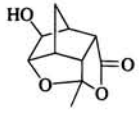
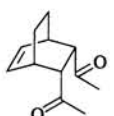
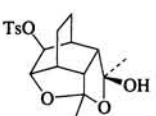


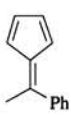
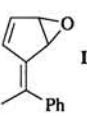
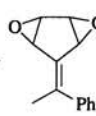
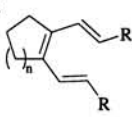
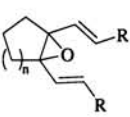




Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																					
C ₁₁₋₁₄ 	DMD, acetone/CH ₃ CN	 (100) <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Temp</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>H</td> <td>0°</td> </tr> <tr> <td>H</td> <td>H</td> <td>0°</td> </tr> <tr> <td>MeO</td> <td>H</td> <td>-40°</td> </tr> <tr> <td>MeO</td> <td>MeO</td> <td>-40°</td> </tr> <tr> <td>CF₃CH₂O</td> <td>MeO</td> <td>-40°</td> </tr> <tr> <td>EtO</td> <td>MeO</td> <td>-40°</td> </tr> </tbody> </table>	R ¹	R ²	Temp	Cl	H	0°	H	H	0°	MeO	H	-40°	MeO	MeO	-40°	CF ₃ CH ₂ O	MeO	-40°	EtO	MeO	-40°	186
R ¹	R ²	Temp																						
Cl	H	0°																						
H	H	0°																						
MeO	H	-40°																						
MeO	MeO	-40°																						
CF ₃ CH ₂ O	MeO	-40°																						
EtO	MeO	-40°																						
C ₁₁ 	1. DMD, acetone, -78° 2. rt, 30 min	 (90)	185																					
	1. DMD (1 equiv), acetone, -78° 2. rt, 30 min 3. HCl (1 M), rt, 10 min	 (84)	185																					
	1. DMD (3 equiv), acetone, -78° 2. rt, 30 min 3. HCl (1 M), rt, 10 min	 (80)	185																					
	1. DMD, acetone, -78° 2. rt, 30 min 3. HCl (1 M), rt, 10 min	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> </tr> </thead> <tbody> <tr> <td>MeO (85)</td> </tr> <tr> <td>MeS (85)</td> </tr> </tbody> </table>	R	MeO (85)	MeS (85)	185																		
R																								
MeO (85)																								
MeS (85)																								
C ₁₂ 	1. DMD, acetone, -78° 2. rt, 30 min 3. HCl (1 M), rt, 10 min 4. TsCl, pyridine, 25°, 24 h	 (68)	185																					
	DMD, acetone/CH ₂ Cl ₂ , 0° to rt, Ar, 5 h	 (97)	187																					
C ₁₃ 	DMD (1.0 equiv), acetone, CH ₂ Cl ₂ , N ₂ , -10°, 3 h	 I (67) +  II (14)	180																					
	DMD (3.1 equiv), acetone, CH ₂ Cl ₂ , N ₂ , 0°, 4 h	I (0) + II (89)	180																					
C ₁₃₋₂₂ 	DMD (-78°), acetone, -20° to 20°	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>n</th> <th>R</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>CO₂Me</td> <td>50 h (64)</td> </tr> <tr> <td>2</td> <td>CO₂Bu-<i>t</i></td> <td>44 h (44)</td> </tr> <tr> <td>1</td> <td>Ph</td> <td>16 h (66)</td> </tr> <tr> <td>2</td> <td>Ph</td> <td>7 h (73)</td> </tr> </tbody> </table>	n	R	Time	1	CO ₂ Me	50 h (64)	2	CO ₂ Bu- <i>t</i>	44 h (44)	1	Ph	16 h (66)	2	Ph	7 h (73)	188						
n	R	Time																						
1	CO ₂ Me	50 h (64)																						
2	CO ₂ Bu- <i>t</i>	44 h (44)																						
1	Ph	16 h (66)																						
2	Ph	7 h (73)																						
C ₁₄ 	DMD, acetone, rt, 40 min	 (100)	184																					
	DMD, acetone, 22°, 2 h	 I (—)	162																					

TABLE 1A. EPOXIDATION OF UNFUNCTIONALIZED OLEFINS BY ISOLATED DIOXIRANES (Continued)




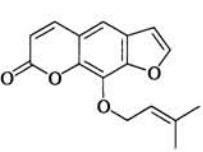
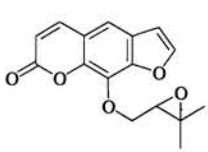
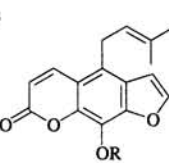
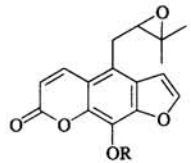
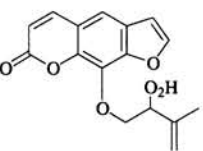
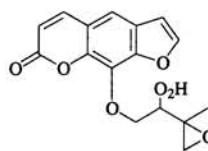
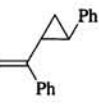
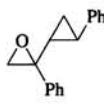

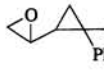
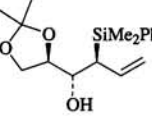
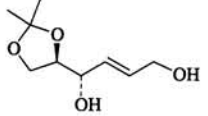
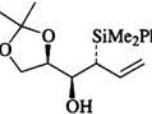
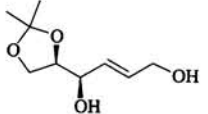
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Cyclohexanone dioxirane, cyclohexanone/CH ₂ Cl ₂ , -20°, 4.5 h	I (97)	156												
	DMD, acetone/solvents, 2°	I (—)	189												
	DMD, acetone, rt, 8 h	I (99)	181												
	Ethylmethyldioxirane, 2-butanone/ acetone, rt, 3 h	 I (—)	162												
	DMD, acetone, 22°	I (—)	162												
	Cyclohexanone dioxirane, cyclohexanone/acetone, -20°, 1.5 h	I (100)	156												
	DMD, acetone, rt, 6 h	I (100)	181												
	1. DMD, acetone, dark, rt, 8 h 2. NaBr or LiBr, Amberlyst 15, rt, 12 h	 (82)	171												
C ₁₆ 	DMD, acetone, 0°, 2 h	 (99)	190												
C ₁₆₋₁₈ 	DMD, acetone, 0°	 <table border="1" data-bbox="1171 1228 1345 1343"> <thead> <tr> <th>R</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>2 h</td> <td>(100)</td> </tr> <tr> <td>Me</td> <td>0.5 h</td> <td>(100)</td> </tr> <tr> <td>Ac</td> <td>0.5 h</td> <td>(100)</td> </tr> </tbody> </table>	R	Time	Yield (%)	H	2 h	(100)	Me	0.5 h	(100)	Ac	0.5 h	(100)	190
R	Time	Yield (%)													
H	2 h	(100)													
Me	0.5 h	(100)													
Ac	0.5 h	(100)													
	DMD, acetone, 20°, 6 h	 (96)	190												
C ₁₇ 	DMD, acetone, 20°, 3.5 h	 (100)	183												
	DMD, acetone, 20°, 1 h	 (>95)	13												
	1. DMD, acetone, 23° 2. HOAc, MeOH	 (88)	191												
	1. DMD, acetone, 23° 2. HOAc, MeOH	 (83)	191												

TABLE 1A. EPOXIDATION OF UNFUNCTIONALIZED OLEFINS BY ISOLATED DIOXIRANES (Continued)

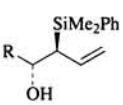
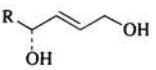
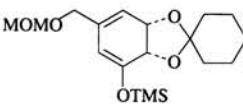
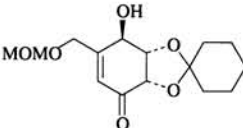
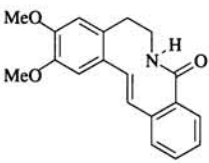
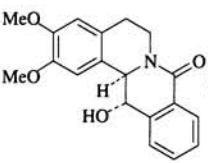
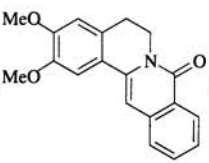
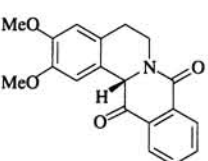
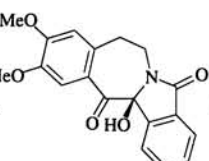
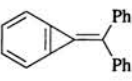
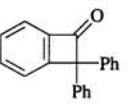
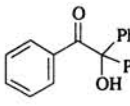
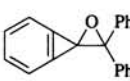
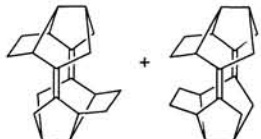

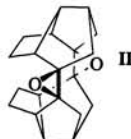
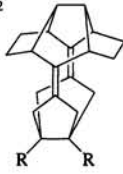
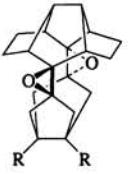
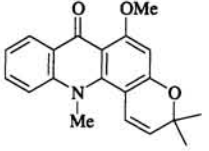
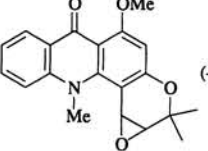
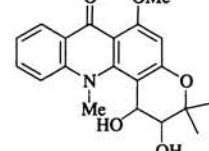
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.									
C ₁₈ 	1. DMD, acetone, 23° 2. HOAc, MeOH	 R C ₆ H ₁₁ (95) n-C ₆ H ₁₃ (89)	191									
	DMD, acetone/CH ₂ Cl ₂ , -78°, 10 min	 (70)	192									
C ₁₉ 	DMD, acetone, rt, 24 h	 (40) +  (31)	193									
	DMD, acetone, rt, 2 d	 (21) +  (-) 70										
C ₂₀ 	K ₂ CO ₃ , DMD (0°), acetone, N ₂	 I <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>Temp</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>rt</td> <td>—</td> <td>(30)</td> </tr> <tr> <td>50°</td> <td>2 h</td> <td>(57)</td> </tr> </tbody> </table>	Temp	Time	Yield (%)	rt	—	(30)	50°	2 h	(57)	194
Temp	Time	Yield (%)										
rt	—	(30)										
50°	2 h	(57)										
	1. K ₂ CO ₃ , DMD, acetone, N ₂ , -20°, 60 min 2. H ₂ SO ₄ (2 M), -20° to rt, 60 min	 II (74)	194									
	1. K ₂ CO ₃ , DMD, acetone, N ₂ , -20°, 60 min 2. H ₂ O, 0°, 14 h	I (8) + II (53)	194									
	1. DMD- <i>d</i> ₆ (-90°), acetone- <i>d</i> ₆ , -30°, 50 min 2. -10°, 50 min	 (-)	194									
	1. DMD, acetone/CH ₂ Cl ₂ , 0° 2. rt, 15 h	 I +  II I + II (14)	195									
C ₂₀₋₂₂ 	1. DMD, acetone/CH ₂ Cl ₂ , 0° 2. rt, 15 h	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(64)</td> </tr> <tr> <td>Me</td> <td>(59)</td> </tr> </tbody> </table>	R	Yield (%)	H	(64)	Me	(59)	195			
R	Yield (%)											
H	(64)											
Me	(59)											
C ₂₀ 	DMD, acetone, -60°, 3 h	 (-) +  (-)	196, 197									

TABLE 1A. EPOXIDATION OF UNFUNCTIONALIZED OLEFINS BY ISOLATED DIOXIRANES (Continued)



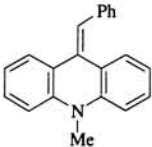
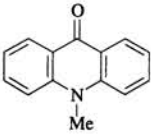
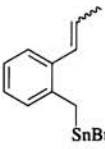
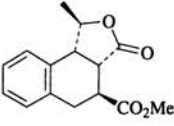
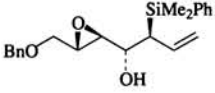
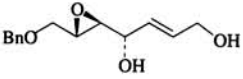
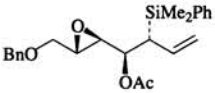
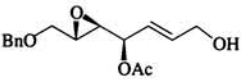
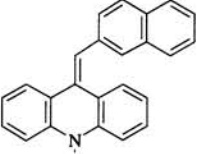
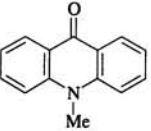
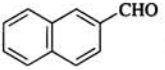
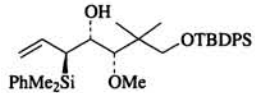
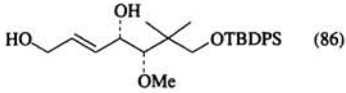
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₁		DMD, acetone	 (82)	198
		DMD, acetone/CH ₂ Cl ₂	 (—) + PhCHO (—)	197
C ₂₂		DMD, CF ₃ CO ₂ H, dimethyl fumarate, CH ₂ Cl ₂ , rt, 2 h	 (78)	199
		1. DMD, acetone, 23° 2. HOAc, MeOH	 (91)	191
C ₂₄		1. DMD, acetone, 23° 2. HOAc, MeOH	 (60)	191
C ₂₅		DMD, acetone/CH ₂ Cl ₂	 (—) +  (—)	197
C ₃₄		1. DMD, acetone, K ₂ CO ₃ , 23° 2. MeOH, HOAc	 (86)	200

TABLE 1B. EPOXIDATION OF OLEFINIC SUBSTRATES WITH ELECTRON DONORS BY ISOLATED DIOXIRANES


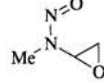






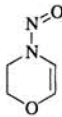
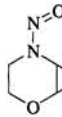




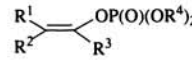
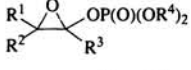
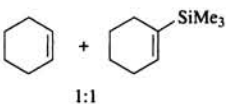



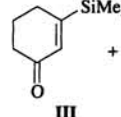
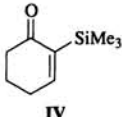




Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																						
C ₃ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , dark, rt, 3 h	 (~100)	201, 202																																																																						
C ₄ 	DMD, acetone/CHCl ₃	 (—)	203																																																																						
	DMD, acetone	 (—)	51																																																																						
	DMD	 (—)	204																																																																						
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , dark, rt, 3 h	 (95)	201																																																																						
	DMD	 (—)	204																																																																						
C ₅ 	DMD, acetone	 (—)	204, 51																																																																						
C ₅₋₁₂ 	DMD, acetone/CH ₂ Cl ₂ , N ₂	 <table border="1" data-bbox="998 1274 1406 1549"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Temp</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>Me</td> <td>Me</td> <td>0°</td> <td>4.5 h</td> <td>(98)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Me</td> <td>Me</td> <td>-10°</td> <td>2.5 h</td> <td>(~100)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Me</td> <td>Me</td> <td>-10°</td> <td>2.5 h</td> <td>(~100)</td> </tr> <tr> <td>H</td> <td>H</td> <td>Me</td> <td>Et</td> <td>0°</td> <td>3.5 h</td> <td>(99)</td> </tr> <tr> <td>H</td> <td>-(CH₂)₄</td> <td>Me</td> <td>Me</td> <td>0°</td> <td>5 h</td> <td>(~100)</td> </tr> <tr> <td>H</td> <td>n-C₅H₁₁</td> <td>H</td> <td>Me</td> <td>0°</td> <td>6 h</td> <td>(99)</td> </tr> <tr> <td>H</td> <td>H</td> <td>Ph</td> <td>Me</td> <td>-10°</td> <td>3.5 h</td> <td>(96)</td> </tr> <tr> <td>Me</td> <td>-(CH₂)₄</td> <td>Et</td> <td>Me</td> <td>-10°</td> <td>3 h</td> <td>(99)</td> </tr> <tr> <td>H</td> <td>H</td> <td>Ph</td> <td>Et</td> <td>-10°</td> <td>2 h</td> <td>(99)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Temp	Time		H	H	Me	Me	0°	4.5 h	(98)	H	Me	Me	Me	-10°	2.5 h	(~100)	Me	H	Me	Me	-10°	2.5 h	(~100)	H	H	Me	Et	0°	3.5 h	(99)	H	-(CH ₂) ₄	Me	Me	0°	5 h	(~100)	H	n-C ₅ H ₁₁	H	Me	0°	6 h	(99)	H	H	Ph	Me	-10°	3.5 h	(96)	Me	-(CH ₂) ₄	Et	Me	-10°	3 h	(99)	H	H	Ph	Et	-10°	2 h	(99)	205, 44
R ¹	R ²	R ³	R ⁴	Temp	Time																																																																				
H	H	Me	Me	0°	4.5 h	(98)																																																																			
H	Me	Me	Me	-10°	2.5 h	(~100)																																																																			
Me	H	Me	Me	-10°	2.5 h	(~100)																																																																			
H	H	Me	Et	0°	3.5 h	(99)																																																																			
H	-(CH ₂) ₄	Me	Me	0°	5 h	(~100)																																																																			
H	n-C ₅ H ₁₁	H	Me	0°	6 h	(99)																																																																			
H	H	Ph	Me	-10°	3.5 h	(96)																																																																			
Me	-(CH ₂) ₄	Et	Me	-10°	3 h	(99)																																																																			
H	H	Ph	Et	-10°	2 h	(99)																																																																			
C _{5,9} 	DMD (1 equiv), acetone, rt, 10 min	 (87) +  (I) +  (II) +  (III) +  (IV) I+II+III+IV (13) I:II:III:IV = 38:23:8:31	74																																																																						
C ₆ 	DMD-d ₆ , -20°, 5 min	 (—)	204																																																																						
	DMD-d ₆ , -20°, 5 min	 (—)	204																																																																						

TABLE 1B. EPOXIDATION OF OLEFINIC SUBSTRATES WITH ELECTRON DONORS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
C ₇₋₁₄ 	DMD, acetone, 0°, 5 min	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>CN</td> <td>(72)</td> </tr> <tr> <td>Me</td> <td>CO₂Me</td> <td>(76)</td> </tr> <tr> <td>Bn</td> <td>CN</td> <td>(69)</td> </tr> <tr> <td>Bn</td> <td>CO₂Me</td> <td>(60)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	Me	CN	(72)	Me	CO ₂ Me	(76)	Bn	CN	(69)	Bn	CO ₂ Me	(60)	206, 207																									
R ¹	R ²	Yield (%)																																									
Me	CN	(72)																																									
Me	CO ₂ Me	(76)																																									
Bn	CN	(69)																																									
Bn	CO ₂ Me	(60)																																									
C ₇ 	DMD, acetone, 25°	 I (—) + II (—) $k_H/k_D = 0.773 \pm 0.029$	208																																								
	DMD, acetone, -78°	I (—) + II (—) $k_H/k_D = 0.681 \pm 0.032$	208																																								
	DMD, acetone, 25°	II (—) + III (—) $k_H/k_D = 0.847 \pm 0.043$	208																																								
	DMD, acetone, -78°	II (—) + III (—) $k_H/k_D = 0.898 \pm 0.036$	208																																								
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , dark, rt, 3 h	(95)	201																																								
C ₇₋₁₃ 	DMD, acetone, rt, 4 to 10 h	(95)	74																																								
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>Me</td> <td>Me</td> <td>(>95)</td> </tr> <tr> <td>H</td> <td><i>n</i>-Bu</td> <td>H</td> <td>Me</td> <td>(>95)</td> </tr> <tr> <td>Me</td> <td><i>n</i>-Bu</td> <td>H</td> <td>Me</td> <td>(>81)</td> </tr> <tr> <td>Et</td> <td><i>n</i>-Bu</td> <td>H</td> <td>Me</td> <td>(>95)</td> </tr> <tr> <td>Me</td> <td>C₆H₁₁</td> <td>H</td> <td>Me</td> <td>(>95)</td> </tr> <tr> <td>Et</td> <td>H</td> <td>Me</td> <td>Ph</td> <td>(>95)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>Ph</td> <td>(>95)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Yield (%)	Me	H	Me	Me	(>95)	H	<i>n</i> -Bu	H	Me	(>95)	Me	<i>n</i> -Bu	H	Me	(>81)	Et	<i>n</i> -Bu	H	Me	(>95)	Me	C ₆ H ₁₁	H	Me	(>95)	Et	H	Me	Ph	(>95)	Me	Me	Me	Ph	(>95)	
R ¹	R ²	R ³	R ⁴	Yield (%)																																							
Me	H	Me	Me	(>95)																																							
H	<i>n</i> -Bu	H	Me	(>95)																																							
Me	<i>n</i> -Bu	H	Me	(>81)																																							
Et	<i>n</i> -Bu	H	Me	(>95)																																							
Me	C ₆ H ₁₁	H	Me	(>95)																																							
Et	H	Me	Ph	(>95)																																							
Me	Me	Me	Ph	(>95)																																							
C ₈ 	DMD, acetone/THF, Ar, -78°, 30 min	(77)	209																																								
C ₈₋₁₁ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -10 to 0°, 3 to 5 h	(99-100)	<table border="1"> <thead> <tr> <th>R¹</th> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>44,</td> </tr> <tr> <td>Me</td> <td>Et</td> <td>205</td> </tr> </tbody> </table>	R ¹	R	Yield (%)	H	Me	44,	Me	Et	205																															
R ¹	R	Yield (%)																																									
H	Me	44,																																									
Me	Et	205																																									
C ₈₋₁₃ 	DMD, acetone, -20°, 30 min	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>—(CH₂)₄</td> <td></td> <td>Me</td> <td>Me</td> <td>(95)</td> </tr> <tr> <td>—(CH₂)₂O(CH₂)₂</td> <td></td> <td>Me</td> <td>Me</td> <td>(61)</td> </tr> <tr> <td>—(CH₂)₅</td> <td></td> <td>Me</td> <td>Me</td> <td>(85)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td><i>i</i>-Pr</td> <td>Me</td> <td>Me</td> <td>(93)</td> </tr> <tr> <td><i>i</i>-Bu</td> <td><i>i</i>-Bu</td> <td>Me</td> <td>Me</td> <td>(91)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td><i>i</i>-Pr</td> <td>—(CH₂)₅</td> <td></td> <td>(96)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Yield (%)	—(CH ₂) ₄		Me	Me	(95)	—(CH ₂) ₂ O(CH ₂) ₂		Me	Me	(61)	—(CH ₂) ₅		Me	Me	(85)	<i>i</i> -Pr	<i>i</i> -Pr	Me	Me	(93)	<i>i</i> -Bu	<i>i</i> -Bu	Me	Me	(91)	<i>i</i> -Pr	<i>i</i> -Pr	—(CH ₂) ₅		(96)	211					
R ¹	R ²	R ³	R ⁴	Yield (%)																																							
—(CH ₂) ₄		Me	Me	(95)																																							
—(CH ₂) ₂ O(CH ₂) ₂		Me	Me	(61)																																							
—(CH ₂) ₅		Me	Me	(85)																																							
<i>i</i> -Pr	<i>i</i> -Pr	Me	Me	(93)																																							
<i>i</i> -Bu	<i>i</i> -Bu	Me	Me	(91)																																							
<i>i</i> -Pr	<i>i</i> -Pr	—(CH ₂) ₅		(96)																																							
C ₉₋₁₄ 	DMD, acetone /THF, N ₂ , -78°, 2 min	 <table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(74)</td> </tr> <tr> <td>MeO</td> <td>(60)</td> </tr> <tr> <td>Ph</td> <td>(92)</td> </tr> </tbody> </table>	R	Yield (%)	Me	(74)	MeO	(60)	Ph	(92)	210																																
R	Yield (%)																																										
Me	(74)																																										
MeO	(60)																																										
Ph	(92)																																										

TABLE 1B. EPOXIDATION OF OLEFINIC SUBSTRATES WITH ELECTRON DONORS BY ISOLATED DIOXIRANES (Continued)

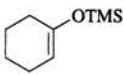
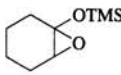


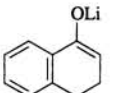
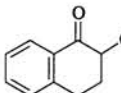
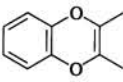
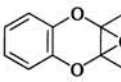
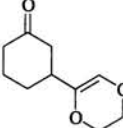
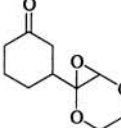

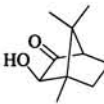
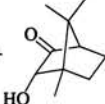

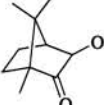
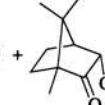
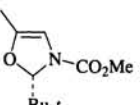
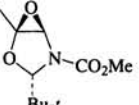
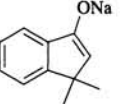
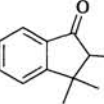
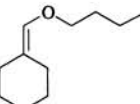
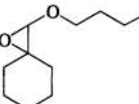
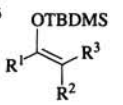
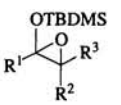
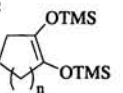
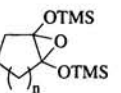
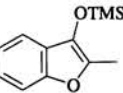
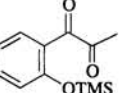
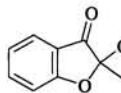
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																								
C ₉ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°, 3 h	 (99)	44, 212, 45																								
	DMD, acetone/CH ₂ Cl ₂ , -40°, 3.5 h	 (36)	64																								
C ₁₀ 	DMD, acetone/THF, Ar, -78°, 10 to 20 min	 (52-82)	209																								
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -70 to -30°, 0.5 to 1 h	 (~100)	213, 204																								
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°	 (~100)	214																								
	DMD, acetone/THF, Ar, -78°, 15 to 30 min	 I +  II (50-74) I:II = 70:30	209																								
	DMD, acetone/THF, N ₂ , -78°, 45 min	 (53) +  (18)	210																								
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°, 2 h		215																								
C ₁₁ 	DMD, acetone /THF, N ₂ , -78°, 2 min	 (80)	210																								
	DMD, acetone, -20°, 30 min	 (98)	211																								
C ₁₁₋₁₆ 	DMD-d ₆ , acetone-d ₆ , -78°, 2 to 5 min	 (—) <table border="1" data-bbox="1128 1572 1319 1802"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>H</td> <td>Me</td> </tr> <tr> <td>—(CH₂)₄—</td> <td>H</td> <td>H</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>—(CH₂)₅—</td> <td>H</td> </tr> <tr> <td>—(CH₂)₄—</td> <td>Me</td> <td>Me</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Me</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Et	H	Me	—(CH ₂) ₄ —	H	H	<i>t</i> -Bu	H	H	H	—(CH ₂) ₅ —	H	—(CH ₂) ₄ —	Me	Me	Ph	H	H	Ph	Me	Me	216
R ¹	R ²	R ³																									
Et	H	Me																									
—(CH ₂) ₄ —	H	H																									
<i>t</i> -Bu	H	H																									
H	—(CH ₂) ₅ —	H																									
—(CH ₂) ₄ —	Me	Me																									
Ph	H	H																									
Ph	Me	Me																									
C ₁₁₋₁₂ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -30°, 3 h	 $\frac{n}{1}$ (97) 2 (98)	213																								
C ₁₂ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -70 to -30°, 0.5 to 1 h	 (72) +  (28)	213																								

TABLE 1B. EPOXIDATION OF OLEFINIC SUBSTRATES WITH ELECTRON DONORS BY ISOLATED DIOXIRANES (Continued)


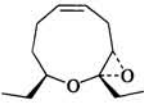

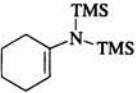
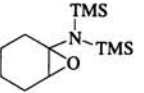
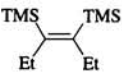
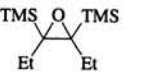
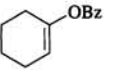
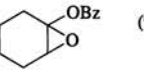
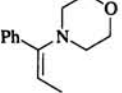
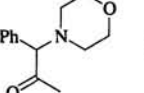
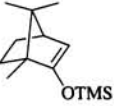
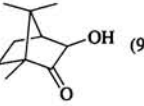
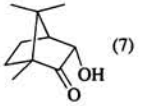
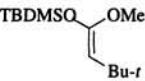
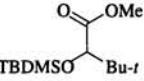
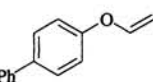
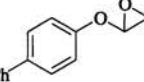
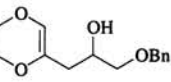
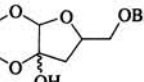

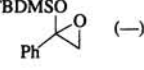
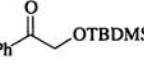
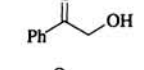
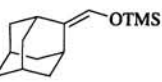
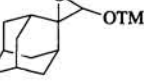
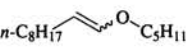
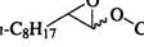

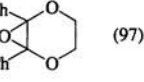
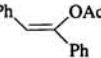
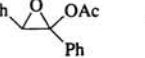
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. DMD, acetone/CH ₂ Cl ₂ , -70°, 10 min 2. -40°, 10 min 3. 2-Methyl-2-butene, <0°, 5 min	 +  (—)	217
	DMD, acetone/CH ₂ Cl ₂ , -50°, 1 h	 (90)	64
	DMD, acetone, 25°, 5 h	 (100)	218
C ₁₃ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°, 3 h	 (96)	212, 44
	DMD, acetone/CH ₂ Cl ₂ , -70°, 75 min	 (77)	64
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -78°, 30 min	 (92) +  (7)	210
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°, 1 h	 (~100)	213
C ₁₄ 	DMD, acetone, rt, 30 min	 (100)	219
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°	 (~100)	214
	DMD- <i>d</i> ₆ , acetone- <i>d</i> ₆ , -78°, 2 to 5 min	 (—) +  (—) +  (—)	216
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°, 3 h	 (98)	44, 45
C ₁₅ 	DMD, acetone/CH ₂ Cl ₂ , 0°, 7 h	 (94)	220
C ₁₆ 	DMD, acetone, rt, < 30 sec	 (97)	221
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°, 7 h	 (84)	44, 222

TABLE 1B. EPOXIDATION OF OLEFINIC SUBSTRATES WITH ELECTRON DONORS BY ISOLATED DIOXIRANES (Continued)

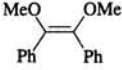

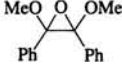
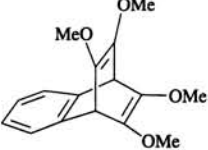
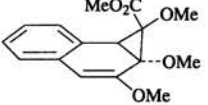
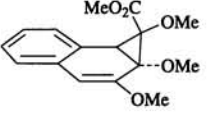
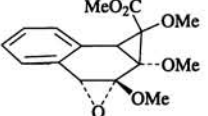
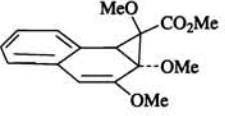
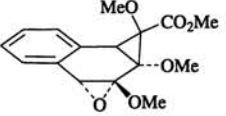
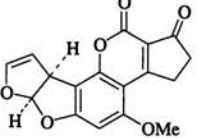
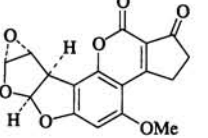
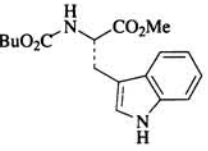
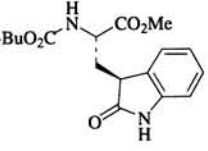
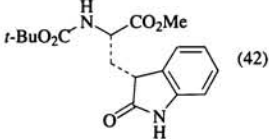
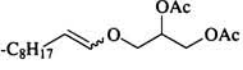
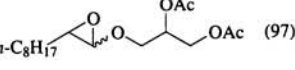
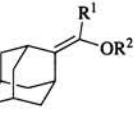
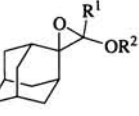
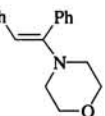
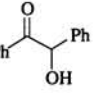
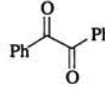
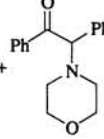
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
		 (—)	223												
	DMD, CH ₂ Cl ₂ /acetone, -40°, 30 min	 (95)	224												
	DMD, CH ₂ Cl ₂ , -30°, 1 h	 (92)	224												
	DMD, CH ₂ Cl ₂ , -30°, 1 h	 (95)	224												
C ₁₇ 	DMD, acetone/CH ₂ Cl ₂ , rt, 15 min	 (—)	225, 51												
	DMD, acetone/CH ₂ Cl ₂ , 10°, 2 d	 (42) +  (42)	226												
	DMD, acetone/CH ₂ Cl ₂ , 0°, 7 h	 (97)	220												
C ₁₈₋₂₄ 	TFD, TFP/CH ₂ Cl ₂ , -20°, 4 to 6 min	 (92-97) <table border="1" data-bbox="1211 1648 1324 1809"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>Me</td> </tr> <tr> <td>1-Naph</td> <td>Me</td> </tr> <tr> <td>2-Naph</td> <td>Me</td> </tr> <tr> <td>Ph</td> <td>Ph</td> </tr> <tr> <td>Ph</td> <td>Bn</td> </tr> </tbody> </table>	R ¹	R ²	Ph	Me	1-Naph	Me	2-Naph	Me	Ph	Ph	Ph	Bn	227
R ¹	R ²														
Ph	Me														
1-Naph	Me														
2-Naph	Me														
Ph	Ph														
Ph	Bn														
C ₁₈ 	DMD (3 equiv), acetone/CH ₂ Cl ₂ , -70°	 I +  II +  III (—) I:II:III = 19:48:33	228												

TABLE 1B. EPOXIDATION OF OLEFINIC SUBSTRATES WITH ELECTRON DONORS BY ISOLATED DIOXIRANES (Continued)


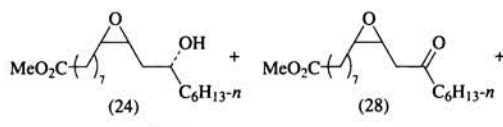
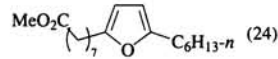
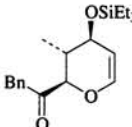
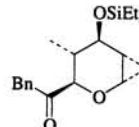
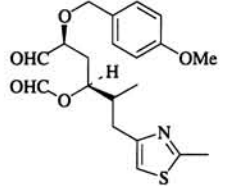
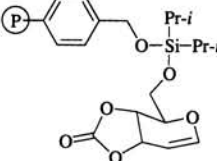
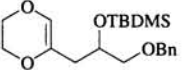
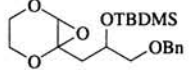
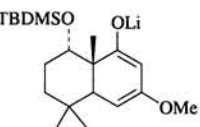
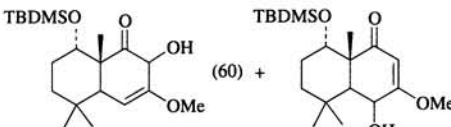
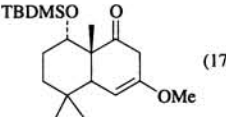
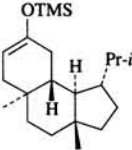
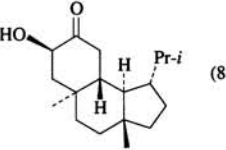
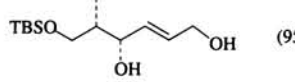
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₉ 	DMD (1.5 equiv), acetone/CH ₂ Cl ₂ , -70°	I + II + III (—) I:II:III = 21:27:52	228
	DMD, acetone, rt	 (24) + (28) +  (24)	69
C ₂₀ 	DMD, acetone/CH ₂ Cl ₂ , 0°	 (>99)	229
	1. DMD, K ₂ CO ₃ , CH ₂ Cl ₂ /acetone, 0° 2. NaIO ₄ , H ₂ O/THF	 (92)	230
	DMD, acetone/CH ₂ Cl ₂ , 0°	(—)	231
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°	 (~94)	214
	DMD, acetone/THF/HMPA, Ar, -78°, 30 min	 (60) + (15) +  (17)	209, 191
C ₂₁ 	DMD, acetone/THF, -78°	 (81)	54
	1. DMD, acetone, 23° 2. HOAc, MeOH	 (95)	191

TABLE 1B. EPOXIDATION OF OLEFINIC SUBSTRATES WITH ELECTRON DONORS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
<p>C₂₂</p>	DMD (-78°), acetone, rt, 30 min	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>OMe</td> <td>H</td> <td>9 h</td> <td>(47)</td> <td>(31)</td> </tr> <tr> <td>H</td> <td>OMe</td> <td>6 d</td> <td>(96)</td> <td>(0)</td> </tr> </tbody> </table>	R ¹	R ²	Time	I	II	OMe	H	9 h	(47)	(31)	H	OMe	6 d	(96)	(0)	70, 193
R ¹	R ²	Time	I	II														
OMe	H	9 h	(47)	(31)														
H	OMe	6 d	(96)	(0)														
<p>C₂₅</p>	DMD, acetone/CH ₂ Cl ₂ , 0°	 (>99)	229															

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES



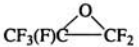
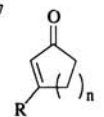
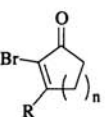
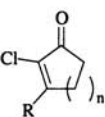
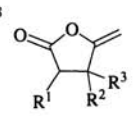
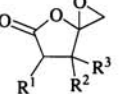
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																									
C ₂	CF ₂ =CFCI	Difluorodioxirane, CFCI ₃	 (>95)	232																									
	CF ₂ =CHF	Difluorodioxirane, CFCI ₃	 (>95)	232																									
C ₃	CF ₃ CF=CF ₂	Difluorodioxirane, CFCI ₃	 (>95)	232																									
C ₅₋₇		1. DMD, acetone, dark, rt, 8 h 2. NaBr or LiBr, Amberlyst 15, rt, 12 h	 <table border="1" data-bbox="1154 1067 1302 1205"> <thead> <tr> <th>n</th> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>H</td> <td>(95)</td> </tr> <tr> <td>1</td> <td>Me</td> <td>(96)</td> </tr> <tr> <td>2</td> <td>H</td> <td>(95)</td> </tr> <tr> <td>2</td> <td>Me</td> <td>(96)</td> </tr> </tbody> </table>	n	R	Yield (%)	1	H	(95)	1	Me	(96)	2	H	(95)	2	Me	(96)	171										
n	R	Yield (%)																											
1	H	(95)																											
1	Me	(96)																											
2	H	(95)																											
2	Me	(96)																											
		1. DMD, acetone, dark, rt, 8 h 2. NaCl or LiCl, Amberlyst 15, rt, 12 h	 <table border="1" data-bbox="1154 1251 1302 1389"> <thead> <tr> <th>n</th> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>H</td> <td>(88)</td> </tr> <tr> <td>1</td> <td>Me</td> <td>(93)</td> </tr> <tr> <td>2</td> <td>H</td> <td>(90)</td> </tr> <tr> <td>2</td> <td>Me</td> <td>(92)</td> </tr> </tbody> </table>	n	R	Yield (%)	1	H	(88)	1	Me	(93)	2	H	(90)	2	Me	(92)	171										
n	R	Yield (%)																											
1	H	(88)																											
1	Me	(93)																											
2	H	(90)																											
2	Me	(92)																											
C ₅₋₈		DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°	 <table border="1" data-bbox="1180 1446 1406 1584"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>2 h</td> <td>(91)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>H</td> <td>3.5 h</td> <td>(95)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>3.5 h</td> <td>(94)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Me</td> <td>3 h</td> <td>(96)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Time	Yield (%)	H	H	H	2 h	(91)	H	Me	H	3.5 h	(95)	Me	H	H	3.5 h	(94)	H	Me	Me	3 h	(96)	44, 212
R ¹	R ²	R ³	Time	Yield (%)																									
H	H	H	2 h	(91)																									
H	Me	H	3.5 h	(95)																									
Me	H	H	3.5 h	(94)																									
H	Me	Me	3 h	(96)																									

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

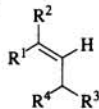
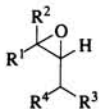
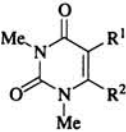
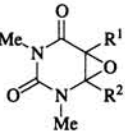
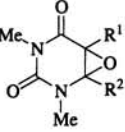
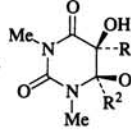
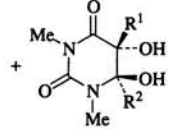
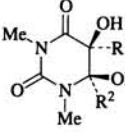
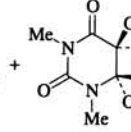
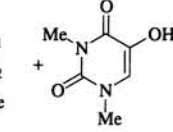
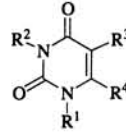
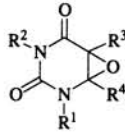
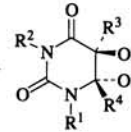
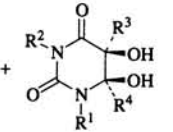


Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																			
C ₅₋₁₃ 	DMD, acetone/CH ₂ Cl ₂ , -20°		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>CO₂H</td> <td>H</td> <td>H</td> <td>23 h</td> <td>(93)</td> </tr> <tr> <td>Me</td> <td>CO₂H</td> <td>Me</td> <td>Ph</td> <td>20 h</td> <td>(96)</td> </tr> <tr> <td>CO₂Me</td> <td>Me</td> <td>Me</td> <td>Ph</td> <td>20 h</td> <td>(99)</td> </tr> <tr> <td>Me</td> <td>CO₂Me</td> <td>Me</td> <td>Ph</td> <td>16 h</td> <td>(98)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Time	Yield (%)	Me	CO ₂ H	H	H	23 h	(93)	Me	CO ₂ H	Me	Ph	20 h	(96)	CO ₂ Me	Me	Me	Ph	20 h	(99)	Me	CO ₂ Me	Me	Ph	16 h	(98)	53																																				
			R ¹	R ²	R ³	R ⁴	Time	Yield (%)																																																														
			Me	CO ₂ H	H	H	23 h	(93)																																																														
			Me	CO ₂ H	Me	Ph	20 h	(96)																																																														
CO ₂ Me	Me	Me	Ph	20 h	(99)																																																																	
Me	CO ₂ Me	Me	Ph	16 h	(98)																																																																	
C ₆₋₇ 	DMD, acetone/CH ₂ Cl ₂ /CH ₃ CN, porphyrin catalyst, imidazole, 20°		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Catalyst</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>FeTDMPPCI^a</td> <td>(20)</td> </tr> <tr> <td>H</td> <td>H</td> <td>MnTDMPPCI^a</td> <td>(40)</td> </tr> <tr> <td>H</td> <td>H</td> <td>Mn(Cl16)TDMPPCI^b</td> <td>(68)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>MnTDMPPCI^a</td> <td>(52)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Mn(Cl16)TDMPPCI^b</td> <td>(70)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>MnTDMPPCI^a</td> <td>(21)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Mn(Cl16)TDMPPCI^b</td> <td>(49)</td> </tr> </tbody> </table>	R ¹	R ²	Catalyst	Yield (%)	H	H	FeTDMPPCI ^a	(20)	H	H	MnTDMPPCI ^a	(40)	H	H	Mn(Cl16)TDMPPCI ^b	(68)	H	Me	MnTDMPPCI ^a	(52)	H	Me	Mn(Cl16)TDMPPCI ^b	(70)	Me	H	MnTDMPPCI ^a	(21)	Me	H	Mn(Cl16)TDMPPCI ^b	(49)	233																																		
			R ¹	R ²	Catalyst	Yield (%)																																																																
			H	H	FeTDMPPCI ^a	(20)																																																																
			H	H	MnTDMPPCI ^a	(40)																																																																
			H	H	Mn(Cl16)TDMPPCI ^b	(68)																																																																
			H	Me	MnTDMPPCI ^a	(52)																																																																
	H	Me	Mn(Cl16)TDMPPCI ^b	(70)																																																																		
	Me	H	MnTDMPPCI ^a	(21)																																																																		
	Me	H	Mn(Cl16)TDMPPCI ^b	(49)																																																																		
	DMD, acetone/CH ₂ Cl ₂ , 25°				234, 235																																																																	
<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(10)</td> <td>(53)</td> <td>(25)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>(35)</td> <td>(30)</td> <td>(8)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>(37)</td> <td>(53)</td> <td>(0)</td> </tr> </tbody> </table>					R ¹	R ²	I	II	III	H	H	(10)	(53)	(25)	Me	H	(35)	(30)	(8)	H	Me	(37)	(53)	(0)																																														
R ¹	R ²	I	II	III																																																																		
H	H	(10)	(53)	(25)																																																																		
Me	H	(35)	(30)	(8)																																																																		
H	Me	(37)	(53)	(0)																																																																		
DMD, acetone/CH ₂ Cl ₂ , Na ₂ SO ₄ , 25°				<table border="1"> <tbody> <tr> <td>H</td> <td>H</td> <td>(50)</td> <td>(—)</td> <td>(—)</td> </tr> </tbody> </table>	H	H	(50)	(—)	(—)																																																													
H	H	(50)	(—)	(—)																																																																		
DMD, acetone/MeOH, 25°				234, 235																																																																		
				<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(38)</td> <td>(35)</td> <td>(11)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>(45)</td> <td>(40)</td> <td>(0)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>(82)</td> <td>(0)</td> <td>(0)</td> </tr> </tbody> </table>	R ¹	R ²	I	II	III	H	H	(38)	(35)	(11)	Me	H	(45)	(40)	(0)	H	Me	(82)	(0)	(0)																																														
				R ¹	R ²	I	II	III																																																														
H	H	(38)	(35)	(11)																																																																		
Me	H	(45)	(40)	(0)																																																																		
H	Me	(82)	(0)	(0)																																																																		
C ₆₋₁₀ 	DMD, acetone/CH ₂ Cl ₂ , additive, 25°				235																																																																	
					<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Additive</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>H</td> <td>—</td> <td>(10)</td> <td>(25)</td> <td>(50)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>H</td> <td>Na₂SO₄</td> <td>(50)</td> <td>(7)</td> <td>(15)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>H</td> <td>H₂O</td> <td>(0)</td> <td>(30)</td> <td>(65)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>H</td> <td>—</td> <td>(30)</td> <td>(57)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>Me</td> <td>—</td> <td>(37)</td> <td>(tr)</td> <td>(53)</td> </tr> <tr> <td>Deoxyribose</td> <td>H</td> <td>H</td> <td>H</td> <td>—</td> <td>(—)</td> <td>(—)</td> <td>(70)</td> </tr> <tr> <td>Deoxyribose</td> <td>H</td> <td>Me</td> <td>H</td> <td>—</td> <td>(10)</td> <td>(12)</td> <td>(33)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Additive	I	II	III	Me	Me	H	H	—	(10)	(25)	(50)	Me	Me	H	H	Na ₂ SO ₄	(50)	(7)	(15)	Me	Me	H	H	H ₂ O	(0)	(30)	(65)	Me	Me	Me	H	—	(30)	(57)	(0)	Me	Me	H	Me	—	(37)	(tr)	(53)	Deoxyribose	H	H	H	—	(—)	(—)	(70)	Deoxyribose	H	Me	H	—	(10)	(12)	(33)	
					R ¹	R ²	R ³	R ⁴	Additive	I	II	III																																																										
					Me	Me	H	H	—	(10)	(25)	(50)																																																										
					Me	Me	H	H	Na ₂ SO ₄	(50)	(7)	(15)																																																										
					Me	Me	H	H	H ₂ O	(0)	(30)	(65)																																																										
					Me	Me	Me	H	—	(30)	(57)	(0)																																																										
Me	Me	H	Me	—	(37)	(tr)	(53)																																																															
Deoxyribose	H	H	H	—	(—)	(—)	(70)																																																															
Deoxyribose	H	Me	H	—	(10)	(12)	(33)																																																															
C ₆ 	DMD, acetone, 30°		(—)	$k_2 = (1.3 \pm 0.09) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$	236																																																																	

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)



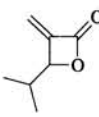
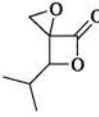


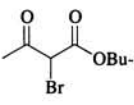
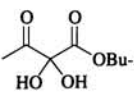
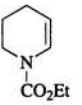
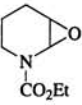
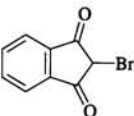
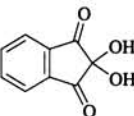
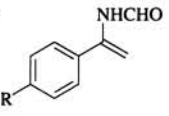
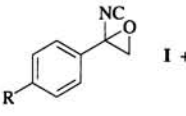
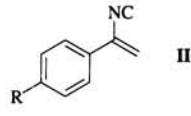
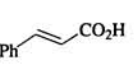
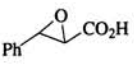
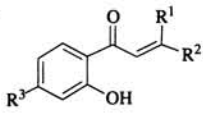
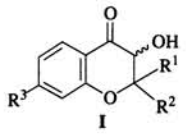
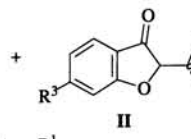
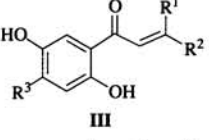
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
	DMD, acetone, 30°	 (—) $k_2 = (5.7 \pm 0.9) \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$	236																																				
C ₇ 	DMD, acetone, 20°, 6 d	 (40)	237																																				
	DMD, acetone, 20°, 3 d	 (37)	237																																				
C ₈ 	DMD, acetone/CH ₂ Cl ₂ , DMAP, 0° to rt	 (96)	240																																				
	DMD, acetone, 0° to rt, overnight	 (97)	239																																				
C ₉ 	DMD, acetone/CH ₂ Cl ₂ , DMAP, 0° to rt	 (80)	240																																				
C ₉₋₁₀ 	1. DMD, acetone/CH ₂ Cl ₂ , -40° 2. (CF ₃ SO ₂) ₂ O, <i>i</i> -Pr ₂ NEt, -78°	 I +  II	238																																				
		<table border="1"> <thead> <tr> <th>R</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>(41)</td> <td>(8)</td> </tr> <tr> <td>Cl</td> <td>(43)</td> <td>(7)</td> </tr> <tr> <td>CN</td> <td>(68)</td> <td>(0)</td> </tr> </tbody> </table>	R	I	II	Br	(41)	(8)	Cl	(43)	(7)	CN	(68)	(0)																									
R	I	II																																					
Br	(41)	(8)																																					
Cl	(43)	(7)																																					
CN	(68)	(0)																																					
C ₉ 	DMD, acetone, 30°	 (—) $k_2 = (0.66 \pm 0.07) \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$	236																																				
C ₉₋₁₈ 	DMD, CH ₂ Cl ₂ /acetone, 0 to 5°	 I +  II +  III	241, 242																																				
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(5)</td> <td>(53)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>(39)</td> <td>(26)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>MeO</td> <td>(4)</td> <td>(31)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>MeO</td> <td>(22)</td> <td>(5)</td> <td>(6)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>TsO</td> <td>(55)</td> <td>(14)</td> <td>(0)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	I	II	III	H	H	H	(5)	(53)	(0)	Me	Me	H	(39)	(26)	(0)	Me	H	MeO	(4)	(31)	(0)	Me	Me	MeO	(22)	(5)	(6)	Me	Me	TsO	(55)	(14)	(0)	
R ¹	R ²	R ³	I	II	III																																		
H	H	H	(5)	(53)	(0)																																		
Me	Me	H	(39)	(26)	(0)																																		
Me	H	MeO	(4)	(31)	(0)																																		
Me	Me	MeO	(22)	(5)	(6)																																		
Me	Me	TsO	(55)	(14)	(0)																																		

TABLE IC. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

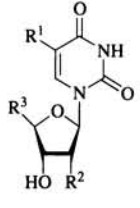
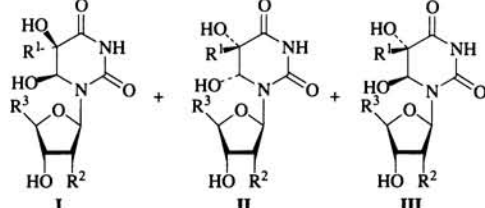
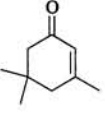
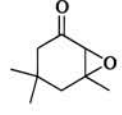
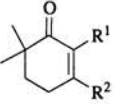
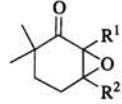
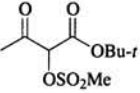
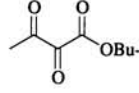
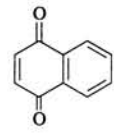
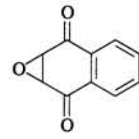
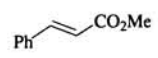
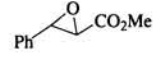
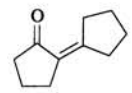
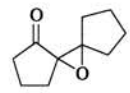
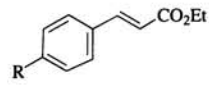
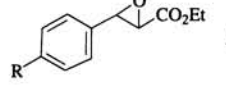
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																			
<p>C₉₋₁₀</p> 	DMD, acetone/H ₂ O, 25°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>I+II</th> <th>III</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>OH</td> <td>CH₂OH</td> <td>(85)</td> <td>(0)</td> <td>83:17</td> </tr> <tr> <td>Me</td> <td>H</td> <td>CO₂H</td> <td>(37)</td> <td>(39)</td> <td>—</td> </tr> <tr> <td>Me</td> <td>H</td> <td>CH₂OH</td> <td>(68)</td> <td>(23)</td> <td>—</td> </tr> </tbody> </table>	R ¹	R ²	R ³	I+II	III	I:II	H	OH	CH ₂ OH	(85)	(0)	83:17	Me	H	CO ₂ H	(37)	(39)	—	Me	H	CH ₂ OH	(68)	(23)	—	234											
R ¹	R ²	R ³	I+II	III	I:II																																	
H	OH	CH ₂ OH	(85)	(0)	83:17																																	
Me	H	CO ₂ H	(37)	(39)	—																																	
Me	H	CH ₂ OH	(68)	(23)	—																																	
<p>C₉</p> 	Cyclohexanone dioxirane, cyclohexanone/CH ₂ Cl ₂ , -10°, 6 h	 (83)	156																																			
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 20°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>20 h (86)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>24 h (90)</td> </tr> </tbody> </table>	R ¹	R ²	Time	H	Me	20 h (86)	Me	H	24 h (90)	34, 53																										
R ¹	R ²	Time																																				
H	Me	20 h (86)																																				
Me	H	24 h (90)																																				
	DMD, acetone/CH ₃ CN, NaOMe, 0°	 (85)	240																																			
<p>C₁₀</p> 	DMD (large excess), acetone, heat	 (—)	244																																			
	DMD, acetone, 30°	 (—) $k_2 = (0.63 \pm 0.06) \times 10^{-3} \text{ (M}^{-1}\text{s}^{-1}\text{)}$	236																																			
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 20°, 20 h	 (94)	34, 53																																			
<p>C₁₁₋₁₄</p> 	DMD, acetone, rt	 I <table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(71)</td> </tr> <tr> <td>Cl</td> <td>(55)</td> </tr> <tr> <td>Me</td> <td>(42)</td> </tr> <tr> <td>CF₃</td> <td>(43)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>(52)</td> </tr> </tbody> </table>	R	Yield (%)	H	(71)	Cl	(55)	Me	(42)	CF ₃	(43)	<i>i</i> -Pr	(52)	80																							
R	Yield (%)																																					
H	(71)																																					
Cl	(55)																																					
Me	(42)																																					
CF ₃	(43)																																					
<i>i</i> -Pr	(52)																																					
	DMD, acetone, 20.5°, 1.5 h	<table border="1"> <thead> <tr> <th>R</th> <th>log k_R/k_H</th> <th>R</th> <th>Temp</th> <th>$k_2 \times 10^4 \text{ (M}^{-1}\text{s}^{-1}\text{)}$</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>-0.302</td> <td>H</td> <td>283 K</td> <td>2.87</td> </tr> <tr> <td>F</td> <td>-0.086</td> <td>H</td> <td>283 K</td> <td>6.01</td> </tr> <tr> <td>H</td> <td>0</td> <td>H</td> <td>293 K</td> <td>6.88</td> </tr> <tr> <td>CF₃</td> <td>-0.828</td> <td>H</td> <td>298 K</td> <td>9.08</td> </tr> <tr> <td>Me</td> <td>0.238</td> <td>H</td> <td>303 K</td> <td>17.90</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>0.316</td> <td></td> <td></td> <td></td> </tr> </tbody> </table>	R	log k_R/k_H	R	Temp	$k_2 \times 10^4 \text{ (M}^{-1}\text{s}^{-1}\text{)}$	Cl	-0.302	H	283 K	2.87	F	-0.086	H	283 K	6.01	H	0	H	293 K	6.88	CF ₃	-0.828	H	298 K	9.08	Me	0.238	H	303 K	17.90	<i>i</i> -Pr	0.316				80
R	log k_R/k_H	R	Temp	$k_2 \times 10^4 \text{ (M}^{-1}\text{s}^{-1}\text{)}$																																		
Cl	-0.302	H	283 K	2.87																																		
F	-0.086	H	283 K	6.01																																		
H	0	H	293 K	6.88																																		
CF ₃	-0.828	H	298 K	9.08																																		
Me	0.238	H	303 K	17.90																																		
<i>i</i> -Pr	0.316																																					
	DMD, acetone, 25°, >30 h	R = H, I (63)	162																																			

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

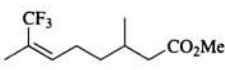
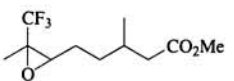
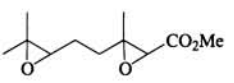
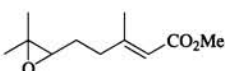
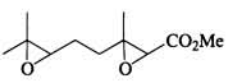
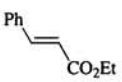
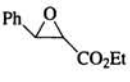
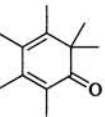
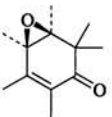
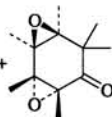
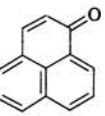
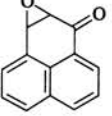
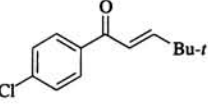
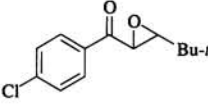
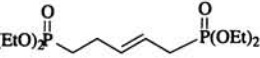
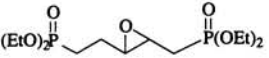
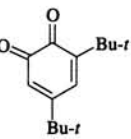
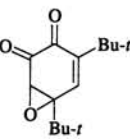
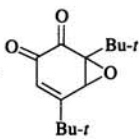
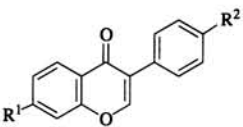
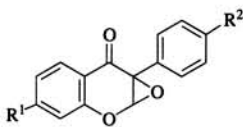
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																									
	DMD, acetone/CH ₂ Cl ₂ , 0°, 48 h	 I (93)	78																									
	TFD, TFP/(CH ₂ Cl ₂), 0°, 30 min	I (93)	78																									
	DMD, acetone/CH ₂ Cl ₂ , 0°, 48 h	 I (90)	78																									
	DMD, acetone/CH ₂ Cl ₂ , 0°, 48 h	 I (90)	78																									
	TFD, TFP/(CH ₂ Cl ₂), -70°, 2 h	I (90)	78																									
	DMD, acetone, rt, 24 h	 I (100)	181																									
	DMD, acetone/solvent (v/v = 1:1), 25°	I (—) <table border="1" data-bbox="1111 734 1362 1102"> <thead> <tr> <th>Solvent</th> <th>$k_2 \times 10^4$ (M⁻¹s⁻¹)</th> </tr> </thead> <tbody> <tr><td>AcOH</td><td>29.66 ± 0.12</td></tr> <tr><td>sulfolane</td><td>25.26 ± 0.26</td></tr> <tr><td>CHCl₃</td><td>16.30 ± 0.30</td></tr> <tr><td>CH₂Cl₂</td><td>14.66 ± 0.57</td></tr> <tr><td>Cl(CH₂)₂Cl</td><td>12.55 ± 0.52</td></tr> <tr><td>PhCl</td><td>19.00 ± 0.23</td></tr> <tr><td>C₆H₆</td><td>9.41 ± 0.10</td></tr> <tr><td>acetone</td><td>8.66 ± 0.22</td></tr> <tr><td>2-butanone</td><td>8.10 ± 0.14</td></tr> <tr><td>CCl₄</td><td>7.98 ± 0.02</td></tr> <tr><td>AcOMe</td><td>7.74 ± 0.04</td></tr> <tr><td>AcOEt</td><td>6.81 ± 0.20</td></tr> </tbody> </table>	Solvent	$k_2 \times 10^4$ (M ⁻¹ s ⁻¹)	AcOH	29.66 ± 0.12	sulfolane	25.26 ± 0.26	CHCl ₃	16.30 ± 0.30	CH ₂ Cl ₂	14.66 ± 0.57	Cl(CH ₂) ₂ Cl	12.55 ± 0.52	PhCl	19.00 ± 0.23	C ₆ H ₆	9.41 ± 0.10	acetone	8.66 ± 0.22	2-butanone	8.10 ± 0.14	CCl ₄	7.98 ± 0.02	AcOMe	7.74 ± 0.04	AcOEt	6.81 ± 0.20
Solvent	$k_2 \times 10^4$ (M ⁻¹ s ⁻¹)																											
AcOH	29.66 ± 0.12																											
sulfolane	25.26 ± 0.26																											
CHCl ₃	16.30 ± 0.30																											
CH ₂ Cl ₂	14.66 ± 0.57																											
Cl(CH ₂) ₂ Cl	12.55 ± 0.52																											
PhCl	19.00 ± 0.23																											
C ₆ H ₆	9.41 ± 0.10																											
acetone	8.66 ± 0.22																											
2-butanone	8.10 ± 0.14																											
CCl ₄	7.98 ± 0.02																											
AcOMe	7.74 ± 0.04																											
AcOEt	6.81 ± 0.20																											
	DMD (3 equiv), acetone, rt, 27 h	 I (—) +  II (—) I:II = 20:80	245																									
	DMD (4 equiv), acetone, rt, 47 h	II (90)	245																									
	DMD, acetone, 30°	 (—) $k_2 = (0.68 \pm 0.01) \times 10^{-3}$ (M ⁻¹ s ⁻¹)	236																									
		DMD, acetone, 30°	 (—) $k_2 = (0.70 \pm 0.02) \times 10^{-3}$ (M ⁻¹ s ⁻¹)	236																								
	DMD, acetone, rt, 24 h	 (100)	76																									
	DMD, acetone	 I +  II (52) I:II = 20:1	246																									
		DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°		<table border="1" data-bbox="1223 1894 1423 2043"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time</th> </tr> </thead> <tbody> <tr><td>H</td><td>Cl</td><td>110 h (100)</td></tr> <tr><td>OH</td><td>H</td><td>128 h (100)</td></tr> <tr><td>MeO</td><td>H</td><td>121 h (100)</td></tr> <tr><td>AcO</td><td>H</td><td>135 h (100)</td></tr> </tbody> </table>	R ¹	R ²	Time	H	Cl	110 h (100)	OH	H	128 h (100)	MeO	H	121 h (100)	AcO	H	135 h (100)	57								
R ¹		R ²	Time																									
H		Cl	110 h (100)																									
OH		H	128 h (100)																									
MeO	H	121 h (100)																										
AcO	H	135 h (100)																										

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

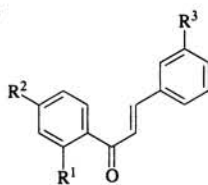
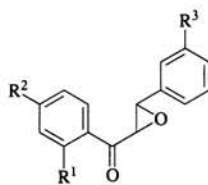
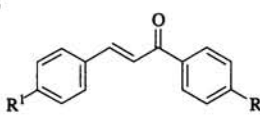
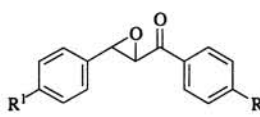
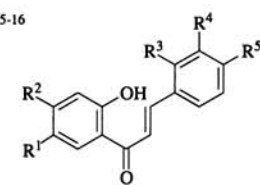
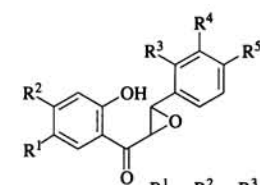
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																								
C ₁₅₋₁₇ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°, 20 to 24 h	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Yield (%)</th> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Br</td> <td>H</td> <td>(98)</td> <td>H</td> <td>MeO</td> <td>H</td> <td>(99)</td> </tr> <tr> <td>H</td> <td>H</td> <td>NO₂</td> <td>(57)</td> <td>OH</td> <td>H</td> <td>Me</td> <td>(~100)</td> </tr> <tr> <td>OH</td> <td>H</td> <td>H</td> <td>(~100)</td> <td>OH</td> <td>H</td> <td>MeO</td> <td>(~100)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(97)</td> <td>H</td> <td>Me</td> <td>Me</td> <td>(99)</td> </tr> <tr> <td>H</td> <td>Br</td> <td>MeO</td> <td>(98)</td> <td>H</td> <td>Me</td> <td>MeO</td> <td>(99)</td> </tr> <tr> <td>H</td> <td>H</td> <td>Me</td> <td>(~100)</td> <td>H</td> <td>MeO</td> <td>Me</td> <td>(99)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>H</td> <td>(~100)</td> <td>H</td> <td>MeO</td> <td>MeO</td> <td>(96)</td> </tr> <tr> <td>H</td> <td>H</td> <td>MeO</td> <td>(99)</td> <td></td> <td></td> <td></td> <td></td> </tr> </tbody> </table>	R ¹	R ²	R ³	Yield (%)	R ¹	R ²	R ³	Yield (%)	H	Br	H	(98)	H	MeO	H	(99)	H	H	NO ₂	(57)	OH	H	Me	(~100)	OH	H	H	(~100)	OH	H	MeO	(~100)	H	H	H	(97)	H	Me	Me	(99)	H	Br	MeO	(98)	H	Me	MeO	(99)	H	H	Me	(~100)	H	MeO	Me	(99)	H	Me	H	(~100)	H	MeO	MeO	(96)	H	H	MeO	(99)					34, 53
R ¹	R ²	R ³	Yield (%)	R ¹	R ²	R ³	Yield (%)																																																																				
H	Br	H	(98)	H	MeO	H	(99)																																																																				
H	H	NO ₂	(57)	OH	H	Me	(~100)																																																																				
OH	H	H	(~100)	OH	H	MeO	(~100)																																																																				
H	H	H	(97)	H	Me	Me	(99)																																																																				
H	Br	MeO	(98)	H	Me	MeO	(99)																																																																				
H	H	Me	(~100)	H	MeO	Me	(99)																																																																				
H	Me	H	(~100)	H	MeO	MeO	(96)																																																																				
H	H	MeO	(99)																																																																								
C ₁₅₋₁₆ 	DMD, acetone, 30°	 (—)	236																																																																								
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>k₂ × 10³ (M⁻¹s⁻¹)</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>H</td> <td>1.03 ± 0.05</td> </tr> <tr> <td>H</td> <td>Br</td> <td>1.39 ± 0.05</td> </tr> <tr> <td>Cl</td> <td>H</td> <td>0.95 ± 0.04</td> </tr> <tr> <td>H</td> <td>Cl</td> <td>1.47 ± 0.03</td> </tr> <tr> <td>F</td> <td>H</td> <td>1.58 ± 0.01</td> </tr> <tr> <td>H</td> <td>F</td> <td>1.54 ± 0.04</td> </tr> <tr> <td>NO₂</td> <td>H</td> <td>0.25 ± 0.03</td> </tr> <tr> <td>H</td> <td>NO₂</td> <td>1.07 ± 0.13</td> </tr> <tr> <td>H</td> <td>H</td> <td>1.54 ± 0.13</td> </tr> <tr> <td>CN</td> <td>H</td> <td>0.36 ± 0.03</td> </tr> <tr> <td>H</td> <td>CN</td> <td>1.24 ± 0.05</td> </tr> <tr> <td>Me</td> <td>H</td> <td>3.1 ± 0.2</td> </tr> <tr> <td>H</td> <td>Me</td> <td>1.86 ± 0.04</td> </tr> <tr> <td>MeO</td> <td>H</td> <td>11.5 ± 0.1</td> </tr> <tr> <td>H</td> <td>MeO</td> <td>2.12 ± 0.06</td> </tr> </tbody> </table>	R ¹	R ²	k ₂ × 10 ³ (M ⁻¹ s ⁻¹)	Br	H	1.03 ± 0.05	H	Br	1.39 ± 0.05	Cl	H	0.95 ± 0.04	H	Cl	1.47 ± 0.03	F	H	1.58 ± 0.01	H	F	1.54 ± 0.04	NO ₂	H	0.25 ± 0.03	H	NO ₂	1.07 ± 0.13	H	H	1.54 ± 0.13	CN	H	0.36 ± 0.03	H	CN	1.24 ± 0.05	Me	H	3.1 ± 0.2	H	Me	1.86 ± 0.04	MeO	H	11.5 ± 0.1	H	MeO	2.12 ± 0.06																									
R ¹	R ²	k ₂ × 10 ³ (M ⁻¹ s ⁻¹)																																																																									
Br	H	1.03 ± 0.05																																																																									
H	Br	1.39 ± 0.05																																																																									
Cl	H	0.95 ± 0.04																																																																									
H	Cl	1.47 ± 0.03																																																																									
F	H	1.58 ± 0.01																																																																									
H	F	1.54 ± 0.04																																																																									
NO ₂	H	0.25 ± 0.03																																																																									
H	NO ₂	1.07 ± 0.13																																																																									
H	H	1.54 ± 0.13																																																																									
CN	H	0.36 ± 0.03																																																																									
H	CN	1.24 ± 0.05																																																																									
Me	H	3.1 ± 0.2																																																																									
H	Me	1.86 ± 0.04																																																																									
MeO	H	11.5 ± 0.1																																																																									
H	MeO	2.12 ± 0.06																																																																									
C ₁₅₋₁₆ 	DMD, acetone/CH ₂ Cl ₂ , N ₂	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>R⁵</th> <th>Temp</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>-20°</td> <td>59 h</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>Cl</td> <td>-20°</td> <td>57 h</td> <td>(100)</td> </tr> <tr> <td>Cl</td> <td>H</td> <td>H</td> <td>H</td> <td>MeO</td> <td>-5°</td> <td>50 h</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>H</td> <td>H</td> <td>H</td> <td>-20°</td> <td>30 h</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>H</td> <td>MeO</td> <td>H</td> <td>H</td> <td>0°</td> <td>62 h</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>MeO</td> <td>H</td> <td>0°</td> <td>56 h</td> <td>(100)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>H</td> <td>MeO</td> <td>0°</td> <td>37 h</td> <td>(99)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	R ⁵	Temp	Time	Yield (%)	Cl	H	H	H	H	-20°	59 h	(100)	H	H	H	H	Cl	-20°	57 h	(100)	Cl	H	H	H	MeO	-5°	50 h	(100)	H	Me	H	H	H	-20°	30 h	(100)	H	H	MeO	H	H	0°	62 h	(100)	H	H	H	MeO	H	0°	56 h	(100)	Me	H	H	H	MeO	0°	37 h	(99)	247								
R ¹	R ²	R ³	R ⁴	R ⁵	Temp	Time	Yield (%)																																																																				
Cl	H	H	H	H	-20°	59 h	(100)																																																																				
H	H	H	H	Cl	-20°	57 h	(100)																																																																				
Cl	H	H	H	MeO	-5°	50 h	(100)																																																																				
H	Me	H	H	H	-20°	30 h	(100)																																																																				
H	H	MeO	H	H	0°	62 h	(100)																																																																				
H	H	H	MeO	H	0°	56 h	(100)																																																																				
Me	H	H	H	MeO	0°	37 h	(99)																																																																				

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

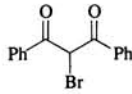
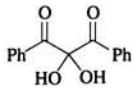
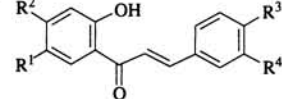
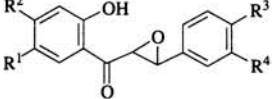
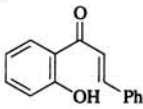
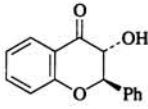
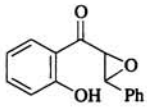

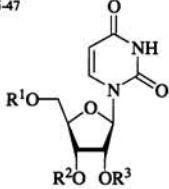
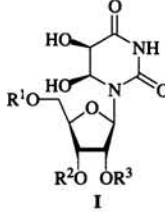
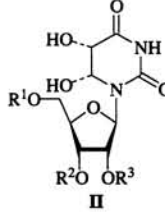
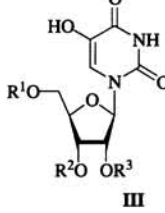
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																
C ₁₅ 	DMD, acetone/CH ₂ Cl ₂ , DMAP, 0° to rt	 (70)	240																																																
C ₁₅₋₁₉ 	DMD, CH ₂ Cl ₂ /acetone, 0°	 (—)	241, 242																																																
		<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>Br</td><td>H</td></tr> <tr><td>Cl</td><td>H</td><td>H</td><td>H</td></tr> <tr><td>H</td><td>H</td><td>F</td><td>H</td></tr> <tr><td>H</td><td>H</td><td>H</td><td>H</td></tr> <tr><td>H</td><td>OH</td><td>OH</td><td>OH</td></tr> <tr><td>H</td><td>H</td><td>CN</td><td>H</td></tr> <tr><td>H</td><td>H</td><td>Me</td><td>H</td></tr> <tr><td>H</td><td>Me</td><td>H</td><td>H</td></tr> <tr><td>H</td><td>H</td><td>MeO</td><td>H</td></tr> <tr><td>H</td><td>OH</td><td>—O(CH₂)₂O—</td><td></td></tr> <tr><td>H</td><td>MOMO</td><td>—O(CH₂)₂O—</td><td></td></tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	H	H	Br	H	Cl	H	H	H	H	H	F	H	H	H	H	H	H	OH	OH	OH	H	H	CN	H	H	H	Me	H	H	Me	H	H	H	H	MeO	H	H	OH	—O(CH ₂) ₂ O—		H	MOMO	—O(CH ₂) ₂ O—		
R ¹	R ²	R ³	R ⁴																																																
H	H	Br	H																																																
Cl	H	H	H																																																
H	H	F	H																																																
H	H	H	H																																																
H	OH	OH	OH																																																
H	H	CN	H																																																
H	H	Me	H																																																
H	Me	H	H																																																
H	H	MeO	H																																																
H	OH	—O(CH ₂) ₂ O—																																																	
H	MOMO	—O(CH ₂) ₂ O—																																																	
C ₁₅ 	DMD, acetone/CH ₂ Cl ₂ , 0° to rt, ~81.5 h	 I (74) +  II (20)	248																																																
	1. DMD, acetone/MeCN, AcOH/NaOAc, 0° 2. rt, ~25 h	 II (60)	248																																																
C ₁₅₋₄₇ 	DMD, CH ₂ Cl ₂ , 25°	 I +  II +  III	234, 235																																																
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>I+II</th> <th>III</th> </tr> </thead> <tbody> <tr><td>Ac</td><td>Ac</td><td>Ac</td><td>(70)</td><td>(18)</td></tr> <tr><td>Tr</td><td>H</td><td>H</td><td>(57)</td><td>(27)</td></tr> <tr><td>PhCO</td><td>PhCO</td><td>PhCO</td><td>(65)</td><td>(0)</td></tr> <tr><td>Tr</td><td>H</td><td>Tr</td><td>(63)</td><td>(0)</td></tr> <tr><td>Tr</td><td>Tr</td><td>H</td><td>(69)</td><td>(0)</td></tr> </tbody> </table>	R ¹	R ²	R ³	I+II	III	Ac	Ac	Ac	(70)	(18)	Tr	H	H	(57)	(27)	PhCO	PhCO	PhCO	(65)	(0)	Tr	H	Tr	(63)	(0)	Tr	Tr	H	(69)	(0)																			
R ¹	R ²	R ³	I+II	III																																															
Ac	Ac	Ac	(70)	(18)																																															
Tr	H	H	(57)	(27)																																															
PhCO	PhCO	PhCO	(65)	(0)																																															
Tr	H	Tr	(63)	(0)																																															
Tr	Tr	H	(69)	(0)																																															

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

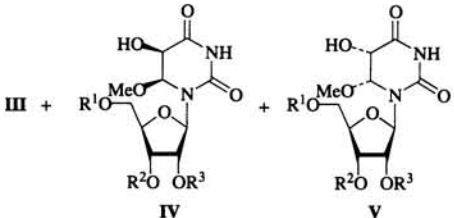
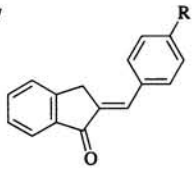
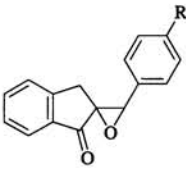
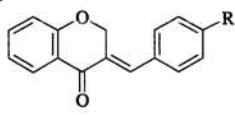
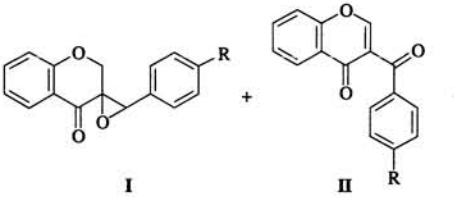
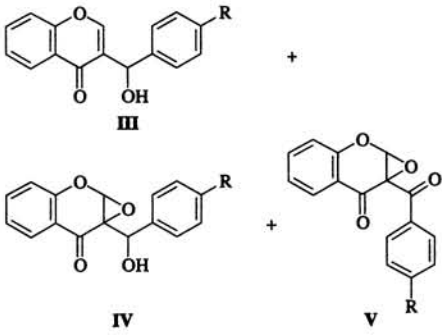
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																	
	DMD, acetone/MeOH, 25°	 III + V	234, 235																																																	
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>III</th> <th>IV+V</th> </tr> </thead> <tbody> <tr> <td>Ac</td> <td>Ac</td> <td>Ac</td> <td>(11)</td> <td>(75)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	III	IV+V	Ac	Ac	Ac	(11)	(75)																																								
R ¹	R ²	R ³	III	IV+V																																																
Ac	Ac	Ac	(11)	(75)																																																
C ₁₆₋₁₇	DMD, acetone/CH ₂ Cl ₂ , rt	  <table border="1"> <thead> <tr> <th>R</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>168 h (76)</td> </tr> <tr> <td>Cl</td> <td>168 h (72)</td> </tr> <tr> <td>F</td> <td>120 h (83)</td> </tr> <tr> <td>H</td> <td>72 h (71)</td> </tr> <tr> <td>CN</td> <td>168 h (77)</td> </tr> <tr> <td>Me</td> <td>72 h (94)</td> </tr> <tr> <td>MeO</td> <td>72 h (87)</td> </tr> </tbody> </table>	R	Time	Br	168 h (76)	Cl	168 h (72)	F	120 h (83)	H	72 h (71)	CN	168 h (77)	Me	72 h (94)	MeO	72 h (87)	249																																	
R	Time																																																			
Br	168 h (76)																																																			
Cl	168 h (72)																																																			
F	120 h (83)																																																			
H	72 h (71)																																																			
CN	168 h (77)																																																			
Me	72 h (94)																																																			
MeO	72 h (87)																																																			
C ₁₆₋₁₈	DMD, acetone/CH ₂ Cl ₂ , dark, rt	  I + II	250																																																	
		 III + V																																																		
		<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>I</th> <th>II</th> <th>III</th> <th>IV</th> <th>V</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>360 h</td> <td>(48)</td> <td>(29)</td> <td>(0)</td> <td>(0)</td> <td>(0)</td> </tr> <tr> <td>Cl</td> <td>456 h</td> <td>(47)</td> <td>(30)</td> <td>(0)</td> <td>(0)</td> <td>(0)</td> </tr> <tr> <td>H</td> <td>168 h</td> <td>(47)</td> <td>(21)</td> <td>(0)</td> <td>(0)</td> <td>(5)</td> </tr> <tr> <td>Me</td> <td>144 h</td> <td>(51)</td> <td>(28)</td> <td>(0)</td> <td>(4)</td> <td>(0)</td> </tr> <tr> <td>MeO</td> <td>144 h</td> <td>(38)</td> <td>(19)</td> <td>(5)</td> <td>(0)</td> <td>(7)</td> </tr> <tr> <td>EtO</td> <td>168 h</td> <td>(41)</td> <td>(16)</td> <td>(0)</td> <td>(0)</td> <td>(8)</td> </tr> </tbody> </table>	R	Time	I	II	III	IV	V	Br	360 h	(48)	(29)	(0)	(0)	(0)	Cl	456 h	(47)	(30)	(0)	(0)	(0)	H	168 h	(47)	(21)	(0)	(0)	(5)	Me	144 h	(51)	(28)	(0)	(4)	(0)	MeO	144 h	(38)	(19)	(5)	(0)	(7)	EtO	168 h	(41)	(16)	(0)	(0)	(8)	
R	Time	I	II	III	IV	V																																														
Br	360 h	(48)	(29)	(0)	(0)	(0)																																														
Cl	456 h	(47)	(30)	(0)	(0)	(0)																																														
H	168 h	(47)	(21)	(0)	(0)	(5)																																														
Me	144 h	(51)	(28)	(0)	(4)	(0)																																														
MeO	144 h	(38)	(19)	(5)	(0)	(7)																																														
EtO	168 h	(41)	(16)	(0)	(0)	(8)																																														

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

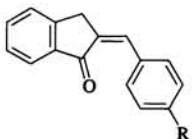
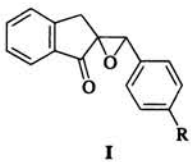
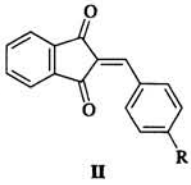
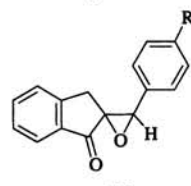
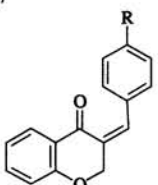
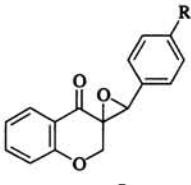
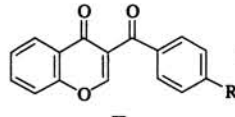
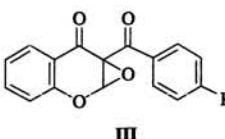
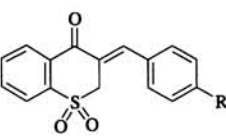
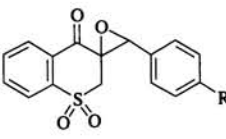
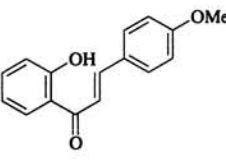
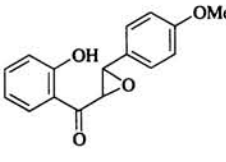
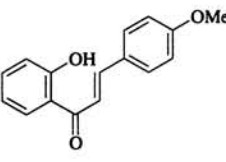
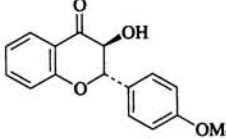
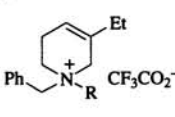
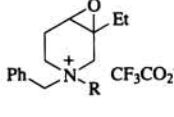
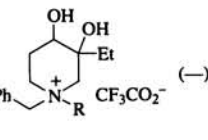
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																									
	DMD, acetone/CH ₂ Cl ₂ , rt	   <table border="1" data-bbox="1206 654 1397 769"> <thead> <tr> <th>R</th> <th>Time</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>192 h</td> <td>(56)</td> <td>(0)</td> </tr> <tr> <td>H</td> <td>120 h</td> <td>(39)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>96 h</td> <td>(35)</td> <td>(5)</td> </tr> </tbody> </table>	R	Time	I	II	Cl	192 h	(56)	(0)	H	120 h	(39)	(0)	Me	96 h	(35)	(5)	251									
R	Time	I	II																									
Cl	192 h	(56)	(0)																									
H	120 h	(39)	(0)																									
Me	96 h	(35)	(5)																									
	DMD, acetone/CH ₂ Cl ₂ , dark, rt	   <table border="1" data-bbox="1206 1090 1466 1228"> <thead> <tr> <th>R</th> <th>Time</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>528 h</td> <td>(23)</td> <td>(43)</td> <td>(0)</td> </tr> <tr> <td>H</td> <td>288 h</td> <td>(36)</td> <td>(23)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>192 h</td> <td>(42)</td> <td>(21)</td> <td>(0)</td> </tr> <tr> <td>MeO</td> <td>360 h</td> <td>(28)</td> <td>(19)</td> <td>(4)</td> </tr> </tbody> </table>	R	Time	I	II	III	Cl	528 h	(23)	(43)	(0)	H	288 h	(36)	(23)	(0)	Me	192 h	(42)	(21)	(0)	MeO	360 h	(28)	(19)	(4)	250
R	Time	I	II	III																								
Cl	528 h	(23)	(43)	(0)																								
H	288 h	(36)	(23)	(0)																								
Me	192 h	(42)	(21)	(0)																								
MeO	360 h	(28)	(19)	(4)																								
	TFD, TFP/CH ₂ Cl ₂ , 20°	 <table border="1" data-bbox="1241 1274 1397 1389"> <thead> <tr> <th>R</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>3 d</td> <td>(69)</td> </tr> <tr> <td>H</td> <td>2.5 d</td> <td>(31)</td> </tr> <tr> <td>Me</td> <td>3 d</td> <td>(14)</td> </tr> </tbody> </table>	R	Time		Cl	3 d	(69)	H	2.5 d	(31)	Me	3 d	(14)	66													
R	Time																											
Cl	3 d	(69)																										
H	2.5 d	(31)																										
Me	3 d	(14)																										
	DMD, acetone/CH ₂ Cl ₂ , 0° to rt, 24 h	 (100)	248																									
	DMD, acetone/MeCN, AcOH/NaOAc, 0° to rt, 20 h	 (62)	248																									
	DMD, acetone/CH ₂ Cl ₂ , 0°, 4 h or 1. TFD, -78° 2. -20°, 30 min	  (—) + (—)	60a																									
		R = H, Me, MeO																										

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

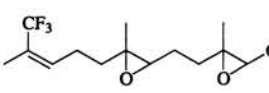
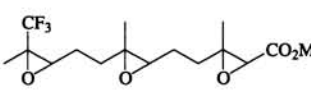
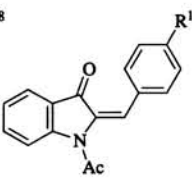
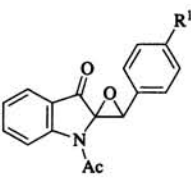
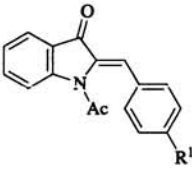
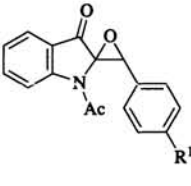
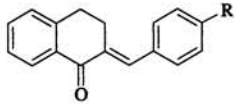
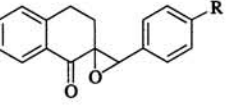
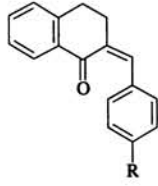
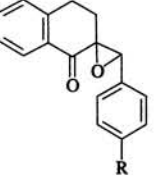
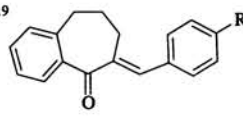
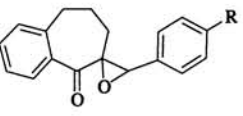
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																									
C ₁₆ 	DMD, acetone/(CH ₂ Cl ₂), -20°, 8 d	 I (93)	78																									
	TFD, TFP (CH ₂ Cl ₂), -20°, 1 h	I (94)	78																									
C ₁₇₋₁₈ 	DMD, acetone/CH ₂ Cl ₂ , rt, dark		<table border="1"> <thead> <tr> <th>R¹</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>113 h</td> <td>(86)</td> </tr> <tr> <td>Cl</td> <td>144 h</td> <td>(85)</td> </tr> <tr> <td>F</td> <td>109 h</td> <td>(92)</td> </tr> <tr> <td>H</td> <td>109 h</td> <td>(71)</td> </tr> <tr> <td>Me</td> <td>74 h</td> <td>(81)</td> </tr> <tr> <td>MeO</td> <td>113 h</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	Time		Br	113 h	(86)	Cl	144 h	(85)	F	109 h	(92)	H	109 h	(71)	Me	74 h	(81)	MeO	113 h	(—)	252			
		R ¹	Time																									
Br	113 h	(86)																										
Cl	144 h	(85)																										
F	109 h	(92)																										
H	109 h	(71)																										
Me	74 h	(81)																										
MeO	113 h	(—)																										
	DMD, acetone/CH ₂ Cl ₂ , rt, dark		<table border="1"> <thead> <tr> <th>R¹</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>121 h</td> <td>(87)</td> </tr> <tr> <td>Cl</td> <td>144 h</td> <td>(87)</td> </tr> <tr> <td>F</td> <td>109 h</td> <td>(89)</td> </tr> <tr> <td>NO₂</td> <td>150 h</td> <td>(84)</td> </tr> <tr> <td>H</td> <td>109 h</td> <td>(83)</td> </tr> <tr> <td>Me</td> <td>89 h</td> <td>(85)</td> </tr> <tr> <td>MeO</td> <td>—</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	Time		Br	121 h	(87)	Cl	144 h	(87)	F	109 h	(89)	NO ₂	150 h	(84)	H	109 h	(83)	Me	89 h	(85)	MeO	—	(—)	252
		R ¹	Time																									
Br	121 h	(87)																										
Cl	144 h	(87)																										
F	109 h	(89)																										
NO ₂	150 h	(84)																										
H	109 h	(83)																										
Me	89 h	(85)																										
MeO	—	(—)																										
	DMD, acetone/CH ₂ Cl ₂ , dark, rt		<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>72 h</td> <td>(89)</td> </tr> <tr> <td>Cl</td> <td>72 h</td> <td>(81)</td> </tr> <tr> <td>F</td> <td>48 h</td> <td>(79)</td> </tr> <tr> <td>H</td> <td>48 h</td> <td>(79)</td> </tr> <tr> <td>CN</td> <td>72 h</td> <td>(83)</td> </tr> <tr> <td>Me</td> <td>48 h</td> <td>(85)</td> </tr> <tr> <td>MeO</td> <td>48 h</td> <td>(85)</td> </tr> </tbody> </table>	R	Time		Br	72 h	(89)	Cl	72 h	(81)	F	48 h	(79)	H	48 h	(79)	CN	72 h	(83)	Me	48 h	(85)	MeO	48 h	(85)	253
		R	Time																									
Br	72 h	(89)																										
Cl	72 h	(81)																										
F	48 h	(79)																										
H	48 h	(79)																										
CN	72 h	(83)																										
Me	48 h	(85)																										
MeO	48 h	(85)																										
	DMD, acetone/CH ₂ Cl ₂ , dark, rt		<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>20 h</td> <td>(30)</td> </tr> <tr> <td>H</td> <td>144 h</td> <td>(28)</td> </tr> <tr> <td>Me</td> <td>120 h</td> <td>(23)</td> </tr> </tbody> </table>	R	Time		Cl	20 h	(30)	H	144 h	(28)	Me	120 h	(23)	253												
		R	Time																									
Cl	20 h	(30)																										
H	144 h	(28)																										
Me	120 h	(23)																										
C ₁₈₋₁₉ 	DMD, acetone/CH ₂ Cl ₂ , rt		<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>216 h</td> <td>(73)</td> </tr> <tr> <td>Cl</td> <td>192 h</td> <td>(79)</td> </tr> <tr> <td>F</td> <td>192 h</td> <td>(79)</td> </tr> <tr> <td>H</td> <td>168 h</td> <td>(83)</td> </tr> <tr> <td>CN</td> <td>216 h</td> <td>(96)</td> </tr> <tr> <td>Me</td> <td>168 h</td> <td>(90)</td> </tr> <tr> <td>MeO</td> <td>120 h</td> <td>(78)</td> </tr> </tbody> </table>	R	Time		Br	216 h	(73)	Cl	192 h	(79)	F	192 h	(79)	H	168 h	(83)	CN	216 h	(96)	Me	168 h	(90)	MeO	120 h	(78)	251
		R	Time																									
Br	216 h	(73)																										
Cl	192 h	(79)																										
F	192 h	(79)																										
H	168 h	(83)																										
CN	216 h	(96)																										
Me	168 h	(90)																										
MeO	120 h	(78)																										

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

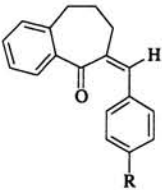
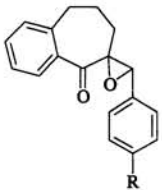
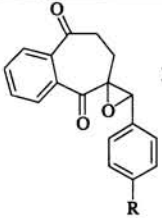
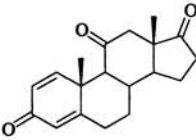
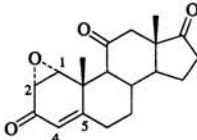
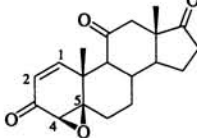
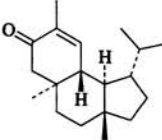
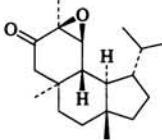
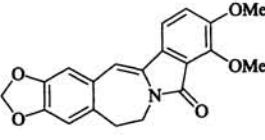
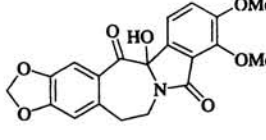

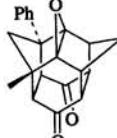
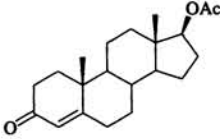
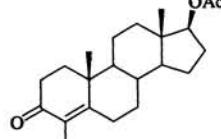
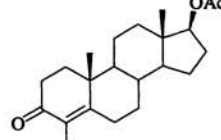
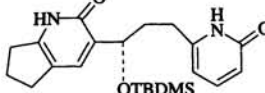
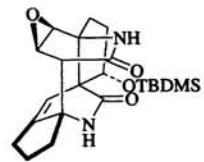
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																
	DMD, acetone/CH ₂ Cl ₂ , rt	 I +  II	251																
		<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>I (%)</th> <th>II (%)</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>336 h</td> <td>(61)</td> <td>(8)</td> </tr> <tr> <td>H</td> <td>240 h</td> <td>(50)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>216 h</td> <td>(53)</td> <td>(7)</td> </tr> </tbody> </table>	R	Time	I (%)	II (%)	Cl	336 h	(61)	(8)	H	240 h	(50)	(0)	Me	216 h	(53)	(7)	
R	Time	I (%)	II (%)																
Cl	336 h	(61)	(8)																
H	240 h	(50)	(0)																
Me	216 h	(53)	(7)																
C₁₉ 	DMD, CH ₂ Cl ₂ /acetone, -20°, 20 h	 (80) + 4β,5β-epoxide (15) + 4α,5α-epoxide (5)	77																
	DMD, CH ₂ Cl ₂ /acetone, -20°, 28 h	 (81) + 4α,5α-epoxide (12) + 1α,2α-epoxide (6) + 1β,2β-epoxide (1)	77																
	DMD, acetone/CH ₂ Cl ₂ , rt	 (72)	54																
C₂₀ 	1. DMD, acetone/CH ₂ Cl ₂ , 0° 2. NaHCO ₃	 (38)	254																
C₂₁ 	DMD, acetone, -30°, 10 min	 (—)	256																
	1. DMD, acetone, dark, rt, 8 h 2. NaBr or LiBr, Amberlyst 15, rt, 12 h	 (97)	171																
	1. DMD, acetone, dark, rt, 8 h 2. NaCl or LiCl, Amberlyst 15, rt, 12 h	 (89)	171																
	1. hv, toluene, <5° 2. DMD, 0 to 5°	 (—)	257																

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

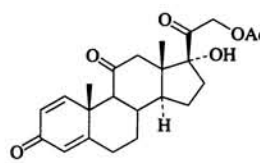
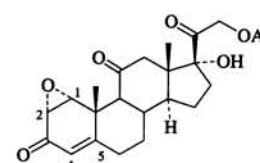
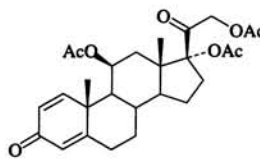
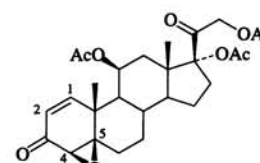
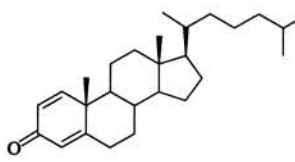
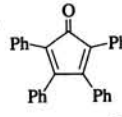
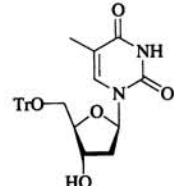
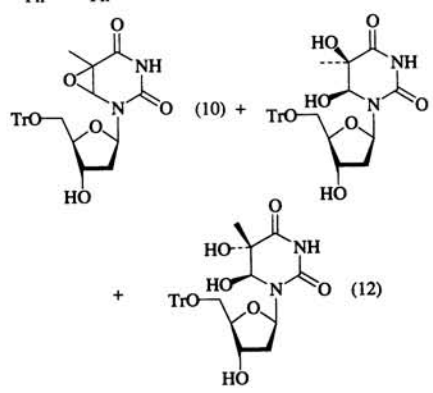
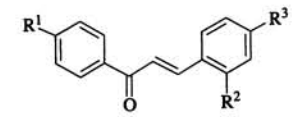
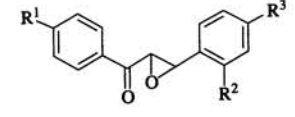
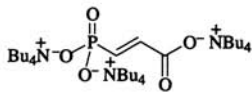
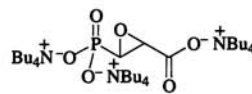
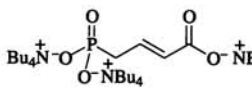
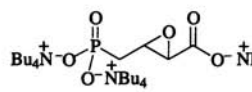
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																												
C ₂₃ 	DMD, acetone, 20°, 20 h	 I (80)	258																												
	DMD, acetone/CH ₂ Cl ₂ , -20°, 20 h	I (80) + 4β,5β-epoxide (16) + 4α,5α-epoxide (4)	77																												
C ₂₇ 	DMD, acetone/CH ₂ Cl ₂ , -20°, 24 h	 (49) + 4α,5α-epoxide (11) + 1α,2α-epoxide (17) + 1β,2β-epoxide (3)	77																												
	DMD, acetone/CH ₂ Cl ₂ , -20°, 24 h	(39)	77																												
	DMD, acetone/CH ₂ Cl ₂ , -20°, 72 h	(40)	77																												
C ₂₉ 	DMD (large excess), acetone, heat	(-)	5																												
	DMD, acetone/CH ₂ Cl ₂ , 25°	 (10) + (43) + (12)	234																												
C ₂₉ 	DMD, acetone/CH ₂ Cl ₂ , 20°, 48 h		259																												
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th></th> </tr> </thead> <tbody> <tr> <td><i>O</i>-β-D-glucosyl-Ac₄</td> <td>H</td> <td>H</td> <td>(84)</td> </tr> <tr> <td>H</td> <td><i>O</i>-β-D-glucosyl-Ac₄</td> <td>H</td> <td>(88)</td> </tr> <tr> <td>H</td> <td>H</td> <td><i>O</i>-β-D-glucosyl-Ac₄</td> <td>(87)</td> </tr> <tr> <td><i>O</i>-β-cellobiosyl-Ac₇</td> <td>H</td> <td>H</td> <td>(78)</td> </tr> <tr> <td>H</td> <td><i>O</i>-β-cellobiosyl-Ac₇</td> <td>H</td> <td>(82)</td> </tr> <tr> <td>H</td> <td>H</td> <td><i>O</i>-β-cellobiosyl-Ac₇</td> <td>(81)</td> </tr> </tbody> </table>	R ¹	R ²	R ³		<i>O</i> -β-D-glucosyl-Ac ₄	H	H	(84)	H	<i>O</i> -β-D-glucosyl-Ac ₄	H	(88)	H	H	<i>O</i> -β-D-glucosyl-Ac ₄	(87)	<i>O</i> -β-cellobiosyl-Ac ₇	H	H	(78)	H	<i>O</i> -β-cellobiosyl-Ac ₇	H	(82)	H	H	<i>O</i> -β-cellobiosyl-Ac ₇	(81)	
R ¹	R ²	R ³																													
<i>O</i> -β-D-glucosyl-Ac ₄	H	H	(84)																												
H	<i>O</i> -β-D-glucosyl-Ac ₄	H	(88)																												
H	H	<i>O</i> -β-D-glucosyl-Ac ₄	(87)																												
<i>O</i> -β-cellobiosyl-Ac ₇	H	H	(78)																												
H	<i>O</i> -β-cellobiosyl-Ac ₇	H	(82)																												
H	H	<i>O</i> -β-cellobiosyl-Ac ₇	(81)																												

TABLE 1C. EPOXIDATION OF OLEFINS WITH ELECTRON ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅₁		DMD, acetone, rt, 4 d	 (100)	76
C ₅₂		DMD, acetone, rt, 4 d	 (100)	76

^a TDMPP = 5,10,15,20-tetrakis(2,6-dimethoxyphenyl)porphyrin dianion

^b (Cl16)TDMPP = 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dimethoxy-3,5-dichlorophenyl)porphyrin dianion

TABLE 1D. EPOXIDATION OF OLEFINS WITH ELECTRON DONORS AND ACCEPTORS BY ISOLATED DIOXIRANES


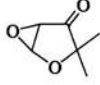

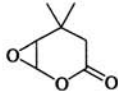
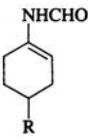
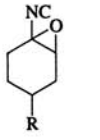
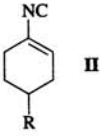

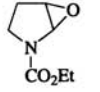
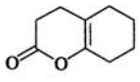
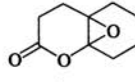
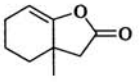
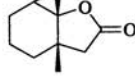
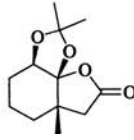
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
C ₆ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 0°, 23 h	 (~100)	56										
C ₇ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°, 3 h	 (79)	44, 212										
C ₇₋₁₃ 	1. DMD, acetone/CH ₂ Cl ₂ , -40° 2. (CF ₃ SO ₂) ₂ O, <i>i</i> -Pr ₂ NEt, -78°	 I +  II	<table border="1"> <thead> <tr> <th>R</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(36)</td> <td>(22)</td> </tr> <tr> <td>Ph</td> <td>(33)</td> <td>(8)</td> </tr> </tbody> </table>	R	I	II	H	(36)	(22)	Ph	(33)	(8)	238
R	I	II											
H	(36)	(22)											
Ph	(33)	(8)											
C ₇ 	DMD, acetone, 0° to rt, overnight	 (97)	239										
C ₉ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°, 3 h	 (83)	44, 212										
	DMD, acetone, -78° to rt	 (97)	243										
	1. Moist DMD, acetone, -78° to rt, 18 h 2. Acetone, CuSO ₄ , H ₂ SO ₄ , 50°, 3 d	 (17)	243										

TABLE 1D. EPOXIDATION OF OLEFINS WITH ELECTRON DONORS AND ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

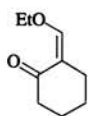
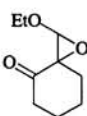
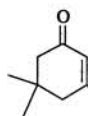
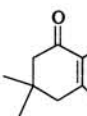
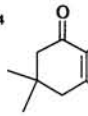
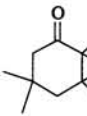










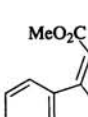
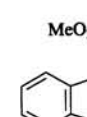
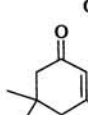
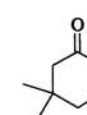
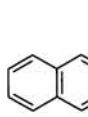
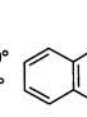
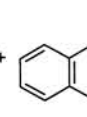


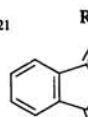
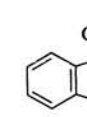
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°, 11.5 h	 (~100)	56																				
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 0°, 11 h	 (99)	56																				
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Et</td> <td>26 h</td> <td>(98)</td> </tr> <tr> <td>Me</td> <td>Et</td> <td>17 h</td> <td>(~100)</td> </tr> <tr> <td>H</td> <td><i>n</i>-Bu</td> <td>11 h</td> <td>(99)</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>24 h</td> <td>(97)</td> </tr> </tbody> </table>	R ¹	R ²	Time		H	Et	26 h	(98)	Me	Et	17 h	(~100)	H	<i>n</i> -Bu	11 h	(99)	H	Ph	24 h	(97)	56
R ¹	R ²	Time																					
H	Et	26 h	(98)																				
Me	Et	17 h	(~100)																				
H	<i>n</i> -Bu	11 h	(99)																				
H	Ph	24 h	(97)																				
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 20°, 48 h	 (98)	205																				
	DMD- <i>d</i> ₆ , acetone- <i>d</i> ₆ , -50°	 (100)	167																				
	1. DMD, acetone/CH ₂ Cl ₂ , -78°, 3 h 2. -20°, 24 h	 (79)	167																				
	DMD- <i>d</i> ₆ , acetone- <i>d</i> ₆ , -50°	 (100)	167																				
	DMD, acetone/MeOH, -78°, 2 h	 (40)	167																				
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 20°, 12 h	 (93)	45																				
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 20°, 91 h	 (98)	205																				
	1. DMD, acetone/CH ₂ Cl ₂ , -40° 2. (CF ₃ SO ₂) ₂ O, <i>i</i> -Pr ₂ NEt, -78°	 (30) +  (8)	238																				
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°, 3 h	 (96)	44, 212																				
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>6 h</td> <td>(~100)</td> </tr> <tr> <td>Ph</td> <td>88 h</td> <td>(~100)</td> </tr> </tbody> </table>	R	Time		H	6 h	(~100)	Ph	88 h	(~100)	212, 44											
R	Time																						
H	6 h	(~100)																					
Ph	88 h	(~100)																					

TABLE 1D. EPOXIDATION OF OLEFINS WITH ELECTRON DONORS AND ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

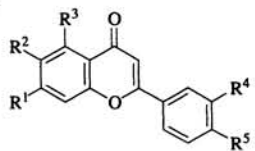
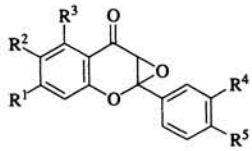
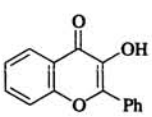
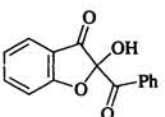
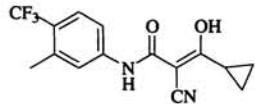
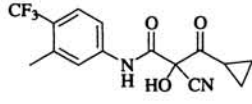
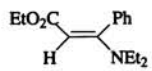
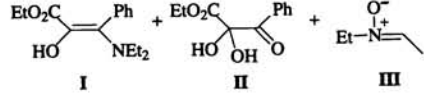
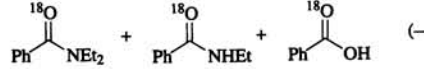
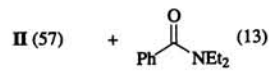
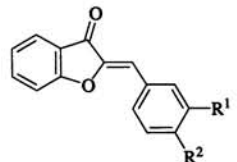
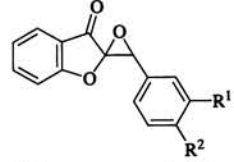
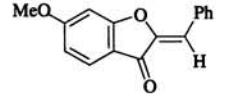
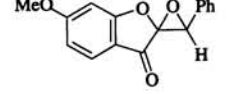
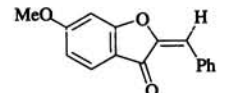
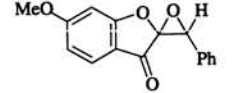
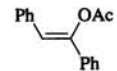
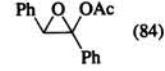
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																																								
C ₁₅₋₁₇ 	DMD, acetone/CH ₂ Cl ₂ , N ₂	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>R⁵</th> <th>Temp</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td><td>H</td><td>H</td><td>Cl</td><td>0°</td><td>61 h</td><td>(92)</td></tr> <tr><td>H</td><td>H</td><td>H</td><td>Cl</td><td>H</td><td>-20°</td><td>28 h</td><td>(~100)</td></tr> <tr><td>H</td><td>H</td><td>H</td><td>H</td><td>NO₂</td><td>-20°</td><td>72 h</td><td>(~100)</td></tr> <tr><td>H</td><td>H</td><td>H</td><td>H</td><td>H</td><td>0°</td><td>36 h</td><td>(~100)</td></tr> <tr><td>H</td><td>Me</td><td>H</td><td>H</td><td>Cl</td><td>-20°</td><td>27 h</td><td>(~100)</td></tr> <tr><td>H</td><td>Me</td><td>H</td><td>Cl</td><td>H</td><td>-20°</td><td>37 h</td><td>(~100)</td></tr> <tr><td>H</td><td>Me</td><td>H</td><td>H</td><td>H</td><td>0°</td><td>41 h</td><td>(~100)</td></tr> <tr><td>H</td><td>H</td><td>H</td><td>H</td><td>Me</td><td>0°</td><td>23 h</td><td>(~100)</td></tr> <tr><td>H</td><td>H</td><td>H</td><td>H</td><td>MeO</td><td>0°</td><td>24 h</td><td>(~100)</td></tr> <tr><td>H</td><td>H</td><td>MeO</td><td>H</td><td>H</td><td>0°</td><td>26 h</td><td>(~100)</td></tr> <tr><td>H</td><td>MeO</td><td>H</td><td>H</td><td>H</td><td>-10°</td><td>48 h</td><td>(~100)</td></tr> <tr><td>MeO</td><td>H</td><td>H</td><td>H</td><td>H</td><td>-10°</td><td>46 h</td><td>(~100)</td></tr> <tr><td>H</td><td>Me</td><td>H</td><td>H</td><td>Me</td><td>-10°</td><td>34 h</td><td>(~100)</td></tr> <tr><td>H</td><td>Me</td><td>H</td><td>H</td><td>MeO</td><td>0°</td><td>23 h</td><td>(~100)</td></tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	R ⁵	Temp	Time		H	H	H	H	Cl	0°	61 h	(92)	H	H	H	Cl	H	-20°	28 h	(~100)	H	H	H	H	NO ₂	-20°	72 h	(~100)	H	H	H	H	H	0°	36 h	(~100)	H	Me	H	H	Cl	-20°	27 h	(~100)	H	Me	H	Cl	H	-20°	37 h	(~100)	H	Me	H	H	H	0°	41 h	(~100)	H	H	H	H	Me	0°	23 h	(~100)	H	H	H	H	MeO	0°	24 h	(~100)	H	H	MeO	H	H	0°	26 h	(~100)	H	MeO	H	H	H	-10°	48 h	(~100)	MeO	H	H	H	H	-10°	46 h	(~100)	H	Me	H	H	Me	-10°	34 h	(~100)	H	Me	H	H	MeO	0°	23 h	(~100)	59, 58
R ¹	R ²	R ³	R ⁴	R ⁵	Temp	Time																																																																																																																					
H	H	H	H	Cl	0°	61 h	(92)																																																																																																																				
H	H	H	Cl	H	-20°	28 h	(~100)																																																																																																																				
H	H	H	H	NO ₂	-20°	72 h	(~100)																																																																																																																				
H	H	H	H	H	0°	36 h	(~100)																																																																																																																				
H	Me	H	H	Cl	-20°	27 h	(~100)																																																																																																																				
H	Me	H	Cl	H	-20°	37 h	(~100)																																																																																																																				
H	Me	H	H	H	0°	41 h	(~100)																																																																																																																				
H	H	H	H	Me	0°	23 h	(~100)																																																																																																																				
H	H	H	H	MeO	0°	24 h	(~100)																																																																																																																				
H	H	MeO	H	H	0°	26 h	(~100)																																																																																																																				
H	MeO	H	H	H	-10°	48 h	(~100)																																																																																																																				
MeO	H	H	H	H	-10°	46 h	(~100)																																																																																																																				
H	Me	H	H	Me	-10°	34 h	(~100)																																																																																																																				
H	Me	H	H	MeO	0°	23 h	(~100)																																																																																																																				
C ₁₅ 	1. DMD, acetone/CH ₂ Cl ₂ , Ar, 0°, 2.3 h 2. rt, ~25 h	 (56)	248																																																																																																																								
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , rt, 24 h	 (80)	260																																																																																																																								
C ₁₅ 	DMD, acetone/CH ₂ Cl ₂ , -70°	 I:II:III = 27:49:24	228																																																																																																																								
	1. DMD, acetone/CH ₂ Cl ₂ , -70° 2. ¹⁸ O ₂	 (—)	228																																																																																																																								
	DMD, acetone/CH ₂ Cl ₂ , 0°	 (13)	228																																																																																																																								
C ₁₆ 	DMD, acetone/CH ₂ Cl ₂ , N ₂	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Temp</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr><td>H</td><td>MeO</td><td>-5°</td><td>11 h</td><td>(100)</td></tr> <tr><td>MeO</td><td>H</td><td>0°</td><td>22 h</td><td>(100)</td></tr> </tbody> </table>	R ¹	R ²	Temp	Time		H	MeO	-5°	11 h	(100)	MeO	H	0°	22 h	(100)	57																																																																																																									
R ¹	R ²	Temp	Time																																																																																																																								
H	MeO	-5°	11 h	(100)																																																																																																																							
MeO	H	0°	22 h	(100)																																																																																																																							
	DMD, acetone/CHCl ₃ , rt, 34 h	 (83)	248																																																																																																																								
	1. DMD, acetone/CH ₂ Cl ₂ , 0°, 1 h 2. rt, 36 h	 (33)	248																																																																																																																								
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°, 7 h	 (84)	44, 45																																																																																																																								

TABLE 1D. EPOXIDATION OF OLEFINS WITH ELECTRON DONORS AND ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

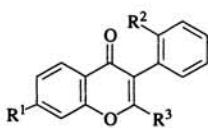
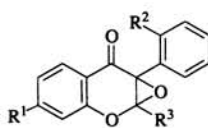
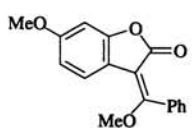
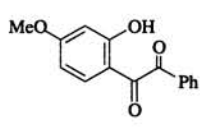
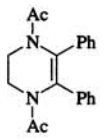
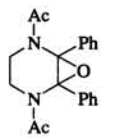
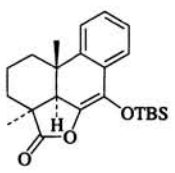
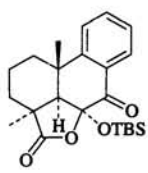
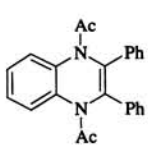
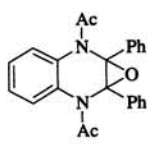
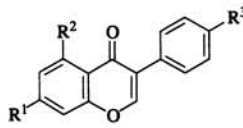
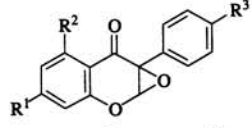
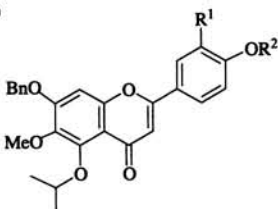
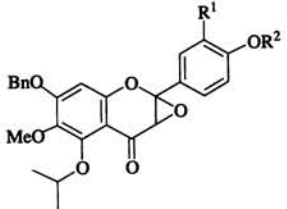
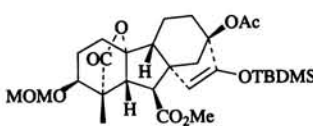
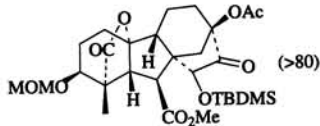
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
C ₁₇₋₂₃ 	DMD, acetone/CH ₂ Cl ₂ , -20°, ~15 d	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th></th> </tr> </thead> <tbody> <tr> <td>MeO</td> <td>H</td> <td>Me</td> <td>(38)</td> </tr> <tr> <td>Ms</td> <td>H</td> <td>Me</td> <td>(23)</td> </tr> <tr> <td>MeO</td> <td>H</td> <td>Et</td> <td>(38)</td> </tr> <tr> <td>MeO</td> <td>MeO</td> <td>Me</td> <td>(14)</td> </tr> <tr> <td>Ms</td> <td>H</td> <td>Et</td> <td>(27)</td> </tr> <tr> <td>MeO</td> <td>MeO</td> <td>Et</td> <td>(17)</td> </tr> <tr> <td>MeO</td> <td>H</td> <td>Ph</td> <td>(16)</td> </tr> <tr> <td>MeO</td> <td>MeO</td> <td>Ph</td> <td>(19)</td> </tr> </tbody> </table>	R ¹	R ²	R ³		MeO	H	Me	(38)	Ms	H	Me	(23)	MeO	H	Et	(38)	MeO	MeO	Me	(14)	Ms	H	Et	(27)	MeO	MeO	Et	(17)	MeO	H	Ph	(16)	MeO	MeO	Ph	(19)	60
R ¹	R ²	R ³																																					
MeO	H	Me	(38)																																				
Ms	H	Me	(23)																																				
MeO	H	Et	(38)																																				
MeO	MeO	Me	(14)																																				
Ms	H	Et	(27)																																				
MeO	MeO	Et	(17)																																				
MeO	H	Ph	(16)																																				
MeO	MeO	Ph	(19)																																				
C ₁₇ 	1. DMD, acetone/CH ₂ Cl ₂ , Ar, 0°, 2.3 h 2. rt, ~25 h	 (33)	248																																				
C ₂₀ 	DMD, acetone, 0°, 6 h	 (94)	255																																				
C ₂₃ 	DMD, acetone/CH ₂ Cl ₂ , -78°, 30 min	 (>85%)	243																																				
C ₂₄ 	DMD, acetone, 0°, 48 h	 (—)	255																																				
C ₂₅ 	DMD, acetone/CH ₂ Cl ₂ , 20°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td><i>O</i>-β-D-glucosyl-Ac₄</td> <td>H</td> <td>H</td> <td>96 h (76)</td> </tr> <tr> <td><i>O</i>-β-D-glucosyl-Ac₄</td> <td>H</td> <td>MeO</td> <td>60 h (88)</td> </tr> <tr> <td>AcO</td> <td>AcO</td> <td><i>O</i>-β-D-glucosyl-Ac₄</td> <td>80 h (80)</td> </tr> <tr> <td><i>O</i>-β-cellobiosyl-Ac₇</td> <td>H</td> <td>H</td> <td>72 h (83)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Time	<i>O</i> -β-D-glucosyl-Ac ₄	H	H	96 h (76)	<i>O</i> -β-D-glucosyl-Ac ₄	H	MeO	60 h (88)	AcO	AcO	<i>O</i> -β-D-glucosyl-Ac ₄	80 h (80)	<i>O</i> -β-cellobiosyl-Ac ₇	H	H	72 h (83)	259																
R ¹	R ²	R ³	Time																																				
<i>O</i> -β-D-glucosyl-Ac ₄	H	H	96 h (76)																																				
<i>O</i> -β-D-glucosyl-Ac ₄	H	MeO	60 h (88)																																				
AcO	AcO	<i>O</i> -β-D-glucosyl-Ac ₄	80 h (80)																																				
<i>O</i> -β-cellobiosyl-Ac ₇	H	H	72 h (83)																																				
C ₂₇₋₄₀ 	1. DMD, acetone, 0°, 5 to 7 h 2. TsOH, CH ₂ Cl ₂ , 0°, 10 to 15 min	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>(71)</td> </tr> <tr> <td>H</td> <td>Bn</td> <td>(67)</td> </tr> <tr> <td>MeO</td> <td>Bn</td> <td>(56)</td> </tr> <tr> <td>BnO</td> <td>Me</td> <td>(74)</td> </tr> <tr> <td>BnO</td> <td>Bn</td> <td>(70)</td> </tr> </tbody> </table>	R ¹	R ²		H	Me	(71)	H	Bn	(67)	MeO	Bn	(56)	BnO	Me	(74)	BnO	Bn	(70)	261																		
R ¹	R ²																																						
H	Me	(71)																																					
H	Bn	(67)																																					
MeO	Bn	(56)																																					
BnO	Me	(74)																																					
BnO	Bn	(70)																																					
C ₂₉ 	DMD, acetone/CH ₂ Cl ₂ , -40°, overnight	 (>80)	262																																				

TABLE 1D. EPOXIDATION OF OLEFINS WITH ELECTRON DONERS AND ACCEPTORS BY ISOLATED DIOXIRANES (Continued)

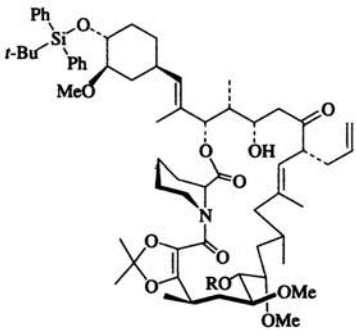
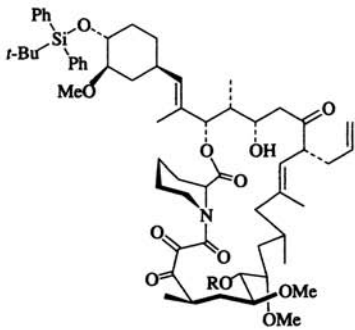
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>^{C₆₉}</p>  <p>R = TBDMS</p>	DMD, acetone, -26°, 1 h	 <p>(100)</p>	263

TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES

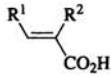
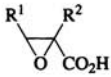
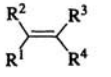
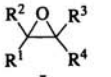
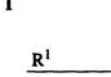
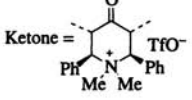
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																														
C ₄ 	Acetone, Oxone [®] , NaHCO ₃ , H ₂ O, EDTA, 24° to 27°		264																																																																														
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>2.75 h</td> <td>(62)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>2.0 h</td> <td>(92)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>2.5 h</td> <td>(92)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>2.25 h</td> <td>(90)</td> </tr> </tbody> </table>	R ¹	R ²	Time	Yield (%)	Me	H	2.75 h	(62)	Ph	H	2.0 h	(92)	Ph	Me	2.5 h	(92)	Ph	Ph	2.25 h	(90)																																																											
R ¹	R ²	Time	Yield (%)																																																																														
Me	H	2.75 h	(62)																																																																														
Ph	H	2.0 h	(92)																																																																														
Ph	Me	2.5 h	(92)																																																																														
Ph	Ph	2.25 h	(90)																																																																														
C ₅₋₂₀ 	TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0 to 1°		35																																																																														
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>AcO</td> <td>H</td> <td>H</td> <td>20 min</td> <td>(97)</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>H</td> <td>H</td> <td>15 min</td> <td>(96)</td> </tr> <tr> <td>4-CF₃C₆H₄</td> <td>H</td> <td>HO₂C</td> <td>H</td> <td>2 h</td> <td>(96)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>MeO₂C</td> <td>H</td> <td>2 h</td> <td>(97)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>Ph</td> <td>30 min</td> <td>(99)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>PhCO</td> <td>H</td> <td>1.3 h</td> <td>(99)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Time	Yield (%)	Me	AcO	H	H	20 min	(97)	Me	Ph	H	H	15 min	(96)	4-CF ₃ C ₆ H ₄	H	HO ₂ C	H	2 h	(96)	Ph	H	MeO ₂ C	H	2 h	(97)	Ph	H	H	Ph	30 min	(99)	Ph	H	PhCO	H	1.3 h	(99)																																					
R ¹	R ²	R ³	R ⁴	Time	Yield (%)																																																																												
Me	AcO	H	H	20 min	(97)																																																																												
Me	Ph	H	H	15 min	(96)																																																																												
4-CF ₃ C ₆ H ₄	H	HO ₂ C	H	2 h	(96)																																																																												
Ph	H	MeO ₂ C	H	2 h	(97)																																																																												
Ph	H	H	Ph	30 min	(99)																																																																												
Ph	H	PhCO	H	1.3 h	(99)																																																																												
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt		38																																																																														
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>-(CH₂)₄-</td> <td>H</td> <td>H</td> <td>0.75 h</td> <td>(85)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>H</td> <td>7 h</td> <td>(82)</td> </tr> <tr> <td>n-C₆H₁₃</td> <td>H</td> <td>H</td> <td>H</td> <td>8 h</td> <td>(90)</td> </tr> <tr> <td>n-C₅H₁₁</td> <td>H</td> <td>Me</td> <td>H</td> <td>8 h</td> <td>(87)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>H</td> <td>3 h</td> <td>(85)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CH₂OH</td> <td>H</td> <td>0.5 h</td> <td>(96)</td> </tr> <tr> <td>(CH₂)₈CH₂OH</td> <td>H</td> <td>H</td> <td>H</td> <td>2.5 h</td> <td>(94)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Ph</td> <td>H</td> <td>1.5 h</td> <td>(97)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>Ph</td> <td>3 h</td> <td>(91)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Ph</td> <td>H</td> <td>2.5 h</td> <td>(95)</td> </tr> <tr> <td>n-C₈H₁₇</td> <td>H</td> <td>H</td> <td>(CH₂)₇CO₂Me</td> <td>2 h</td> <td>(94)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>Ph</td> <td>H</td> <td>4.5 h</td> <td>(96)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Time	Yield (%)	Me	-(CH ₂) ₄ -	H	H	0.75 h	(85)	Ph	H	H	H	7 h	(82)	n-C ₆ H ₁₃	H	H	H	8 h	(90)	n-C ₅ H ₁₁	H	Me	H	8 h	(87)	Ph	H	Me	H	3 h	(85)	Ph	H	CH ₂ OH	H	0.5 h	(96)	(CH ₂) ₈ CH ₂ OH	H	H	H	2.5 h	(94)	Ph	H	Ph	H	1.5 h	(97)	Ph	H	H	Ph	3 h	(91)	Ph	Me	Ph	H	2.5 h	(95)	n-C ₈ H ₁₇	H	H	(CH ₂) ₇ CO ₂ Me	2 h	(94)	Ph	Ph	Ph	H	4.5 h	(96)	
R ¹	R ²	R ³	R ⁴	Time	Yield (%)																																																																												
Me	-(CH ₂) ₄ -	H	H	0.75 h	(85)																																																																												
Ph	H	H	H	7 h	(82)																																																																												
n-C ₆ H ₁₃	H	H	H	8 h	(90)																																																																												
n-C ₅ H ₁₁	H	Me	H	8 h	(87)																																																																												
Ph	H	Me	H	3 h	(85)																																																																												
Ph	H	CH ₂ OH	H	0.5 h	(96)																																																																												
(CH ₂) ₈ CH ₂ OH	H	H	H	2.5 h	(94)																																																																												
Ph	H	Ph	H	1.5 h	(97)																																																																												
Ph	H	H	Ph	3 h	(91)																																																																												
Ph	Me	Ph	H	2.5 h	(95)																																																																												
n-C ₈ H ₁₇	H	H	(CH ₂) ₇ CO ₂ Me	2 h	(94)																																																																												
Ph	Ph	Ph	H	4.5 h	(96)																																																																												

TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)

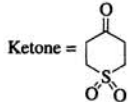
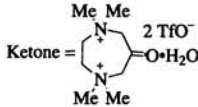



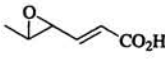


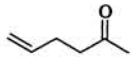
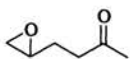
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																	
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt	I	38																																																																	
	Ketone = 	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>—(CH₂)₄—</td> <td>H</td> <td>H</td> <td>0.5 h (83)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>H</td> <td>4.5 h (80)</td> </tr> <tr> <td>n-C₆H₁₃</td> <td>H</td> <td>H</td> <td>H</td> <td>2.5 h (92)</td> </tr> <tr> <td>n-C₅H₁₁</td> <td>H</td> <td>Me</td> <td>H</td> <td>1.5 h (81)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>H</td> <td>4.5 h (87)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CH₂OH</td> <td>H</td> <td>1.5 h (95)</td> </tr> <tr> <td>(CH₂)₉OH</td> <td>H</td> <td>H</td> <td>H</td> <td>3.5 h (95)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Ph</td> <td>H</td> <td>5 h (95)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>Ph</td> <td>4 h (95)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Ph</td> <td>H</td> <td>4 h (97)</td> </tr> <tr> <td>n-C₈H₁₇</td> <td>H</td> <td>H</td> <td>(CH₂)₇CO₂Me</td> <td>3 h (96)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>Ph</td> <td>H</td> <td>6 h (97)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Time	Me	—(CH ₂) ₄ —	H	H	0.5 h (83)	Ph	H	H	H	4.5 h (80)	n-C ₆ H ₁₃	H	H	H	2.5 h (92)	n-C ₅ H ₁₁	H	Me	H	1.5 h (81)	Ph	H	Me	H	4.5 h (87)	Ph	H	CH ₂ OH	H	1.5 h (95)	(CH ₂) ₉ OH	H	H	H	3.5 h (95)	Ph	H	Ph	H	5 h (95)	Ph	H	H	Ph	4 h (95)	Ph	Me	Ph	H	4 h (97)	n-C ₈ H ₁₇	H	H	(CH ₂) ₇ CO ₂ Me	3 h (96)	Ph	Ph	Ph	H	6 h (97)	
R ¹	R ²	R ³	R ⁴	Time																																																																
Me	—(CH ₂) ₄ —	H	H	0.5 h (83)																																																																
Ph	H	H	H	4.5 h (80)																																																																
n-C ₆ H ₁₃	H	H	H	2.5 h (92)																																																																
n-C ₅ H ₁₁	H	Me	H	1.5 h (81)																																																																
Ph	H	Me	H	4.5 h (87)																																																																
Ph	H	CH ₂ OH	H	1.5 h (95)																																																																
(CH ₂) ₉ OH	H	H	H	3.5 h (95)																																																																
Ph	H	Ph	H	5 h (95)																																																																
Ph	H	H	Ph	4 h (95)																																																																
Ph	Me	Ph	H	4 h (97)																																																																
n-C ₈ H ₁₇	H	H	(CH ₂) ₇ CO ₂ Me	3 h (96)																																																																
Ph	Ph	Ph	H	6 h (97)																																																																
	Ketone, Oxone [®] , CH ₃ CN/buffer, (pH 7.0), 0°	I	37																																																																	
	Ketone = 	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>n-C₆H₁₃</td> <td>H</td> <td>H</td> <td>H</td> <td>11 h (74)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>H</td> <td>8 h (83)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>Me</td> <td>6 h (78)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CH₂OH</td> <td>H</td> <td>11 h (94)</td> </tr> <tr> <td>Ph</td> <td>—(CH₂)₄—</td> <td>H</td> <td>H</td> <td>4 h (93)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>(CH₂)₃OBn</td> <td>H</td> <td>22 h (89)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Ph</td> <td>H</td> <td>22 h (33)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Time	n-C ₆ H ₁₃	H	H	H	11 h (74)	Ph	H	Me	H	8 h (83)	Ph	H	H	Me	6 h (78)	Ph	H	CH ₂ OH	H	11 h (94)	Ph	—(CH ₂) ₄ —	H	H	4 h (93)	Me	H	(CH ₂) ₃ OBn	H	22 h (89)	Ph	H	Ph	H	22 h (33)																										
R ¹	R ²	R ³	R ⁴	Time																																																																
n-C ₆ H ₁₃	H	H	H	11 h (74)																																																																
Ph	H	Me	H	8 h (83)																																																																
Ph	H	H	Me	6 h (78)																																																																
Ph	H	CH ₂ OH	H	11 h (94)																																																																
Ph	—(CH ₂) ₄ —	H	H	4 h (93)																																																																
Me	H	(CH ₂) ₃ OBn	H	22 h (89)																																																																
Ph	H	Ph	H	22 h (33)																																																																
	Acetone, Oxone [®] , phosphate buffer (pH 7.65)/CH ₂ Cl ₂ , 18-crown-6, EDTA, 5 to 8°, 16 h	 (70-90)	42																																																																	
	Acetone, Oxone [®] , H ₂ O (pH 7.0-7.5), 18-crown-6, 2 to 8°, 2.0 h	 (77)	32																																																																	
	Acetone, Oxone [®] , benzene/H ₂ O, (pH 7.0-7.5), Bu ₄ NHSO ₄ , 2 to 8°, 3.0 h	 I (72)	32																																																																	
	Acetone, Oxone [®] , CH ₂ Cl ₂ /H ₂ O, (pH 7.0-7.5), Bu ₄ NHSO ₄ , 2 to 8°, 4.0 h	I (78)	32																																																																	
	Acetone, Oxone [®] , benzene/H ₂ O, (pH 7.0-7.5), Bu ₄ NHSO ₄ , 2 to 8°, 4.0 h	I (32)	32																																																																	
	Acetone, NaHCO ₃ , CH ₂ Cl ₂ /H ₂ O, NaHSO ₅ , 0° to 5°, N ₂ , 2 h	I (95)	265																																																																	
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 24 h	I	266																																																																	
		<table border="1"> <thead> <tr> <th>Ketone</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>C₆H₅COCF₃</td> <td>(38)</td> </tr> <tr> <td>4-CF₃COC₆H₄CO₂H</td> <td>(5)</td> </tr> <tr> <td>4-CF₃COC₆H₄CO₂Me</td> <td>(0)</td> </tr> </tbody> </table>	Ketone	Yield (%)	C ₆ H ₅ COCF ₃	(38)	4-CF ₃ COC ₆ H ₄ CO ₂ H	(5)	4-CF ₃ COC ₆ H ₄ CO ₂ Me	(0)																																																										
Ketone	Yield (%)																																																																			
C ₆ H ₅ COCF ₃	(38)																																																																			
4-CF ₃ COC ₆ H ₄ CO ₂ H	(5)																																																																			
4-CF ₃ COC ₆ H ₄ CO ₂ Me	(0)																																																																			
	Acetone, Oxone [®] , H ₂ O (pH 7.0-7.5), 18-crown-6, 2 to 8°, 2.0 h	 (96)	32																																																																	

TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)

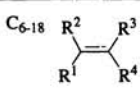
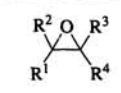






Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
 C_{6-18}	Acetone, Oxone [®] , CH ₃ CN, DMM, K ₂ CO ₃ buffer, Bu ₄ NHSO ₄ , EDTA	 R^1 R^2 R^3 R^4	36																				
				R^1	R^2	R^3	R^4	Time															
				<i>n</i> -Pr	H	CH ₂ OH	H	2 h (79)															
				Et	H	(CH ₂) ₂ OH	H	2 h (80)															
				Et	H	H	(CH ₂) ₂ OH	4 h (90)															
				Ph	H	CH ₂ Cl	H	2 h (72)															
				Ph	H	CH ₂ OH	H	2 h (67)															
				Ph	Me	H	H	4 h (91)															
				Ph	H	Me	H	4 h (84)															
				H	—(CH ₂) ₄ —		C≡CMe	1.5 h (88)															
				<i>n</i> -C ₈ H ₁₇	H	H	H	4 h (67)															
				2-MeC ₆ H ₄	H	Me	Me	4 h (75)															
				H	—(CH ₂) ₄ —		Ph	2 h (84)															
				<i>i</i> -Pr ₃ SiCH ₂	H	H	H	4 h (77)															
				Bn	H	(CH ₂) ₂ CO ₂ Me	H	2 h (85)															
				Ph	H	Ph	H	4 h (86)															
				<i>n</i> -C ₆ H ₁₃	H	<i>n</i> -C ₆ H ₁₃	H	1.5 h (92)															
Ph	Me	Ph	H	2 h (98)																			
Ph	H	CH ₂ OTBDMS	H	2 h (77)																			
H	Ph	<i>n</i> -C ₁₀ H ₂₁	H	4 h (72)																			
 C_7	Acetone, Oxone [®] , H ₂ O (pH 7.5-8.0)/ CH ₂ Cl ₂ , 18-crown-6, 0 to 5°	 I (95)	162																				
				2-Butanone, Oxone [®] , NaHCO ₃ , 20 to 30 min	I (68)	267																	
				2-Butanone, Oxone [®] , iron(III) tetrakis(2,6-dichlorophenyl)- porphyrin chloride [(TDCPP)FeCl], NaHCO ₃ , 20 to 30 min	I (68)	267																	
				2-Butanone, Oxone [®] , NaHCO ₃ , 0°, 24 h, with prior incubation	I (16)	267																	
				2-Butanone, Oxone [®] , NaHCO ₃ , (TDCPP)FeCl, 0°, 24 h, with prior incubation	I (14)	267																	
	Acetone, Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, Bu ₄ NHSO ₄ , EDTA, rt, 4 h	 (50)	36																				
	Ketone, TMSOTf, CH ₂ Cl ₂	 <table border="1"> <thead> <tr> <th>Ketone</th> <th>Temp</th> <th>Time</th> <th>% Convn</th> </tr> </thead> <tbody> <tr> <td>cyclohexanone</td> <td>-32°</td> <td>3 h</td> <td>94 (97)</td> </tr> <tr> <td>acetone</td> <td>-32°</td> <td>3 h</td> <td>75 (96)</td> </tr> <tr> <td>acetone</td> <td>-75°</td> <td>16 h</td> <td>23 (95)</td> </tr> <tr> <td>4-heptanone</td> <td>-32°</td> <td>3 h</td> <td>80 (95)</td> </tr> </tbody> </table>	Ketone	Temp	Time	% Convn	cyclohexanone	-32°	3 h	94 (97)	acetone	-32°	3 h	75 (96)	acetone	-75°	16 h	23 (95)	4-heptanone	-32°	3 h	80 (95)	268
Ketone	Temp	Time	% Convn																				
cyclohexanone	-32°	3 h	94 (97)																				
acetone	-32°	3 h	75 (96)																				
acetone	-75°	16 h	23 (95)																				
4-heptanone	-32°	3 h	80 (95)																				

TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)

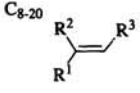
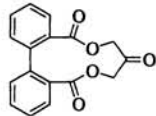




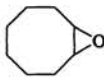
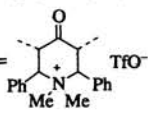
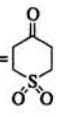

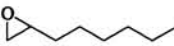
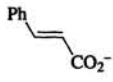
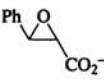

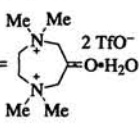
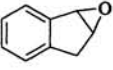
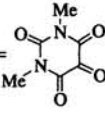
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																												
C_{8-20} 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt Ketone = 	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>4-ClC₆H₄</td> <td>H</td> <td>H</td> <td>1 h</td> <td>(80)</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>H</td> <td>1 h</td> <td>(75)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CH₂OH</td> <td>2.5 h</td> <td>(92)</td> </tr> <tr> <td>4-CF₃C₆H₄</td> <td>H</td> <td>CO₂H</td> <td>2 h</td> <td>(85)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CO₂Me</td> <td>2 h</td> <td>(96)</td> </tr> <tr> <td>(CH₂)₉OH</td> <td>H</td> <td>H</td> <td>5 h</td> <td>(94)</td> </tr> <tr> <td>Ph</td> <td>—(CH₂)₄—</td> <td></td> <td>2 h</td> <td>(86)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Ph</td> <td>80 min</td> <td>(94)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>PhCO</td> <td>1 h</td> <td>(96)</td> </tr> <tr> <td><i>n</i>-C₈H₁₇</td> <td>H</td> <td>(CH₂)₇CO₂Me</td> <td>5.5 h</td> <td>(96)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>Ph</td> <td>160 min</td> <td>(91)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Time		4-ClC ₆ H ₄	H	H	1 h	(80)	Me	Ph	H	1 h	(75)	Ph	H	CH ₂ OH	2.5 h	(92)	4-CF ₃ C ₆ H ₄	H	CO ₂ H	2 h	(85)	Ph	H	CO ₂ Me	2 h	(96)	(CH ₂) ₉ OH	H	H	5 h	(94)	Ph	—(CH ₂) ₄ —		2 h	(86)	Ph	H	Ph	80 min	(94)	Ph	H	PhCO	1 h	(96)	<i>n</i> -C ₈ H ₁₇	H	(CH ₂) ₇ CO ₂ Me	5.5 h	(96)	Ph	Ph	Ph	160 min	(91)	39
			R ¹	R ²	R ³	Time																																																									
			4-ClC ₆ H ₄	H	H	1 h	(80)																																																								
			Me	Ph	H	1 h	(75)																																																								
			Ph	H	CH ₂ OH	2.5 h	(92)																																																								
			4-CF ₃ C ₆ H ₄	H	CO ₂ H	2 h	(85)																																																								
			Ph	H	CO ₂ Me	2 h	(96)																																																								
			(CH ₂) ₉ OH	H	H	5 h	(94)																																																								
			Ph	—(CH ₂) ₄ —		2 h	(86)																																																								
			Ph	H	Ph	80 min	(94)																																																								
Ph	H	PhCO	1 h	(96)																																																											
<i>n</i> -C ₈ H ₁₇	H	(CH ₂) ₇ CO ₂ Me	5.5 h	(96)																																																											
Ph	Ph	Ph	160 min	(91)																																																											
C_8 	Acetone, NaHCO ₃ , CH ₂ Cl ₂ /H ₂ O, NaHSO ₅ , 0° to 5°, N ₂ , 2 h	 (70)	265																																																												
	Acetone, NaHCO ₃ , CH ₂ Cl ₂ /H ₂ O, NaHSO ₅ , 0° to 5°, N ₂ , 2 h	 I (71)	265																																																												
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 1.5 h Ketone = 	I (95)	38																																																												
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 0.5 h Ketone = 	I (96)	38																																																												
	Acetone, NaHCO ₃ , CH ₂ Cl ₂ /H ₂ O, NaHSO ₅ , 0 to 5°, N ₂ , 2 h	 (54)	265																																																												
C_9 	Ketone, Oxone [®] , solvent, buffer	 (—)	269																																																												
	Ketone, Oxone [®] , CH ₃ CN/buffer (pH 7.0), 0°, 6 h Ketone = 	 I (85)	37																																																												
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 8 h Ketone = 	I (92)	40																																																												

TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																
	Acetone, Oxone [®] , phosphate buffer, (pH 7.5), 2°, 2 h	I (95)	207																
	Acetone, Oxone [®] , H ₂ O (pH 7.0-7.5), 18-crown-6, 2 to 8°, 2.3 h	I (94)	32																
	Acetone, Oxone [®] , benzene/H ₂ O (pH 7.0-7.5), Bu ₄ NHSO ₄ , 2 to 8°, 3 h	I (90)	32																
	Acetone, Oxone [®] , phosphate buffer (pH 7.0), 2°, 3.5 h	I (90)	31																
	Acetone, Oxone [®] , H ₂ O (pH 7.0-7.5), 18-crown-6, 2 to 8°, 3.5 h	I (>81)	32																
	Acetophenone, Oxone [®] , MeOH, H ₂ O, 0°, 1 h	(100)	270																
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 8 h	(92)	40																
	Ketone =																		
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 8 h	(92)	40																
	Ketone =																		
	Ketone, (TMS) ₂ SO ₅ , CH ₂ Cl ₂	<table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>Ketone</th> <th>Temp</th> <th>Time</th> <th>% Convn</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>-4°</td> <td>1.0 h</td> <td>98 (95)</td> </tr> <tr> <td>acetone</td> <td>-32°</td> <td>3.0 h</td> <td>68 (95)</td> </tr> <tr> <td>cyclohexanone</td> <td>-32°</td> <td>3.0 h</td> <td>88 (97)</td> </tr> </tbody> </table>	Ketone	Temp	Time	% Convn	acetone	-4°	1.0 h	98 (95)	acetone	-32°	3.0 h	68 (95)	cyclohexanone	-32°	3.0 h	88 (97)	268
Ketone	Temp	Time	% Convn																
acetone	-4°	1.0 h	98 (95)																
acetone	-32°	3.0 h	68 (95)																
cyclohexanone	-32°	3.0 h	88 (97)																
	<i>p</i> -O ₂ NC ₆ H ₄ SO ₂ N ₂ , [¹⁸ O]acetone, H ₂ O ₂ , NaOH	+ (38 - 43)	271																
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 8 h	(90)	40																
	Ketone =																		
	Acetone, Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, Bu ₄ NHSO ₄ , EDTA, rt, 1.5 h	(88)	36																

TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)

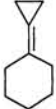
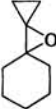
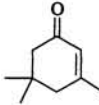
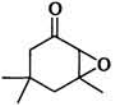
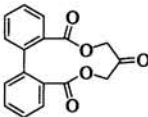
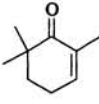
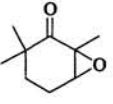
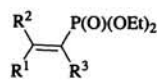
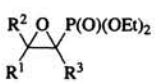
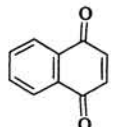
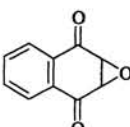
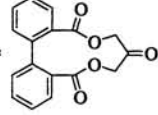
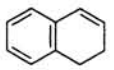
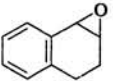
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																
	Acetone, Oxone [®] , phosphate buffer (pH 7.65)/CH ₂ Cl ₂ , 18-crown-6, EDTA, 5 to 8°, 16 h	 (70-90)	42																																																
	TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0 to 1°, 1.5 h	 I (90)	35																																																
	2-Butanone, Oxone [®] , phosphate buffer (pH 7.3-7.5), -20°, 24 h	I (86)	34																																																
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 1.5 h	I (89)	39																																																
	Ketone = 																																																		
	2-Butanone, Oxone [®] , phosphate buffer (pH 7.3-7.5), -20°, 24 h	 (84)	34																																																
C ₉₋₂₀ 	2-Butanone, Oxone [®] , CH ₂ Cl ₂ /phosphate buffer (pH 7.3-7.5), Bu ₄ NHSO ₄ , aq. KOH, 24 h	 <table border="1" data-bbox="1137 1239 1388 1572"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td><i>n</i>-Pr</td> <td>H</td> <td>(58)</td> </tr> <tr> <td>H</td> <td><i>n</i>-Bu</td> <td>H</td> <td>(71)</td> </tr> <tr> <td>Me</td> <td><i>n</i>-Pr</td> <td>H</td> <td>(75)</td> </tr> <tr> <td>Me</td> <td><i>n</i>-Pr</td> <td>Me</td> <td>(79)</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>H</td> <td>(73)</td> </tr> <tr> <td>Ph</td> <td><i>n</i>-Pr</td> <td>H</td> <td>(81)</td> </tr> <tr> <td>Ph</td> <td><i>n</i>-Bu</td> <td>H</td> <td>(80)</td> </tr> <tr> <td><i>n</i>-Bu</td> <td>Ph</td> <td>H</td> <td>(35)</td> </tr> <tr> <td><i>n</i>-Bu</td> <td>Ph</td> <td>Me</td> <td>(20)</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>Ph</td> <td>H</td> <td>(84)</td> </tr> <tr> <td><i>n</i>-C₈H₁₇</td> <td>Ph</td> <td>H</td> <td>(19)</td> </tr> </tbody> </table>	R ¹	R ²	R ³		H	<i>n</i> -Pr	H	(58)	H	<i>n</i> -Bu	H	(71)	Me	<i>n</i> -Pr	H	(75)	Me	<i>n</i> -Pr	Me	(79)	H	Ph	H	(73)	Ph	<i>n</i> -Pr	H	(81)	Ph	<i>n</i> -Bu	H	(80)	<i>n</i> -Bu	Ph	H	(35)	<i>n</i> -Bu	Ph	Me	(20)	4-MeC ₆ H ₄	Ph	H	(84)	<i>n</i> -C ₈ H ₁₇	Ph	H	(19)	272
R ¹	R ²	R ³																																																	
H	<i>n</i> -Pr	H	(58)																																																
H	<i>n</i> -Bu	H	(71)																																																
Me	<i>n</i> -Pr	H	(75)																																																
Me	<i>n</i> -Pr	Me	(79)																																																
H	Ph	H	(73)																																																
Ph	<i>n</i> -Pr	H	(81)																																																
Ph	<i>n</i> -Bu	H	(80)																																																
<i>n</i> -Bu	Ph	H	(35)																																																
<i>n</i> -Bu	Ph	Me	(20)																																																
4-MeC ₆ H ₄	Ph	H	(84)																																																
<i>n</i> -C ₈ H ₁₇	Ph	H	(19)																																																
C ₁₀ 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 6 h	 (88)	39																																																
	Ketone = 																																																		
	Acetone, Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, Bu ₄ NHSO ₄ , EDTA, rt, 4 h	 I (66)	36																																																

TABLE IE. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)

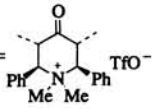
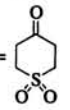
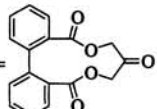

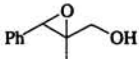
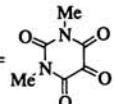
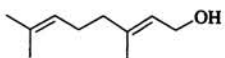
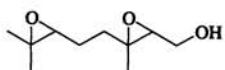
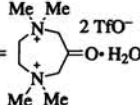
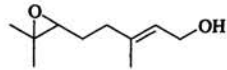
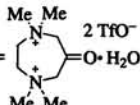


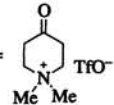
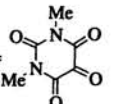
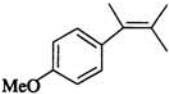
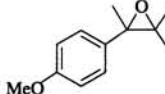
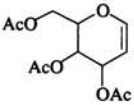
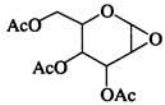
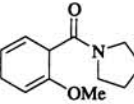
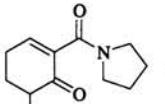

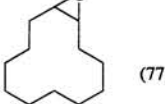

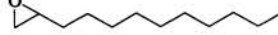
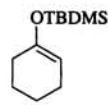
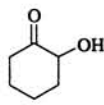
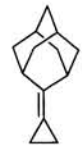
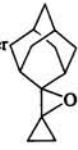


Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 1.5 h	I (83)	38
	Ketone = 		
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 2.5 h	I (85)	38
	Ketone = 		
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 80 min	I (81)	39
	Ketone = 		
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 8 h	 (84)	40
	Ketone = 		
	Ketone, Oxone [®] , CH ₃ CN/buffer (pH 7.0), 0°, 6 h	 I (90)	37
	Ketone = 		
	Ketone, Oxone [®] , CH ₃ CN/buffer, (pH 7.0), 0°, 2.4 h	I +  II (89) I:II = 19:77	37
	Ketone = 		
C ₁₂ 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, 0°, 3 h	 I (90)	273
	Ketone = 		
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 8 h	I (88)	40
	Ketone = 		

TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.											
	Acetone, Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, Bu ₄ NHSO ₄ , EDTA, rt, 2 h	I (84)	36											
	1. Acetone, Oxone [®] , H ₂ O, NaHCO ₃ , 20°, 2.5 h 2. 25°, 2 h	 (85)	274											
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt		<table border="1"> <thead> <tr> <th>Ketone</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>Tentagel S-Br</td> <td>48 h (80)</td> </tr> <tr> <td>C₆H₅COCF₃</td> <td>24 h (100)</td> </tr> <tr> <td>4-CF₃COC₆H₄CO₂H</td> <td>24 h (100)</td> </tr> <tr> <td>4-CF₃COC₆H₄CO₂Me</td> <td>24 h (100)</td> </tr> </tbody> </table>	Ketone	Time	Tentagel S-Br	48 h (80)	C ₆ H ₅ COCF ₃	24 h (100)	4-CF ₃ COC ₆ H ₄ CO ₂ H	24 h (100)	4-CF ₃ COC ₆ H ₄ CO ₂ Me	24 h (100)	266
Ketone	Time													
Tentagel S-Br	48 h (80)													
C ₆ H ₅ COCF ₃	24 h (100)													
4-CF ₃ COC ₆ H ₄ CO ₂ H	24 h (100)													
4-CF ₃ COC ₆ H ₄ CO ₂ Me	24 h (100)													
	Acetone, Oxone [®] , phosphate buffer (pH 7.2), 0°	 (77)	275											
	Acetone, Oxone [®] , benzene/H ₂ O, (pH 7.0-7.5), 18-crown-6, 2 to 8°, 3.0 h	 (77)	32											
	Acetone, Oxone [®] , benzene/H ₂ O, (pH 7.0-7.5), 18-crown-6, 2 to 8°, 3.0 h	 (43)	32											
	1. TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0 to 1°, 30 min 2. NaSH, rt, 2 h	 (97)	35											
	Acetone, Oxone [®] , phosphate buffer (pH 7.65)/CH ₂ Cl ₂ , 18-crown-6, EDTA, 5 to 8°, 16 h	 (70-90)	42											
	Acetone, Oxone [®] , H ₂ O/CH ₂ Cl ₂ , (pH 7.8), Bu ₄ NHSO ₄ , 0°, 24 h	 I (87)	168											
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 8 h	I (70)	40											
	Oxone [®] , various ketones, CH ₂ Cl ₂ /H ₂ O, Bu ₄ NHSO ₄ , 9 to 24 h	I (—)	107											

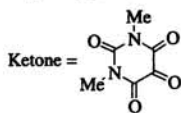


TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)


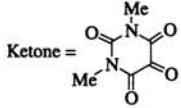
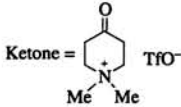
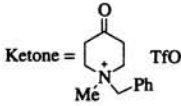
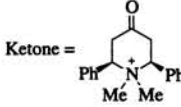
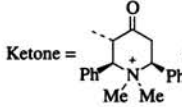
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
C ₁₄ 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 8 h 	 I (70)	40															
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 8 h 	I (70)	40															
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt	I	<table border="1"> <thead> <tr> <th>Ketone</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>Tentagel S-Br</td> <td>48 h (97)</td> </tr> <tr> <td>Hydroxymethyl resin</td> <td>17 h (41)</td> </tr> <tr> <td>Hydroxymethyl resin</td> <td>36 h (64)</td> </tr> <tr> <td>C₆H₅COCF₃</td> <td>24 h (70)</td> </tr> <tr> <td>4-CF₃COC₆H₄CO₂H</td> <td>24 h (81)</td> </tr> <tr> <td>4-CF₃COC₆H₄CO₂Me</td> <td>24 h (91)</td> </tr> </tbody> </table>	Ketone	Time	Tentagel S-Br	48 h (97)	Hydroxymethyl resin	17 h (41)	Hydroxymethyl resin	36 h (64)	C ₆ H ₅ COCF ₃	24 h (70)	4-CF ₃ COC ₆ H ₄ CO ₂ H	24 h (81)	4-CF ₃ COC ₆ H ₄ CO ₂ Me	24 h (91)	266
	Ketone	Time																
	Tentagel S-Br	48 h (97)																
	Hydroxymethyl resin	17 h (41)																
	Hydroxymethyl resin	36 h (64)																
	C ₆ H ₅ COCF ₃	24 h (70)																
4-CF ₃ COC ₆ H ₄ CO ₂ H	24 h (81)																	
4-CF ₃ COC ₆ H ₄ CO ₂ Me	24 h (91)																	
Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 5 min 	I (—)	38																
Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 45 min 	I (95)	38																
Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 2 h 	I (92)	38																
Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 2 h 	I (87)	38																

TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 15 min	I (94)	38
	Ketone =		
		TfO ⁻	
	Cyclohexanone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 12 h	I (—)	38
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 30 min	I (93)	38
	Ketone =		
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 2 to 3 min	I (97)	38
	Ketone =		
	TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 30 min	I (96)	39
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 120 min	I (91)	39
	Ketone =		
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 50 min	I (90)	39
	Ketone =		
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 35 min	I (98)	39
	Ketone =		

TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)

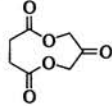
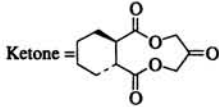
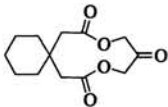
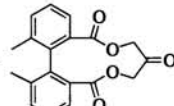
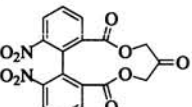
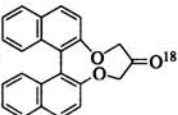
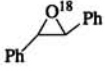
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Ketone = 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 20 min	I (96)	39
Ketone = 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 12 min	I (97)	39
Ketone = 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 10 min	I (96)	39
Ketone = 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 10 min	I (91)	39
Ketone = 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 6 min	I (93)	39
Ketone = 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 45 min	 (→)	112

TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt	 Tentagel S-Br 48 h (61) Hydroxymethyl resin 38 h (51) C ₆ H ₅ COCF ₃ 24 h (100) 4-CF ₃ COC ₆ H ₄ CO ₂ H 24 h (100) 4-CF ₃ COC ₆ H ₄ CO ₂ Me 24 h (97)	266
C ₁₅ 	TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0 to 1°, 1.25 h	 (99)	35
C ₁₅₋₁₆ 	2-Butanone, Oxone [®] , phosphate buffer (pH 7.3-7.5), -20°, 24 h	 R ¹ R ² H Br (40) H H (93) Me H (98) H MeO (94) MeO H (93)	34
	2-Butanone, Oxone [®] , phosphate buffer (pH 7.3-7.5)/CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , -20°, 41 h	R ¹ = H, R ² = Br I (89)	34
C ₁₅ 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt	 Tentagel S-Br 48 h (13) Hydroxymethyl resin 48 h (9) C ₆ H ₅ COCF ₃ 24 h (11) 4-CF ₃ COC ₆ H ₄ CO ₂ H 24 h (34) 4-CF ₃ COC ₆ H ₄ CO ₂ Me 24 h (7)	266
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 8 h	 Ketone =	40
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt	 Ketone Tentagel S-Br 48 h (90) C ₆ H ₅ COCF ₃ 24 h (100) 4-CF ₃ COC ₆ H ₄ CO ₂ H 24 h (100) 4-CF ₃ COC ₆ H ₄ CO ₂ Me 24 h (100)	266
C ₁₆ 	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 2 h	 Ketone =	38
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 2.5 h	I (92) Ketone =	38

TABLE 1E. EPOXIDATION OF OLEFINS BY IN-SITU-GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																		
	Acetone, Oxone [®] , H ₂ O/CH ₂ Cl ₂ , (pH 8.0), Bu ₄ NHSO ₄ , 0°, 6.5 h	(58)	168																		
THPO	TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 30 min	(72)	276																		
C ₁₉	2-Butanone, Oxone [®] , NaHCO ₃ , H ₂ O, Bu ₄ NHSO ₄ , dark, rt, 2 h	(100)	69																		
	2-Butanone, Oxone [®] , NaHCO ₃ , H ₂ O, Bu ₄ NHSO ₄ , dark, rt, 2 h	(89) dr = 50:50	69																		
C ₂₂	Ketone, Oxone [®] , buffer (pH 7.5), CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 0°, 24 h Ketone =	(81)	168																		
C ₂₇	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt	(76)	266																		
		<table border="1"> <thead> <tr> <th>Ketone</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Tentagel C-Br</td> <td>48 h</td> <td>(76)</td> </tr> <tr> <td>Hydroxymethyl resin</td> <td>48 h</td> <td>(37)</td> </tr> <tr> <td>C₆H₅COCF₃</td> <td>24 h</td> <td>(52)</td> </tr> <tr> <td>4-CF₃COC₆H₄CO₂H</td> <td>24 h</td> <td>(100)</td> </tr> <tr> <td>4-CF₃COC₆H₄CO₂Me</td> <td>24 h</td> <td>(72)</td> </tr> </tbody> </table>	Ketone	Time	Yield (%)	Tentagel C-Br	48 h	(76)	Hydroxymethyl resin	48 h	(37)	C ₆ H ₅ COCF ₃	24 h	(52)	4-CF ₃ COC ₆ H ₄ CO ₂ H	24 h	(100)	4-CF ₃ COC ₆ H ₄ CO ₂ Me	24 h	(72)	
Ketone	Time	Yield (%)																			
Tentagel C-Br	48 h	(76)																			
Hydroxymethyl resin	48 h	(37)																			
C ₆ H ₅ COCF ₃	24 h	(52)																			
4-CF ₃ COC ₆ H ₄ CO ₂ H	24 h	(100)																			
4-CF ₃ COC ₆ H ₄ CO ₂ Me	24 h	(72)																			
C ₃₂	Acetone, Oxone [®] , NaHCO ₃ , H ₂ O/CH ₂ Cl ₂ , 18-crown-6, rt, > 1 h	(75)	277																		
C ₅₃	1. TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 2. HCl (1 N), 0°	(88)	278, 278a																		

TABLE 2. CHEMOSELECTIVE OXIDATIONS BY ISOLATED DIOXIRANES




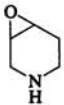
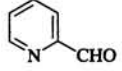
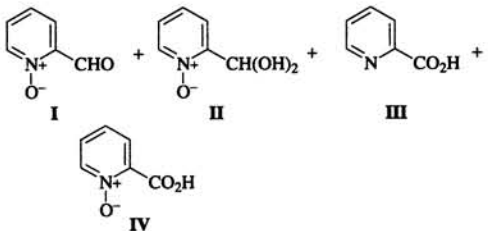

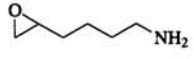
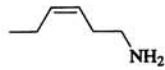
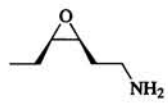
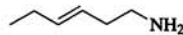

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																															
C ₃ 	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. DMD, acetone/CH ₃ CN, 0°, 8 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	 I (45)	65																																																															
	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. TFD, CH ₂ Cl ₂ /CH ₃ CN, 0°, 0.1 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	I (72)	65																																																															
C ₅ 	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. DMD, acetone/CH ₃ CN, 0°, 8 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	 I (70)	65																																																															
	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. TFD, CH ₂ Cl ₂ , 0°, 0.1 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	I (79)	65																																																															
C ₆ 	DMD (x equiv), acetone		279																																																															
<table border="1"> <thead> <tr> <th>x</th> <th>Temp</th> <th>Time</th> <th>% Convn</th> <th>(I+II)</th> <th>III</th> <th>IV</th> </tr> </thead> <tbody> <tr> <td>1.0</td> <td>0°</td> <td>2 h</td> <td>42</td> <td>(42)</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>1.0</td> <td>0°</td> <td>4 h</td> <td>60</td> <td>(56)</td> <td>(2)</td> <td>(2)</td> </tr> <tr> <td>1.0</td> <td>0°</td> <td>8 h</td> <td>75</td> <td>(68)</td> <td>(5)</td> <td>(2)</td> </tr> <tr> <td>2.0</td> <td>0°</td> <td>2 h</td> <td>72</td> <td>(65)</td> <td>(—)</td> <td>(7)</td> </tr> <tr> <td>1.0</td> <td>-20°</td> <td>12 h</td> <td>67</td> <td>(67)</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>1.5</td> <td>-20°</td> <td>12 h</td> <td>79</td> <td>(79)</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>2.0</td> <td>-20°</td> <td>12 h</td> <td>86</td> <td>(80)</td> <td>(3)</td> <td>(3)</td> </tr> <tr> <td>1.0</td> <td>20°</td> <td>1 h</td> <td>85</td> <td>(79)</td> <td>(3)</td> <td>(3)</td> </tr> </tbody> </table>				x	Temp	Time	% Convn	(I+II)	III	IV	1.0	0°	2 h	42	(42)	(—)	(—)	1.0	0°	4 h	60	(56)	(2)	(2)	1.0	0°	8 h	75	(68)	(5)	(2)	2.0	0°	2 h	72	(65)	(—)	(7)	1.0	-20°	12 h	67	(67)	(—)	(—)	1.5	-20°	12 h	79	(79)	(—)	(—)	2.0	-20°	12 h	86	(80)	(3)	(3)	1.0	20°	1 h	85	(79)	(3)	(3)
x	Temp	Time	% Convn	(I+II)	III	IV																																																												
1.0	0°	2 h	42	(42)	(—)	(—)																																																												
1.0	0°	4 h	60	(56)	(2)	(2)																																																												
1.0	0°	8 h	75	(68)	(5)	(2)																																																												
2.0	0°	2 h	72	(65)	(—)	(7)																																																												
1.0	-20°	12 h	67	(67)	(—)	(—)																																																												
1.5	-20°	12 h	79	(79)	(—)	(—)																																																												
2.0	-20°	12 h	86	(80)	(3)	(3)																																																												
1.0	20°	1 h	85	(79)	(3)	(3)																																																												
	1. 4-MeC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. DMD, acetone/CH ₂ Cl ₂ , 0°, 3.5 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	 (90)	65																																																															
	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. DMD, acetone/CH ₂ Cl ₂ , 0°, 1.5 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	 (81)	65																																																															
	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. DMD, acetone/CH ₂ Cl ₂ , 0°, 3.5 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	 (96)	65																																																															

TABLE 2. CHEMOSELECTIVE OXIDATIONS BY ISOLATED DIOXIRANES (Continued)

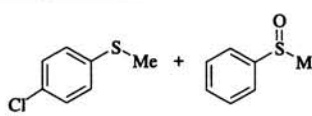
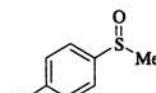
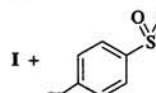
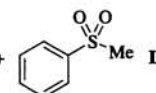
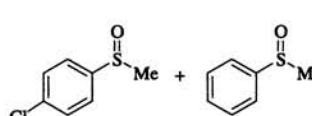
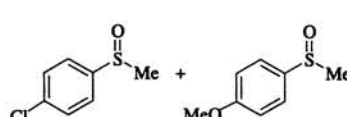
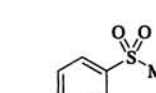
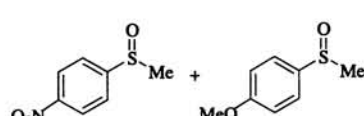
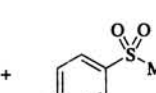
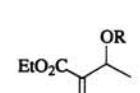
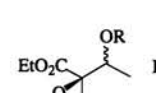
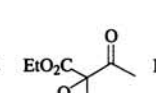
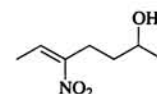
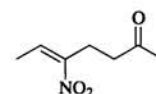
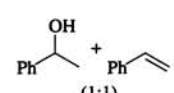
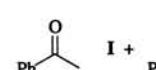
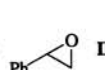
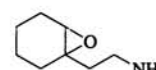
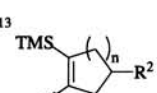
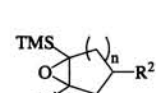
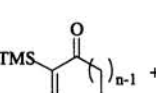
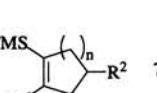
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																			
	DMD, acetone/CHCl ₃ , N ₂ , 0°	 I (100)	280																																			
	TFD, TFP/CHCl ₃ , N ₂ , 0°	I +  II (—) +  III (—) I:II:III = 61:13:26	280																																			
	DMD, acetone/CHCl ₃ , N ₂ , 0°	II + III (—) II:III = 44:56	280																																			
	TFD, TFP/CHCl ₃ , N ₂ , 0°	II + III (—) II:III = 49:51	280																																			
	DMD, acetone/CHCl ₃ , N ₂ , 0°	II +  IV (—) IV:II = 29:71	280																																			
	TFD, TFP/CHCl ₃ , N ₂ , 0°	IV + II (—) IV:II = 44:56	280																																			
	DMD, acetone/CHCl ₃ , N ₂ , 0°	IV +  V (—) V:IV = 5:95	280																																			
	TFD, TFP/CHCl ₃ , N ₂ , 0°	IV + V (—) V:IV = 27:73	280																																			
	DMD, acetone, rt	 I +  II	73																																			
		<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>% Convn</th> <th>I</th> <th>dr of I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>18 h</td> <td>>95</td> <td>(0)</td> <td>—</td> <td>(100)</td> </tr> <tr> <td>Ac</td> <td>48 h</td> <td>>95</td> <td>(100)</td> <td>65:35</td> <td>(0)</td> </tr> </tbody> </table>	R	Time	% Convn	I	dr of I	II	H	18 h	>95	(0)	—	(100)	Ac	48 h	>95	(100)	65:35	(0)																		
R	Time	% Convn	I	dr of I	II																																	
H	18 h	>95	(0)	—	(100)																																	
Ac	48 h	>95	(100)	65:35	(0)																																	
	DMD, acetone, ~25°, overnight	 (75)	281																																			
	DMD, CH ₂ Cl ₂ /acetone, 0°, 8 h	 I +  II I + II (—) I:II = 35:65	73																																			
	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. DMD, acetone, 0°, 1 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	 (80)	65																																			
	DMD, acetone, rt, 4 to 10 h	 I +  II +  III	74																																			
		<table border="1"> <thead> <tr> <th>n</th> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>H</td> <td>H</td> <td>(90)</td> <td>(4)</td> <td>(6)</td> </tr> <tr> <td>2</td> <td>H</td> <td>H</td> <td>(75)</td> <td>(6)</td> <td>(10)</td> </tr> <tr> <td>2</td> <td>Me</td> <td>H</td> <td>(100)</td> <td>(0)</td> <td>(0)</td> </tr> <tr> <td>4</td> <td>H</td> <td>H</td> <td>(100)</td> <td>(0)</td> <td>(0)</td> </tr> <tr> <td>2</td> <td>H</td> <td><i>t</i>-Bu</td> <td>(64)</td> <td>(16)</td> <td>(0)</td> </tr> </tbody> </table>	n	R ¹	R ²	I	II	III	1	H	H	(90)	(4)	(6)	2	H	H	(75)	(6)	(10)	2	Me	H	(100)	(0)	(0)	4	H	H	(100)	(0)	(0)	2	H	<i>t</i> -Bu	(64)	(16)	(0)
n	R ¹	R ²	I	II	III																																	
1	H	H	(90)	(4)	(6)																																	
2	H	H	(75)	(6)	(10)																																	
2	Me	H	(100)	(0)	(0)																																	
4	H	H	(100)	(0)	(0)																																	
2	H	<i>t</i> -Bu	(64)	(16)	(0)																																	

TABLE 2. CHEMOSELECTIVE OXIDATIONS BY ISOLATED DIOXIRANES (Continued)

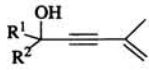
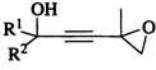
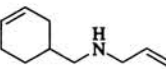
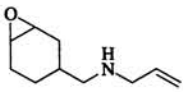




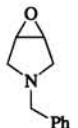

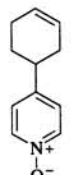
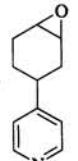

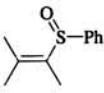
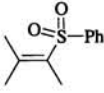

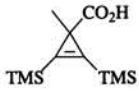
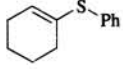
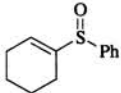
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	DMD	 (—)	71
		$\begin{matrix} R^1 & R^2 \\ H & t\text{-Bu} \\ Ph & Et \\ Ph & Ph \end{matrix}$	
	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. DMD, acetone/CH ₂ Cl ₂ , 0°, 2.5 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	 I (95)	65
	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. TFD, CH ₂ Cl ₂ , 0°, 0.1 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	I (95)	65
C ₁₁ 	DMD, acetone, 0°, <1 h	 (~100)	62
	DMD, acetone, 0°	 (100)	63
	1. BF ₃ •Et ₂ O, 70° 2. TFD, CH ₂ Cl ₂ /TFP, 0° 3. KHCO ₃	 (82)	63
	DMD, acetone, 0°	 (100)	63
	1. BF ₃ •Et ₂ O, 70° 2. DMD, CH ₂ Cl ₂ /acetone, 0° 3. KHCO ₃	 (95)	63
	DMD (1 equiv), acetone/CH ₂ Cl ₂ , -35°, 1 h	 (81)	66
	DMD (3 equiv), acetone/CH ₂ Cl ₂ , -35°, 3 h	 (91)	66
	DMD, acetone, 25°, 35 h	 (~80)	218
C ₁₂ 	DMD (1 equiv), acetone/CH ₂ Cl ₂ , -40°, 5 h	 (67)	66

TABLE 2. CHEMOSELECTIVE OXIDATIONS BY ISOLATED DIOXIRANES (Continued)

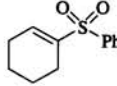
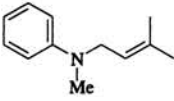
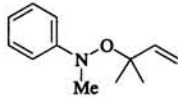
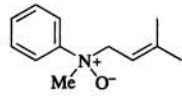
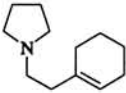
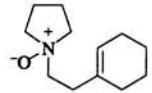
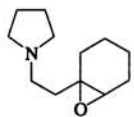
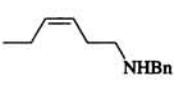
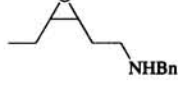
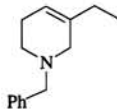
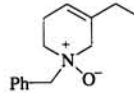
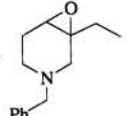
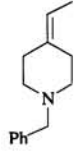
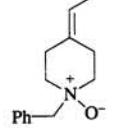
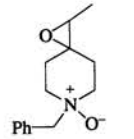
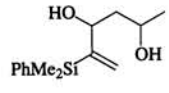
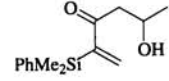
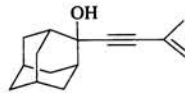
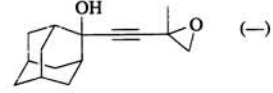
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD (3 equiv), acetone/ CH ₂ Cl ₂ , -40°, 3.5 h	 (62)	66
	DMD, acetone, 0°, <1 h	 (~100) +  (—)	62
	DMD, acetone, 0°, <1 h	 (~100)	63
	1. BF ₃ •Et ₂ O, 70° 2. DMD, acetone/CH ₂ Cl ₂ , 0° 3. KHCO ₃	 (85)	63
C ₁₃ 	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. DMD, acetone/CH ₂ Cl ₂ , 0°, 1.5 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	 (93)	65
C ₁₄ 	DMD, acetone, 0°	 (100)	63
	1. BF ₃ •Et ₂ O, 70° 2. DMD, acetone/CH ₂ Cl ₂ , 0° 3. KHCO ₃	 (97)	63
	DMD, acetone, 0°	 (100)	63
	1. BF ₃ •Et ₂ O, 70° 2. TFD, TFP/CH ₂ Cl ₂ , 0° 3. KHCO ₃	 (70)	63
C ₁₅ 	DMD, acetone, 20°, 16 h	 (—)	282
	DMD	 (—)	71

TABLE 2. CHEMOSELECTIVE OXIDATIONS BY ISOLATED DIOXIRANES (Continued)

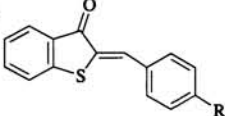
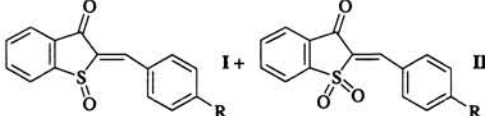
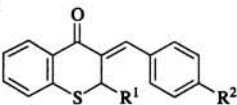
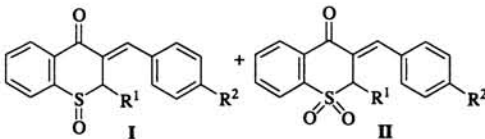
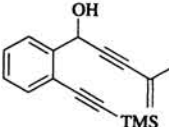
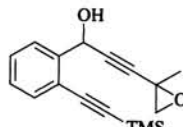
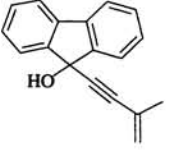
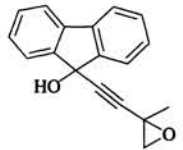
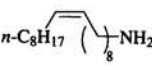
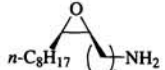
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																																																								
C ₁₅₋₁₆ 	DMD (x equiv), CH ₂ Cl ₂ / acetone, 20°	 <table border="1"> <thead> <tr> <th>R</th> <th>x</th> <th>Time</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>1.4</td> <td>1 h</td> <td>(29)</td> <td>(19)</td> </tr> <tr> <td>Cl</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>1.3</td> <td>1 h</td> <td>(29)</td> <td>(22)</td> </tr> <tr> <td>H</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> <tr> <td>Me</td> <td>1.4</td> <td>1 h</td> <td>(31)</td> <td>(21)</td> </tr> <tr> <td>Me</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> </tbody> </table>	R	x	Time	I	II	Cl	1.4	1 h	(29)	(19)	Cl	2.2	2 h	(0)	(100)	H	1.3	1 h	(29)	(22)	H	2.2	2 h	(0)	(100)	Me	1.4	1 h	(31)	(21)	Me	2.2	2 h	(0)	(100)	66																																																																																					
R	x	Time	I	II																																																																																																																							
Cl	1.4	1 h	(29)	(19)																																																																																																																							
Cl	2.2	2 h	(0)	(100)																																																																																																																							
H	1.3	1 h	(29)	(22)																																																																																																																							
H	2.2	2 h	(0)	(100)																																																																																																																							
Me	1.4	1 h	(31)	(21)																																																																																																																							
Me	2.2	2 h	(0)	(100)																																																																																																																							
C ₁₆₋₂₃ 	DMD (x equiv), CH ₂ Cl ₂ , acetone, 20°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>x</th> <th>Time</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Br</td> <td>1.3</td> <td>1 h</td> <td>(72)</td> <td>(12)</td> </tr> <tr> <td>H</td> <td>Br</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>Cl</td> <td>1.2</td> <td>1 h</td> <td>(76)</td> <td>(10)</td> </tr> <tr> <td>H</td> <td>Cl</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>H</td> <td>1.3</td> <td>1 h</td> <td>(75)</td> <td>(14)</td> </tr> <tr> <td>H</td> <td>H</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>1.3</td> <td>1 h</td> <td>(73)</td> <td>(13)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>MeO</td> <td>1.2</td> <td>1 h</td> <td>(78)</td> <td>(10)</td> </tr> <tr> <td>H</td> <td>MeO</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> </tbody> </table> <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>x</th> <th>Time</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>Cl</td> <td>1.3</td> <td>1 h</td> <td>(81)</td> <td>(13)</td> </tr> <tr> <td>Ph</td> <td>Cl</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>1.2</td> <td>1 h</td> <td>(82)</td> <td>(9)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>1.3</td> <td>1 h</td> <td>(74)</td> <td>(11)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> <tr> <td>Ph</td> <td>MeO</td> <td>1.3</td> <td>1 h</td> <td>(77)</td> <td>(11)</td> </tr> <tr> <td>Ph</td> <td>MeO</td> <td>2.2</td> <td>2 h</td> <td>(0)</td> <td>(100)</td> </tr> </tbody> </table>	R ¹	R ²	x	Time	I	II	H	Br	1.3	1 h	(72)	(12)	H	Br	2.2	2 h	(0)	(100)	H	Cl	1.2	1 h	(76)	(10)	H	Cl	2.2	2 h	(0)	(100)	H	H	1.3	1 h	(75)	(14)	H	H	2.2	2 h	(0)	(100)	H	Me	1.3	1 h	(73)	(13)	H	Me	2.2	2 h	(0)	(100)	H	MeO	1.2	1 h	(78)	(10)	H	MeO	2.2	2 h	(0)	(100)	R ¹	R ²	x	Time	I	II	Ph	Cl	1.3	1 h	(81)	(13)	Ph	Cl	2.2	2 h	(0)	(100)	Ph	H	1.2	1 h	(82)	(9)	Ph	H	2.2	2 h	(0)	(100)	Ph	Me	1.3	1 h	(74)	(11)	Ph	Me	2.2	2 h	(0)	(100)	Ph	MeO	1.3	1 h	(77)	(11)	Ph	MeO	2.2	2 h	(0)	(100)	66
R ¹	R ²	x	Time	I	II																																																																																																																						
H	Br	1.3	1 h	(72)	(12)																																																																																																																						
H	Br	2.2	2 h	(0)	(100)																																																																																																																						
H	Cl	1.2	1 h	(76)	(10)																																																																																																																						
H	Cl	2.2	2 h	(0)	(100)																																																																																																																						
H	H	1.3	1 h	(75)	(14)																																																																																																																						
H	H	2.2	2 h	(0)	(100)																																																																																																																						
H	Me	1.3	1 h	(73)	(13)																																																																																																																						
H	Me	2.2	2 h	(0)	(100)																																																																																																																						
H	MeO	1.2	1 h	(78)	(10)																																																																																																																						
H	MeO	2.2	2 h	(0)	(100)																																																																																																																						
R ¹	R ²	x	Time	I	II																																																																																																																						
Ph	Cl	1.3	1 h	(81)	(13)																																																																																																																						
Ph	Cl	2.2	2 h	(0)	(100)																																																																																																																						
Ph	H	1.2	1 h	(82)	(9)																																																																																																																						
Ph	H	2.2	2 h	(0)	(100)																																																																																																																						
Ph	Me	1.3	1 h	(74)	(11)																																																																																																																						
Ph	Me	2.2	2 h	(0)	(100)																																																																																																																						
Ph	MeO	1.3	1 h	(77)	(11)																																																																																																																						
Ph	MeO	2.2	2 h	(0)	(100)																																																																																																																						
C ₁₇ 	DMD	 (-)	71																																																																																																																								
C ₁₈ 	DMD	 (-)	71																																																																																																																								
	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. DMD, acetone/CH ₂ Cl ₂ , 0°, 2 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	 (98)	65																																																																																																																								

TABLE 2. CHEMOSELECTIVE OXIDATIONS BY ISOLATED DIOXIRANES (Continued)

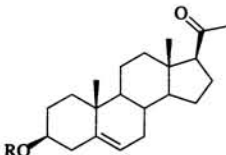
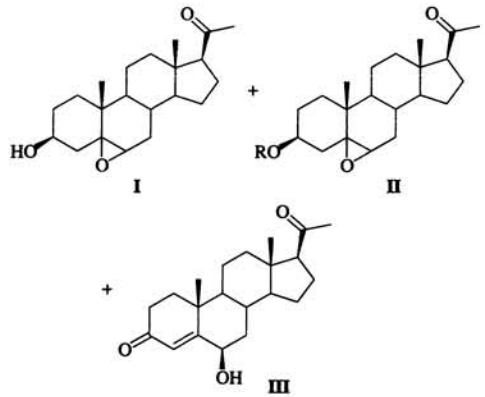

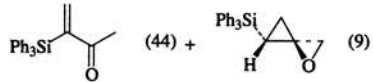
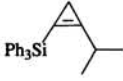
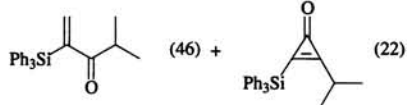
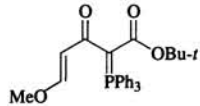
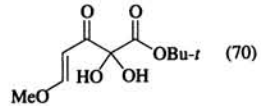
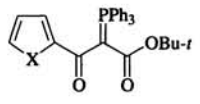
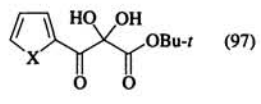
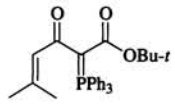
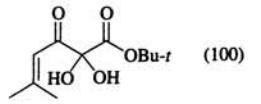
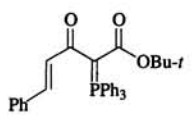
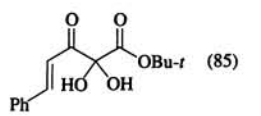
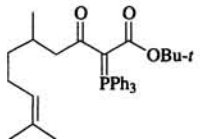
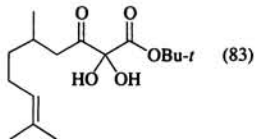
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₂₁₂₈ 	DMD, acetone, rt	 I + II + III	283												
		<table border="1"> <thead> <tr> <th>R</th> <th>I</th> <th>II=I</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(—)</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>Bn</td> <td>(30)</td> <td>(37)</td> <td>(16)</td> </tr> </tbody> </table>	R	I	II=I	III	H	(—)	(—)	(—)	Bn	(30)	(37)	(16)	
R	I	II=I	III												
H	(—)	(—)	(—)												
Bn	(30)	(37)	(16)												
C ₂₂ 	DMD, acetone, rt, 6 h	 (44) + (9)	284												
C ₂₄ 	DMD, acetone, rt, 3.5 h	 (46) + (22)	284												
C ₂₈ 	DMD, acetone/CH ₂ Cl ₂ , -78° to 25°, 4 h	 (70)	285												
C ₂₉ 	DMD, acetone/CH ₂ Cl ₂ , -78° to 25°, 4 h	 (97) X = O, S	285												
	DMD, acetone/CH ₂ Cl ₂ , -78° to 25°, 4 h	 (100)	285												
C ₃₃ 	DMD, acetone/CH ₂ Cl ₂ , -78° to 25°, 4 h	 (85)	285												
C ₃₄ 	DMD, acetone/CH ₂ Cl ₂ , -78° to 25°, 4 h	 (83)	285												

TABLE 3. REGIOSELECTIVE EPOXIDATIONS BY DIOXIRANES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
C ₇₋₁₂ 	DMD, acetone/CH ₂ Cl ₂ , 0°, 3.5 h	(95) R = Me, Ph	286																																				
C ₁₀₋₁₅ 	DMD, acetone or TFD, TFP/CH ₂ Cl ₂		78																																				
		<table border="1"> <thead> <tr> <th>R</th> <th>Dioxirane</th> <th>Temp</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>DMD</td> <td>20°</td> <td>15 min (98)</td> </tr> <tr> <td>H</td> <td>TFD</td> <td>-15°</td> <td>3 min (98)</td> </tr> <tr> <td>THP</td> <td>DMD</td> <td>20°</td> <td>15 min (98)</td> </tr> <tr> <td>THP</td> <td>TFD</td> <td>-40°</td> <td>3 min (99)</td> </tr> </tbody> </table>	R	Dioxirane	Temp	Time	H	DMD	20°	15 min (98)	H	TFD	-15°	3 min (98)	THP	DMD	20°	15 min (98)	THP	TFD	-40°	3 min (99)																	
R	Dioxirane	Temp	Time																																				
H	DMD	20°	15 min (98)																																				
H	TFD	-15°	3 min (98)																																				
THP	DMD	20°	15 min (98)																																				
THP	TFD	-40°	3 min (99)																																				
C ₁₀₋₁₃ 	TFD, solvent, 0 to 10°, 1 to 3 h	I + II	80																																				
		<table border="1"> <thead> <tr> <th>R</th> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>TFP</td> <td>22</td> <td>68:32</td> </tr> <tr> <td>H</td> <td>MeOH/TFP (9:1)</td> <td>21</td> <td>73:27</td> </tr> <tr> <td>H</td> <td>CCl₄/TFP (9:1)</td> <td>25</td> <td>57:43</td> </tr> <tr> <td>Me</td> <td>TFP</td> <td>32</td> <td>73:27</td> </tr> <tr> <td>Me</td> <td>MeOH/TFP (9:1)</td> <td>31</td> <td>68:32</td> </tr> <tr> <td>Me</td> <td>CCl₄/TFP (9:1)</td> <td>32</td> <td>71:29</td> </tr> <tr> <td>Ac</td> <td>TFP</td> <td>30</td> <td>83:17</td> </tr> <tr> <td>TMS</td> <td>TFP</td> <td>33</td> <td>70:30</td> </tr> </tbody> </table>	R	Solvent	% Convn	I:II	H	TFP	22	68:32	H	MeOH/TFP (9:1)	21	73:27	H	CCl ₄ /TFP (9:1)	25	57:43	Me	TFP	32	73:27	Me	MeOH/TFP (9:1)	31	68:32	Me	CCl ₄ /TFP (9:1)	32	71:29	Ac	TFP	30	83:17	TMS	TFP	33	70:30	
R	Solvent	% Convn	I:II																																				
H	TFP	22	68:32																																				
H	MeOH/TFP (9:1)	21	73:27																																				
H	CCl ₄ /TFP (9:1)	25	57:43																																				
Me	TFP	32	73:27																																				
Me	MeOH/TFP (9:1)	31	68:32																																				
Me	CCl ₄ /TFP (9:1)	32	71:29																																				
Ac	TFP	30	83:17																																				
TMS	TFP	33	70:30																																				
C ₁₀ 	DMD (x equiv), solvent, rt, 1 to 3 h	I + II + bis(epoxide) III	72																																				
		<table border="1"> <thead> <tr> <th>x</th> <th>Solvent</th> <th>% Convn</th> <th>I:II:III</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>acetone</td> <td>93</td> <td>73:17:10</td> </tr> <tr> <td>0.3</td> <td>acetone/MeOH (1:9)</td> <td>27</td> <td>88:12:0</td> </tr> <tr> <td>0.3</td> <td>acetone</td> <td>28</td> <td>74:26:0</td> </tr> <tr> <td>0.3</td> <td>CCl₄/acetone (9:1)</td> <td>27</td> <td>51:49:0</td> </tr> <tr> <td>5</td> <td>acetone</td> <td>>95</td> <td><5:<5:95</td> </tr> </tbody> </table>	x	Solvent	% Convn	I:II:III	1	acetone	93	73:17:10	0.3	acetone/MeOH (1:9)	27	88:12:0	0.3	acetone	28	74:26:0	0.3	CCl ₄ /acetone (9:1)	27	51:49:0	5	acetone	>95	<5:<5:95													
x	Solvent	% Convn	I:II:III																																				
1	acetone	93	73:17:10																																				
0.3	acetone/MeOH (1:9)	27	88:12:0																																				
0.3	acetone	28	74:26:0																																				
0.3	CCl ₄ /acetone (9:1)	27	51:49:0																																				
5	acetone	>95	<5:<5:95																																				
	DMD, acetone/CH ₃ CN, buffer, rt	I + II	149a																																				
		<table border="1"> <thead> <tr> <th>pH</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>4.5</td> <td>17</td> <td>5.3:1</td> </tr> <tr> <td>7.2</td> <td>19</td> <td>4.4:1</td> </tr> <tr> <td>8.8</td> <td>18</td> <td>5.2:1</td> </tr> <tr> <td>9.3</td> <td>20</td> <td>5.0:1</td> </tr> <tr> <td>10.0</td> <td>20</td> <td>4.7:1</td> </tr> <tr> <td>10.9</td> <td>16</td> <td>5.2:1</td> </tr> </tbody> </table>	pH	% Convn	I:II	4.5	17	5.3:1	7.2	19	4.4:1	8.8	18	5.2:1	9.3	20	5.0:1	10.0	20	4.7:1	10.9	16	5.2:1																
pH	% Convn	I:II																																					
4.5	17	5.3:1																																					
7.2	19	4.4:1																																					
8.8	18	5.2:1																																					
9.3	20	5.0:1																																					
10.0	20	4.7:1																																					
10.9	16	5.2:1																																					

TABLE 3. REGIOSELECTIVE EPOXIDATIONS BY DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																								
	Fructose dioxirane, CH ₃ CN/H ₂ O, pH 7.5	I + II (5) I:II = 5.7:1	149a																																																								
	Fructose dioxirane =																																																										
C ₁₁ 	DMD, acetone or TFD, TFP/CH ₂ Cl ₂	I (42)	78																																																								
	TFD, TFP/CH ₂ Cl ₂ , 0°, 3 min	I (85) + bis(epoxide) (15)	78																																																								
	DMD, acetone or TFD, TFP/CH ₂ Cl ₂	I + II	78																																																								
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Dioxirane</th> <th>Temp</th> <th>Time</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>CF₃</td> <td>H</td> <td>DMD (excess)</td> <td>0°</td> <td>12 d</td> <td>(0)</td> <td>(85)</td> </tr> <tr> <td>CF₃</td> <td>H</td> <td>TFD (excess)</td> <td>0°</td> <td>1 h</td> <td>(0)</td> <td>(93)</td> </tr> <tr> <td>Me</td> <td>F</td> <td>DMD</td> <td>20°</td> <td>15 min</td> <td>(95)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>F</td> <td>DMD</td> <td>-40°</td> <td>3 min</td> <td>(95)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>F</td> <td>DMD (excess)</td> <td>0°</td> <td>8 d</td> <td>(0)</td> <td>(90)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>DMD</td> <td>20°</td> <td>10 min</td> <td>(96)</td> <td>(0)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>TFD</td> <td>-40°</td> <td>3 min</td> <td>(97)</td> <td>(0)</td> </tr> </tbody> </table>	R ¹	R ²	Dioxirane	Temp	Time	I	II	CF ₃	H	DMD (excess)	0°	12 d	(0)	(85)	CF ₃	H	TFD (excess)	0°	1 h	(0)	(93)	Me	F	DMD	20°	15 min	(95)	(0)	Me	F	DMD	-40°	3 min	(95)	(0)	Me	F	DMD (excess)	0°	8 d	(0)	(90)	Me	H	DMD	20°	10 min	(96)	(0)	Me	H	TFD	-40°	3 min	(97)	(0)	
R ¹	R ²	Dioxirane	Temp	Time	I	II																																																					
CF ₃	H	DMD (excess)	0°	12 d	(0)	(85)																																																					
CF ₃	H	TFD (excess)	0°	1 h	(0)	(93)																																																					
Me	F	DMD	20°	15 min	(95)	(0)																																																					
Me	F	DMD	-40°	3 min	(95)	(0)																																																					
Me	F	DMD (excess)	0°	8 d	(0)	(90)																																																					
Me	H	DMD	20°	10 min	(96)	(0)																																																					
Me	H	TFD	-40°	3 min	(97)	(0)																																																					
	DMD, solvent, 20°	I + II	134a																																																								
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> <th>dr (II)</th> <th>dr (I)</th> </tr> </thead> <tbody> <tr> <td>MeOH/acetone (9:1)</td> <td>41</td> <td>95:5</td> <td>76:24</td> <td>50:50</td> </tr> <tr> <td>acetone</td> <td>35</td> <td>84:16</td> <td>84:16</td> <td>50:50</td> </tr> <tr> <td>CCl₄</td> <td>26</td> <td>32:68</td> <td>94:6</td> <td>50:50</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	dr (II)	dr (I)	MeOH/acetone (9:1)	41	95:5	76:24	50:50	acetone	35	84:16	84:16	50:50	CCl ₄	26	32:68	94:6	50:50																																					
Solvent	% Convn	I:II	dr (II)	dr (I)																																																							
MeOH/acetone (9:1)	41	95:5	76:24	50:50																																																							
acetone	35	84:16	84:16	50:50																																																							
CCl ₄	26	32:68	94:6	50:50																																																							
	TFD, CH ₂ Cl ₂ /TFP, 20°	I + II (—) I:II = 69:31 Convn = 25%; dr of II = 85:15	134a																																																								
	Acetone, Oxone [®] , CH ₃ CN/H ₂ O, 20°	I + II (—) I:II = 57:43 Convn = 18%; dr of II = 90:10	134a																																																								
C ₁₃ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°	(~100)	214																																																								
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°	(~90)	214																																																								
C ₁₄ 	DMD, acetone/CH ₂ Cl ₂ , 0°	(—) + (—) I:II = 70:30	287, 287a																																																								

TABLE 3. REGIOSELECTIVE EPOXIDATIONS BY DIOXIRANES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₁₆		DMD, acetone/CH ₂ Cl ₂ , 20°, 15 min	I (100)	78												
		TFD, TFP/CH ₂ Cl ₂ , -20°, 3 min	I (85) + (15)	78												
		DMD, acetone/CH ₂ Cl ₂ , 20°, 3 d	I (56) + triepoxide (44)	78												
		TFD, TFP/CH ₂ Cl ₂ , -70°, 1 h	I (85) + triepoxide (8)	78												
		DMD, acetone/CH ₃ CN	I + II + III (—)	288												
			<table border="1"> <thead> <tr> <th>Temp</th> <th>% Convn</th> <th>I:II:III</th> </tr> </thead> <tbody> <tr> <td>20°</td> <td>84</td> <td>52:13:22</td> </tr> <tr> <td>-50°</td> <td>95</td> <td>55:9:28</td> </tr> <tr> <td>-15°</td> <td>63</td> <td>42:13:7</td> </tr> </tbody> </table>	Temp	% Convn	I:II:III	20°	84	52:13:22	-50°	95	55:9:28	-15°	63	42:13:7	
Temp	% Convn	I:II:III														
20°	84	52:13:22														
-50°	95	55:9:28														
-15°	63	42:13:7														
		DMD (excess), acetone/ CH ₂ Cl ₂ , rt, 5 min	III (~100)	288												
		DMD, acetone/CH ₂ Cl ₂ rt, 5 min	III (>96)	288												
		DMD (excess), acetone/ CH ₂ Cl ₂ , rt, 3 d	(~100)	288												
		DMD, acetone/CH ₂ Cl ₂ , NaHPO ₄ , rt, 3 min	(—)	288												
		Ketone 12, Oxone®, NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, 0°	I (—) + II (—) +bisepoxide (—) I:II = 4.3:1	149a												
C ₁₈		DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°	(~ 100)	214												

TABLE 3. REGIOSELECTIVE EPOXIDATIONS BY DIOXIRANES (Continued)

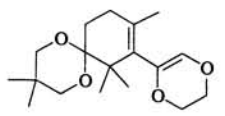
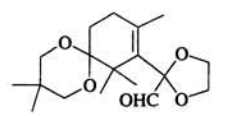
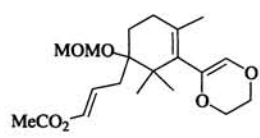
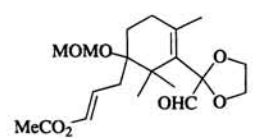
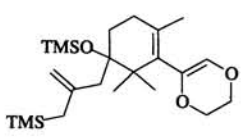
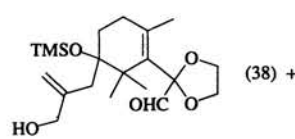
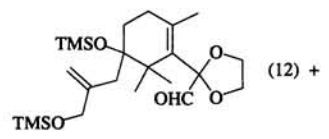
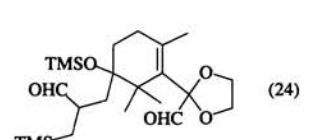
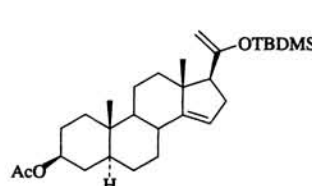
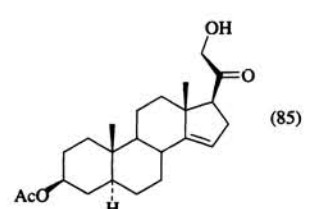
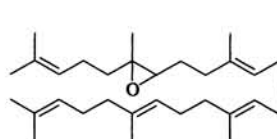
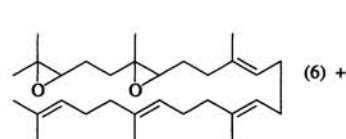
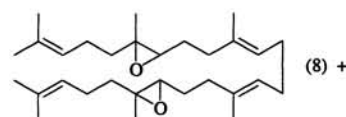
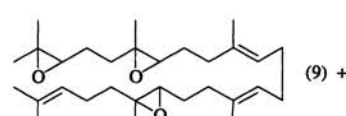
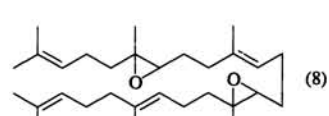
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°	 (~100)	214
C ₂₀ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°	 (84)	214
C ₂₃ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -40°	 (38) +  (12) +  (24)	214
C ₂₉ 	DMD, acetone, rt, 16 h	 (85)	289
C ₃₀ 	DMD, acetone/CH ₂ Cl ₂ , 0°, 1 h	 (6) +  (8) +  (9) +  (8)	290, 291

TABLE 3. REGIOSELECTIVE EPOXIDATIONS BY DIOXIRANES (Continued)

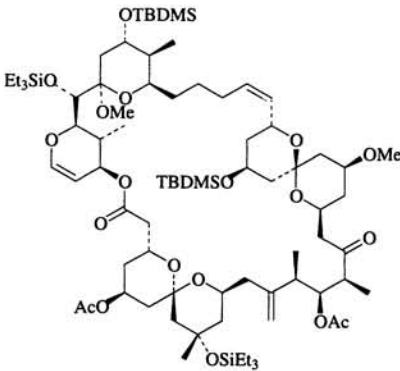
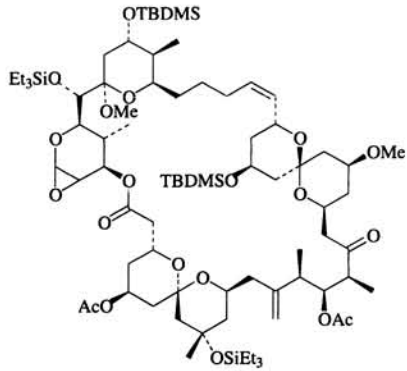
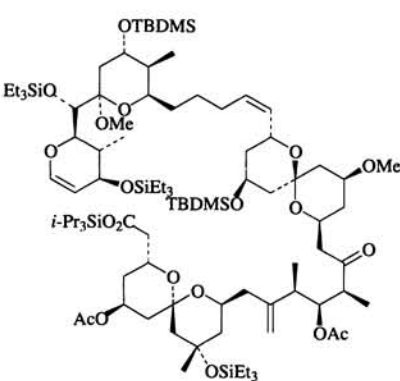
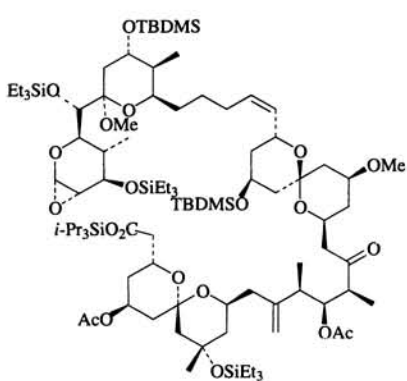
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₇₉</p> 	<p>DMD, acetone/CH₂Cl₂, 0°</p>		<p>(—) 90</p>
<p>C₉₄</p> 	<p>DMD, acetone/CH₂Cl₂, 0°, 5 min</p>		<p>(—) 90</p>

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES

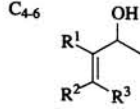
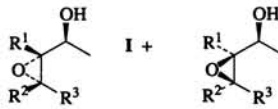
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																																																																																												
$C_{4,6}$ 	DMD, solvent, 0 to 20°, 1 to 8 h	 I + II (>95)	72, 292, 293																																																																																																												
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td><td>H</td><td>acetone</td><td>89</td><td>50:50</td></tr> <tr><td>Me</td><td>H</td><td>H</td><td>MeOH/acetone (9:1)</td><td>>95</td><td>57:43</td></tr> <tr><td>Me</td><td>H</td><td>H</td><td>acetone</td><td>>95</td><td>60:40</td></tr> <tr><td>Me</td><td>H</td><td>H</td><td>CCl₄/acetone (9:1)</td><td>>95</td><td>70:30</td></tr> <tr><td>H</td><td>Me</td><td>H</td><td>acetone</td><td>78</td><td>53:47</td></tr> <tr><td>H</td><td>Me</td><td>H</td><td>CCl₄/acetone (9:1)</td><td>>95</td><td>56:44</td></tr> <tr><td>H</td><td>H</td><td>Me</td><td>MeOH/acetone (9:1)</td><td>86</td><td>64:36</td></tr> <tr><td>H</td><td>H</td><td>Me</td><td>acetone</td><td>>95</td><td>67:33</td></tr> <tr><td>H</td><td>H</td><td>Me</td><td>CCl₄/acetone (9:1)</td><td>>95</td><td>85:15</td></tr> <tr><td>H</td><td>Me</td><td>Me</td><td>MeOH/acetone (9:1)</td><td>>95</td><td>59:41</td></tr> <tr><td>H</td><td>Me</td><td>Me</td><td>acetone</td><td>87</td><td>76:24</td></tr> <tr><td>H</td><td>Me</td><td>Me</td><td>CCl₄/acetone (9:1)</td><td>>95</td><td>82:18</td></tr> <tr><td>Me</td><td>H</td><td>Me</td><td>MeOH/acetone (9:1)</td><td>>95</td><td>82:18</td></tr> <tr><td>Me</td><td>H</td><td>Me</td><td>acetone</td><td>>95</td><td>87:13</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>acetone</td><td>(—)</td><td>51:49</td></tr> <tr><td>Me</td><td>H</td><td>Me</td><td>CCl₄/acetone (9:1)</td><td>>95</td><td>91:9</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>acetone</td><td>>95</td><td>>95:5</td></tr> </tbody> </table>	R ¹	R ²	R ³	Solvent	% Convn	I:II	H	H	H	acetone	89	50:50	Me	H	H	MeOH/acetone (9:1)	>95	57:43	Me	H	H	acetone	>95	60:40	Me	H	H	CCl ₄ /acetone (9:1)	>95	70:30	H	Me	H	acetone	78	53:47	H	Me	H	CCl ₄ /acetone (9:1)	>95	56:44	H	H	Me	MeOH/acetone (9:1)	86	64:36	H	H	Me	acetone	>95	67:33	H	H	Me	CCl ₄ /acetone (9:1)	>95	85:15	H	Me	Me	MeOH/acetone (9:1)	>95	59:41	H	Me	Me	acetone	87	76:24	H	Me	Me	CCl ₄ /acetone (9:1)	>95	82:18	Me	H	Me	MeOH/acetone (9:1)	>95	82:18	Me	H	Me	acetone	>95	87:13	Me	Me	H	acetone	(—)	51:49	Me	H	Me	CCl ₄ /acetone (9:1)	>95	91:9	Me	Me	Me	acetone	>95	>95:5	
R ¹	R ²	R ³	Solvent	% Convn	I:II																																																																																																										
H	H	H	acetone	89	50:50																																																																																																										
Me	H	H	MeOH/acetone (9:1)	>95	57:43																																																																																																										
Me	H	H	acetone	>95	60:40																																																																																																										
Me	H	H	CCl ₄ /acetone (9:1)	>95	70:30																																																																																																										
H	Me	H	acetone	78	53:47																																																																																																										
H	Me	H	CCl ₄ /acetone (9:1)	>95	56:44																																																																																																										
H	H	Me	MeOH/acetone (9:1)	86	64:36																																																																																																										
H	H	Me	acetone	>95	67:33																																																																																																										
H	H	Me	CCl ₄ /acetone (9:1)	>95	85:15																																																																																																										
H	Me	Me	MeOH/acetone (9:1)	>95	59:41																																																																																																										
H	Me	Me	acetone	87	76:24																																																																																																										
H	Me	Me	CCl ₄ /acetone (9:1)	>95	82:18																																																																																																										
Me	H	Me	MeOH/acetone (9:1)	>95	82:18																																																																																																										
Me	H	Me	acetone	>95	87:13																																																																																																										
Me	Me	H	acetone	(—)	51:49																																																																																																										
Me	H	Me	CCl ₄ /acetone (9:1)	>95	91:9																																																																																																										
Me	Me	Me	acetone	>95	>95:5																																																																																																										
	TFD, solvent, 0 to 10°, 15 to 60 min	I + II (>95)	80																																																																																																												
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr><td>H</td><td>H</td><td>H</td><td>CCl₄/TFP (9:1)</td><td>>95</td><td>55:45</td></tr> <tr><td>Me</td><td>H</td><td>H</td><td>TFP</td><td>>95</td><td>53:47</td></tr> <tr><td>Me</td><td>H</td><td>H</td><td>CCl₄/TFP (9:1)</td><td>>95</td><td>62:38</td></tr> </tbody> </table>	R ¹	R ²	R ³	Solvent	% Convn	I:II	H	H	H	CCl ₄ /TFP (9:1)	>95	55:45	Me	H	H	TFP	>95	53:47	Me	H	H	CCl ₄ /TFP (9:1)	>95	62:38																																																																																					
R ¹	R ²	R ³	Solvent	% Convn	I:II																																																																																																										
H	H	H	CCl ₄ /TFP (9:1)	>95	55:45																																																																																																										
Me	H	H	TFP	>95	53:47																																																																																																										
Me	H	H	CCl ₄ /TFP (9:1)	>95	62:38																																																																																																										

TABLE 4. DIASTERESELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

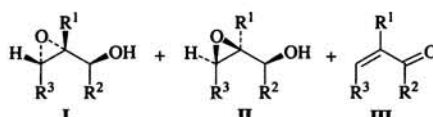
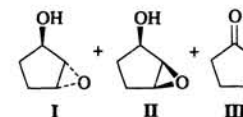
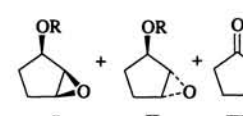
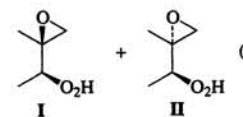
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)				Refs.																																																																						
		R ¹	R ²	R ³	Solvent % Convn I:II																																																																							
		H	Me	H	TFP 95	48:52																																																																						
		H	Me	H	CCl ₄ /TFP (9:1) 76	43:57																																																																						
		H	H	Me	TFP 95	77:23																																																																						
		H	H	Me	CCl ₄ /TFP (9:1) 93	88:12																																																																						
		H	Me	Me	TFP >95	76:24																																																																						
		H	Me	Me	CCl ₄ /TFP (9:1) >95	82:18																																																																						
		Me	H	Me	TFP >95	85:15																																																																						
		Me	H	Me	CCl ₄ /TFP (9:1) 60	90:10																																																																						
C ₄₋₇	DMD, acetone	I + II (—) <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>50:50</td> </tr> <tr> <td>H</td> <td>Me</td> <td>H</td> <td>53:47</td> </tr> <tr> <td>H</td> <td>H</td> <td>Me</td> <td>67:33</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>60:40</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Me</td> <td>76:24</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Me</td> <td>87:13</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>95:5</td> </tr> </tbody> </table>				R ¹	R ²	R ³	I:II	H	H	H	50:50	H	Me	H	53:47	H	H	Me	67:33	Me	H	H	60:40	H	Me	Me	76:24	Me	H	Me	87:13	Me	Me	Me	95:5	292																																						
R ¹	R ²	R ³	I:II																																																																									
H	H	H	50:50																																																																									
H	Me	H	53:47																																																																									
H	H	Me	67:33																																																																									
Me	H	H	60:40																																																																									
H	Me	Me	76:24																																																																									
Me	H	Me	87:13																																																																									
Me	Me	Me	95:5																																																																									
C ₄₋₁₂	DMD, CH ₂ Cl ₂ /acetone, rt, 3.5 h	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>I+II</th> <th>III</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>H</td> <td>(>95)</td> <td>(<5)</td> <td>50:50</td> </tr> <tr> <td>TMS</td> <td>Me</td> <td>H</td> <td>(32)</td> <td>(68)</td> <td>60:40</td> </tr> <tr> <td>TMS</td> <td>-(CH₂)₃-</td> <td>H</td> <td>(<5)</td> <td>(>95)</td> <td>—</td> </tr> <tr> <td>SiMe₂Ph</td> <td>Me</td> <td>H</td> <td>(10)</td> <td>(90)</td> <td>55:45</td> </tr> </tbody> </table>				R ¹	R ²	R ³	I+II	III	I:II	H	Me	H	(>95)	(<5)	50:50	TMS	Me	H	(32)	(68)	60:40	TMS	-(CH ₂) ₃ -	H	(<5)	(>95)	—	SiMe ₂ Ph	Me	H	(10)	(90)	55:45	74																																								
R ¹	R ²	R ³	I+II	III	I:II																																																																							
H	Me	H	(>95)	(<5)	50:50																																																																							
TMS	Me	H	(32)	(68)	60:40																																																																							
TMS	-(CH ₂) ₃ -	H	(<5)	(>95)	—																																																																							
SiMe ₂ Ph	Me	H	(10)	(90)	55:45																																																																							
C ₅	DMD, acetone, rt, 2 h	 (—) I:II = 48:52 (I + II):III = 78:22				83																																																																						
C ₅₋₇	DMD or TFD, solvent, 0°, time	 I + II + III (>95)				294																																																																						
		<table border="1"> <thead> <tr> <th>R</th> <th>Dioxirane</th> <th>Solvent</th> <th>Time</th> <th>% Convn</th> <th>I:II</th> <th>(I+II):III</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>DMD</td> <td>acetone</td> <td>55 min</td> <td>92</td> <td>53:47</td> <td>70:30</td> </tr> <tr> <td>H</td> <td>DMD</td> <td>acetone/CH₂Cl₂ (1:1)</td> <td>40 min</td> <td>95</td> <td>61:39</td> <td>90:10</td> </tr> <tr> <td>H</td> <td>TFD</td> <td>CCl₄</td> <td>10 min</td> <td>95</td> <td>70:30</td> <td>66:34</td> </tr> <tr> <td>Me</td> <td>DMD</td> <td>acetone</td> <td>90 min</td> <td>54</td> <td>20:80</td> <td>95:5</td> </tr> <tr> <td>Me</td> <td>DMD</td> <td>acetone/CH₂Cl₂ (1:1)</td> <td>75 min</td> <td>60</td> <td>30:70</td> <td>95:5</td> </tr> <tr> <td>Me</td> <td>TFD</td> <td>CCl₄</td> <td>20 min</td> <td>70</td> <td>8:92</td> <td>98:2</td> </tr> <tr> <td>Ac</td> <td>DMD</td> <td>acetone</td> <td>150 min</td> <td>60</td> <td>30:70</td> <td>—</td> </tr> <tr> <td>Ac</td> <td>DMD</td> <td>acetone/CH₂Cl₂ (1:1)</td> <td>120 min</td> <td>72</td> <td>36:64</td> <td>—</td> </tr> <tr> <td>Ac</td> <td>TFD</td> <td>CCl₄</td> <td>30 min</td> <td>56</td> <td>38:62</td> <td>—</td> </tr> </tbody> </table>				R	Dioxirane	Solvent	Time	% Convn	I:II	(I+II):III	H	DMD	acetone	55 min	92	53:47	70:30	H	DMD	acetone/CH ₂ Cl ₂ (1:1)	40 min	95	61:39	90:10	H	TFD	CCl ₄	10 min	95	70:30	66:34	Me	DMD	acetone	90 min	54	20:80	95:5	Me	DMD	acetone/CH ₂ Cl ₂ (1:1)	75 min	60	30:70	95:5	Me	TFD	CCl ₄	20 min	70	8:92	98:2	Ac	DMD	acetone	150 min	60	30:70	—	Ac	DMD	acetone/CH ₂ Cl ₂ (1:1)	120 min	72	36:64	—	Ac	TFD	CCl ₄	30 min	56	38:62	—	
R	Dioxirane	Solvent	Time	% Convn	I:II	(I+II):III																																																																						
H	DMD	acetone	55 min	92	53:47	70:30																																																																						
H	DMD	acetone/CH ₂ Cl ₂ (1:1)	40 min	95	61:39	90:10																																																																						
H	TFD	CCl ₄	10 min	95	70:30	66:34																																																																						
Me	DMD	acetone	90 min	54	20:80	95:5																																																																						
Me	DMD	acetone/CH ₂ Cl ₂ (1:1)	75 min	60	30:70	95:5																																																																						
Me	TFD	CCl ₄	20 min	70	8:92	98:2																																																																						
Ac	DMD	acetone	150 min	60	30:70	—																																																																						
Ac	DMD	acetone/CH ₂ Cl ₂ (1:1)	120 min	72	36:64	—																																																																						
Ac	TFD	CCl ₄	30 min	56	38:62	—																																																																						
C ₅	DMD, acetone/CH ₂ Cl ₂ , 20°, 1 h	 (71) I:II = 42:58				170																																																																						

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)


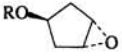
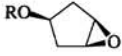
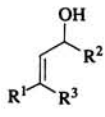
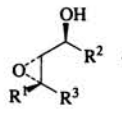
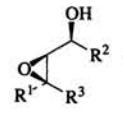
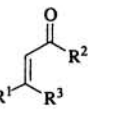
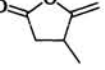
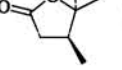
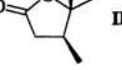
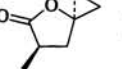
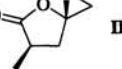
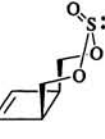

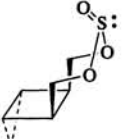

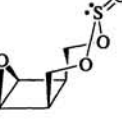
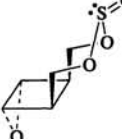
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																																																																				
C ₅₋₆ 	DMD or TFD, solvent, 0°, time	 I +  II (>95)	294																																																																																				
		<table border="1"> <thead> <tr> <th>R</th> <th>Dioxirane</th> <th>Solvent</th> <th>Time</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>DMD</td> <td>acetone</td> <td>70 min</td> <td>96</td> <td>54:46</td> </tr> <tr> <td>H</td> <td>TFD</td> <td>CCl₄</td> <td>18 min</td> <td>85</td> <td>78:22</td> </tr> <tr> <td>Me</td> <td>DMD</td> <td>acetone</td> <td>70 min</td> <td>96</td> <td>15:85</td> </tr> <tr> <td>Me</td> <td>TFD</td> <td>CCl₄</td> <td>18 min</td> <td>85</td> <td>2:98</td> </tr> </tbody> </table>	R	Dioxirane	Solvent	Time	% Convn	I:II	H	DMD	acetone	70 min	96	54:46	H	TFD	CCl ₄	18 min	85	78:22	Me	DMD	acetone	70 min	96	15:85	Me	TFD	CCl ₄	18 min	85	2:98																																																							
		R	Dioxirane	Solvent	Time	% Convn	I:II																																																																																
		H	DMD	acetone	70 min	96	54:46																																																																																
		H	TFD	CCl ₄	18 min	85	78:22																																																																																
Me	DMD	acetone	70 min	96	15:85																																																																																		
Me	TFD	CCl ₄	18 min	85	2:98																																																																																		
C ₅₋₇ 	DMD, acetone/CH ₂ Cl ₂	 I +  II +  III	73																																																																																				
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Temp</th> <th>% Convn</th> <th>I:II</th> <th>(I+II):III</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>0°</td> <td>78</td> <td>53:47</td> <td>81:19</td> </tr> <tr> <td>H</td> <td>—(CH₂)₃—</td> <td>H</td> <td>-20°</td> <td>>95</td> <td>72:28</td> <td>46:54</td> </tr> <tr> <td>H</td> <td>—(CH₂)₃—</td> <td>H</td> <td>0°</td> <td>80</td> <td>53:47</td> <td>70:30</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>-78°</td> <td>>95</td> <td>76:24</td> <td>>95:5</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>0°</td> <td>87</td> <td>77:23</td> <td>>95:5</td> </tr> <tr> <td>Me</td> <td><i>i</i>-Pr</td> <td>H</td> <td>-20°</td> <td>>95</td> <td>63:37</td> <td>47:53</td> </tr> <tr> <td>Me</td> <td><i>i</i>-Pr</td> <td>H</td> <td>0°</td> <td>>95</td> <td>65:35</td> <td>90:10</td> </tr> <tr> <td>H</td> <td>—(CH₂)₃—</td> <td>H</td> <td>0°</td> <td>>95</td> <td>>95:5</td> <td>>95:5</td> </tr> <tr> <td>H</td> <td><i>n</i>-C₃H₁₁</td> <td>H</td> <td>0°</td> <td>>95</td> <td>66:34</td> <td>51:49</td> </tr> <tr> <td>Me</td> <td><i>n</i>-Bu</td> <td>H</td> <td>-20°</td> <td>96</td> <td>52:48</td> <td>47:53</td> </tr> <tr> <td>Me</td> <td><i>n</i>-Bu</td> <td>H</td> <td>0°</td> <td>>95</td> <td>52:48</td> <td>71:29</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Temp	% Convn	I:II	(I+II):III	Me	Me	H	0°	78	53:47	81:19	H	—(CH ₂) ₃ —	H	-20°	>95	72:28	46:54	H	—(CH ₂) ₃ —	H	0°	80	53:47	70:30	Me	Me	Me	-78°	>95	76:24	>95:5	Me	Me	Me	0°	87	77:23	>95:5	Me	<i>i</i> -Pr	H	-20°	>95	63:37	47:53	Me	<i>i</i> -Pr	H	0°	>95	65:35	90:10	H	—(CH ₂) ₃ —	H	0°	>95	>95:5	>95:5	H	<i>n</i> -C ₃ H ₁₁	H	0°	>95	66:34	51:49	Me	<i>n</i> -Bu	H	-20°	96	52:48	47:53	Me	<i>n</i> -Bu	H	0°	>95	52:48	71:29	
		R ¹	R ²	R ³	Temp	% Convn	I:II	(I+II):III																																																																															
		Me	Me	H	0°	78	53:47	81:19																																																																															
		H	—(CH ₂) ₃ —	H	-20°	>95	72:28	46:54																																																																															
		H	—(CH ₂) ₃ —	H	0°	80	53:47	70:30																																																																															
		Me	Me	Me	-78°	>95	76:24	>95:5																																																																															
		Me	Me	Me	0°	87	77:23	>95:5																																																																															
		Me	<i>i</i> -Pr	H	-20°	>95	63:37	47:53																																																																															
		Me	<i>i</i> -Pr	H	0°	>95	65:35	90:10																																																																															
		H	—(CH ₂) ₃ —	H	0°	>95	>95:5	>95:5																																																																															
		H	<i>n</i> -C ₃ H ₁₁	H	0°	>95	66:34	51:49																																																																															
		Me	<i>n</i> -Bu	H	-20°	96	52:48	47:53																																																																															
		Me	<i>n</i> -Bu	H	0°	>95	52:48	71:29																																																																															
		C ₆ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°, 3.5 h	 I +  II (—) I:II = 60:40	44																																																																																		
 I +  II (—) I:II = 65:35	44																																																																																						
	DMD, rt	 I +  II	295																																																																																				
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>Time</th> <th>I+II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>7 h</td> <td>(88)</td> <td>77:23</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>12 h</td> <td>(85)</td> <td>70:30</td> </tr> </tbody> </table>	Solvent	Time	I+II	I:II	acetone	7 h	(88)	77:23	CCl ₄ /acetone (9:1)	12 h	(85)	70:30																																																																									
Solvent	Time	I+II	I:II																																																																																				
acetone	7 h	(88)	77:23																																																																																				
CCl ₄ /acetone (9:1)	12 h	(85)	70:30																																																																																				
	DMD, rt	 I +  II	295																																																																																				
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>Time</th> <th>II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>2 h</td> <td>(95)</td> <td>0:100</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>5 h</td> <td>(95)</td> <td>0:100</td> </tr> </tbody> </table>	Solvent	Time	II	I:II	acetone	2 h	(95)	0:100	CCl ₄ /acetone (9:1)	5 h	(95)	0:100																																																																									
Solvent	Time	II	I:II																																																																																				
acetone	2 h	(95)	0:100																																																																																				
CCl ₄ /acetone (9:1)	5 h	(95)	0:100																																																																																				

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)








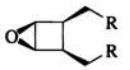
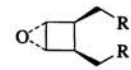




Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																																																	
	DMD, solvent, rt, 60 min	 I +  II <table border="1" data-bbox="1171 447 1440 539"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>76</td> <td>90:10</td> </tr> <tr> <td>CH₂Cl₂/acetone (1:1)</td> <td>74</td> <td>93:7</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	acetone	76	90:10	CH ₂ Cl ₂ /acetone (1:1)	74	93:7	67																																																								
Solvent	% Convn	I:II																																																																		
acetone	76	90:10																																																																		
CH ₂ Cl ₂ /acetone (1:1)	74	93:7																																																																		
	DMD, acetone, rt, 60 min	 I +  II Convsn = 58%; I:II = 92:8	67																																																																	
	DMD, rt	 I +  II <table border="1" data-bbox="928 792 1354 1148"> <thead> <tr> <th>R</th> <th>Solvent</th> <th>Time</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>acetone</td> <td>12 min</td> <td>(99)</td> <td>44:56</td> </tr> <tr> <td>H</td> <td>CCl₄/acetone (9:1)</td> <td>30 min</td> <td>(99)</td> <td>55:45</td> </tr> <tr> <td>OH</td> <td>acetone</td> <td>2 h</td> <td>(70)</td> <td>57:43</td> </tr> <tr> <td>OH</td> <td>CCl₄/acetone (9:1)</td> <td>1 h</td> <td>(80)</td> <td>67:33</td> </tr> <tr> <td>OMe</td> <td>acetone</td> <td>7 h</td> <td>(99)</td> <td>49:51</td> </tr> <tr> <td>OMe</td> <td>CCl₄/acetone (9:1)</td> <td>10 h</td> <td>(99)</td> <td>62:38</td> </tr> <tr> <td>OMs</td> <td>acetone</td> <td>5 h</td> <td>(85)</td> <td>79:21</td> </tr> <tr> <td>OMs</td> <td>CCl₄/acetone (9:1)</td> <td>12 h</td> <td>(99)</td> <td>90:10</td> </tr> <tr> <td>OAc</td> <td>acetone</td> <td>2 h</td> <td>(69)</td> <td>72:28</td> </tr> <tr> <td>OAc</td> <td>CCl₄/acetone (9:1)</td> <td>6 h</td> <td>(99)</td> <td>68:32</td> </tr> <tr> <td>OTs</td> <td>acetone</td> <td>2 h</td> <td>(97)</td> <td>63:37</td> </tr> <tr> <td>OTs</td> <td>CCl₄/acetone (9:1)</td> <td>8 h</td> <td>(99)</td> <td>82:18</td> </tr> </tbody> </table>	R	Solvent	Time	(%)	I:II	H	acetone	12 min	(99)	44:56	H	CCl ₄ /acetone (9:1)	30 min	(99)	55:45	OH	acetone	2 h	(70)	57:43	OH	CCl ₄ /acetone (9:1)	1 h	(80)	67:33	OMe	acetone	7 h	(99)	49:51	OMe	CCl ₄ /acetone (9:1)	10 h	(99)	62:38	OMs	acetone	5 h	(85)	79:21	OMs	CCl ₄ /acetone (9:1)	12 h	(99)	90:10	OAc	acetone	2 h	(69)	72:28	OAc	CCl ₄ /acetone (9:1)	6 h	(99)	68:32	OTs	acetone	2 h	(97)	63:37	OTs	CCl ₄ /acetone (9:1)	8 h	(99)	82:18	295
R	Solvent	Time	(%)	I:II																																																																
H	acetone	12 min	(99)	44:56																																																																
H	CCl ₄ /acetone (9:1)	30 min	(99)	55:45																																																																
OH	acetone	2 h	(70)	57:43																																																																
OH	CCl ₄ /acetone (9:1)	1 h	(80)	67:33																																																																
OMe	acetone	7 h	(99)	49:51																																																																
OMe	CCl ₄ /acetone (9:1)	10 h	(99)	62:38																																																																
OMs	acetone	5 h	(85)	79:21																																																																
OMs	CCl ₄ /acetone (9:1)	12 h	(99)	90:10																																																																
OAc	acetone	2 h	(69)	72:28																																																																
OAc	CCl ₄ /acetone (9:1)	6 h	(99)	68:32																																																																
OTs	acetone	2 h	(97)	63:37																																																																
OTs	CCl ₄ /acetone (9:1)	8 h	(99)	82:18																																																																
	DMD, acetone, 20°, 6 h	 I +  II +  III (93) I:II = 47:53; (I + II):III = 70:30	75																																																																	
	DMD, acetone/CH ₂ Cl ₂ , rt, 4 h	I + II + III I + II (80), III (10); I:II = 25:75	133																																																																	
	DMD, solvent, rt, 60 min	I + II + III <table border="1" data-bbox="980 1526 1362 1779"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> <th>(I+II):III</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>94</td> <td>54:46</td> <td>46:54</td> </tr> <tr> <td>CH₂Cl₂/acetone (1:1)</td> <td>94</td> <td>43:57</td> <td>65:35</td> </tr> <tr> <td>CH₂Cl₂/acetone (9:1)</td> <td>89</td> <td>22:78</td> <td>84:16</td> </tr> <tr> <td>CH₂Cl₂/acetone (97:3)</td> <td>77</td> <td>18:82</td> <td>89:11</td> </tr> <tr> <td>MeOH/acetone (9:1)</td> <td>100</td> <td>66:34</td> <td>75:25</td> </tr> <tr> <td>CHCl₃/acetone (9:1)</td> <td>100</td> <td>88:12</td> <td>88:12</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>87</td> <td>15:85</td> <td>52:48</td> </tr> <tr> <td>CCl₄/acetone (95:5)</td> <td>86</td> <td>6:94</td> <td>59:41</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	(I+II):III	acetone	94	54:46	46:54	CH ₂ Cl ₂ /acetone (1:1)	94	43:57	65:35	CH ₂ Cl ₂ /acetone (9:1)	89	22:78	84:16	CH ₂ Cl ₂ /acetone (97:3)	77	18:82	89:11	MeOH/acetone (9:1)	100	66:34	75:25	CHCl ₃ /acetone (9:1)	100	88:12	88:12	CCl ₄ /acetone (9:1)	87	15:85	52:48	CCl ₄ /acetone (95:5)	86	6:94	59:41	296																													
Solvent	% Convn	I:II	(I+II):III																																																																	
acetone	94	54:46	46:54																																																																	
CH ₂ Cl ₂ /acetone (1:1)	94	43:57	65:35																																																																	
CH ₂ Cl ₂ /acetone (9:1)	89	22:78	84:16																																																																	
CH ₂ Cl ₂ /acetone (97:3)	77	18:82	89:11																																																																	
MeOH/acetone (9:1)	100	66:34	75:25																																																																	
CHCl ₃ /acetone (9:1)	100	88:12	88:12																																																																	
CCl ₄ /acetone (9:1)	87	15:85	52:48																																																																	
CCl ₄ /acetone (95:5)	86	6:94	59:41																																																																	
	Ketone, Oxone®, CH ₂ Cl ₂ /MeOH, buffer (pH 11.0), KOH, rt	I + II <table border="1" data-bbox="954 1882 1354 1986"> <thead> <tr> <th>Ketone</th> <th>Time</th> <th>(%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>1.5 h</td> <td>(69)</td> <td>64:36</td> </tr> <tr> <td>2-methylcyclohexanone</td> <td>3.5 h</td> <td>(63)</td> <td>71:29</td> </tr> <tr> <td>2,6-dimethylcyclohexanone</td> <td>3.0 h</td> <td>(66)</td> <td>77:23</td> </tr> </tbody> </table>	Ketone	Time	(%)	I:II	acetone	1.5 h	(69)	64:36	2-methylcyclohexanone	3.5 h	(63)	71:29	2,6-dimethylcyclohexanone	3.0 h	(66)	77:23	297																																																	
Ketone	Time	(%)	I:II																																																																	
acetone	1.5 h	(69)	64:36																																																																	
2-methylcyclohexanone	3.5 h	(63)	71:29																																																																	
2,6-dimethylcyclohexanone	3.0 h	(66)	77:23																																																																	

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																								
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, rt	I + II (—)	81																																								
		<table border="1"> <thead> <tr> <th>Ketone</th> <th>I:II</th> <th>Ketone</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>MeCOMe</td> <td>1.2:1</td> <td></td> <td>1.9:1</td> </tr> <tr> <td>EtCOEt</td> <td>—</td> <td></td> <td></td> </tr> <tr> <td>ClCH₂COMe</td> <td>2.0:1</td> <td></td> <td></td> </tr> <tr> <td>ClCH₂COCH₂Cl</td> <td>2.7:1</td> <td></td> <td></td> </tr> <tr> <td>CF₃COMe</td> <td>3.3:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>1.3:1</td> <td></td> <td>1.9:1</td> </tr> <tr> <td></td> <td>—</td> <td></td> <td>5.9:1</td> </tr> <tr> <td></td> <td>2.1:1</td> <td></td> <td>1.7:1</td> </tr> <tr> <td></td> <td>1.6:1</td> <td></td> <td>1.9:1</td> </tr> </tbody> </table>	Ketone	I:II	Ketone	I:II	MeCOMe	1.2:1		1.9:1	EtCOEt	—			ClCH ₂ COMe	2.0:1			ClCH ₂ COCH ₂ Cl	2.7:1			CF ₃ COMe	3.3:1				1.3:1		1.9:1		—		5.9:1		2.1:1		1.7:1		1.6:1		1.9:1	
Ketone	I:II	Ketone	I:II																																								
MeCOMe	1.2:1		1.9:1																																								
EtCOEt	—																																										
ClCH ₂ COMe	2.0:1																																										
ClCH ₂ COCH ₂ Cl	2.7:1																																										
CF ₃ COMe	3.3:1																																										
	1.3:1		1.9:1																																								
	—		5.9:1																																								
	2.1:1		1.7:1																																								
	1.6:1		1.9:1																																								
C ₆₋₁₀ 	TFD, solvent, 0 to 10°, 15 to 60 min	 I + II	80																																								
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>TFP</td> <td>70</td> <td>57:43</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>CCl₄/TFP (9:1)</td> <td>78</td> <td>70:30</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>TFP</td> <td>84</td> <td>88:12</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>CCl₄/TFP (9:1)</td> <td>70</td> <td>94:6</td> </tr> <tr> <td>H</td> <td>H</td> <td><i>t</i>-Bu</td> <td>TFP</td> <td>80</td> <td>73:27</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Solvent	% Convn	I:II	H	H	H	TFP	70	57:43	H	H	H	CCl ₄ /TFP (9:1)	78	70:30	Me	Me	Me	TFP	84	88:12	Me	Me	Me	CCl ₄ /TFP (9:1)	70	94:6	H	H	<i>t</i> -Bu	TFP	80	73:27					
R ¹	R ²	R ³	Solvent	% Convn	I:II																																						
H	H	H	TFP	70	57:43																																						
H	H	H	CCl ₄ /TFP (9:1)	78	70:30																																						
Me	Me	Me	TFP	84	88:12																																						
Me	Me	Me	CCl ₄ /TFP (9:1)	70	94:6																																						
H	H	<i>t</i> -Bu	TFP	80	73:27																																						
C ₆ 	DMD, acetone, 20°, 2 to 8 h	 I + II (—) I:II = 91:9	75																																								
	DMD, solvent, rt, 20 h	I + II <table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>100</td> <td>84:16</td> </tr> <tr> <td>CH₂Cl₂/acetone (1:1)</td> <td>100</td> <td>82:18</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	acetone	100	84:16	CH ₂ Cl ₂ /acetone (1:1)	100	82:18	67																															
Solvent	% Convn	I:II																																									
acetone	100	84:16																																									
CH ₂ Cl ₂ /acetone (1:1)	100	82:18																																									
	DMD, acetone, 8 h	 I + II (>95) I:II = 46:54	298																																								
	DMD, acetone, 7 h	 I + II (50) I:II = 90:10	298																																								

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

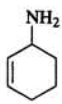
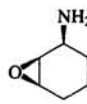
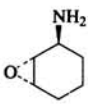




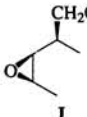
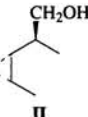

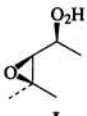
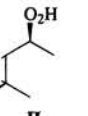
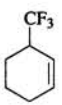
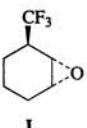
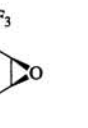
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																
	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. DMD, acetone/CH ₂ Cl ₂ , 0°, 1 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	 I +  II (60) I:II = 90:10	65																
	1. 4-ClC ₆ H ₄ SO ₃ H, Et ₂ O, 0° 2. TFD, CH ₂ Cl ₂ /CH ₃ CN, 0°, 0.1 h 3. K ₂ CO ₃ , MgSO ₄ , CH ₂ Cl ₂ , 0°, 5 h	I + II (72) I:II = 50:50	65																
	DMD, solvent, -20°, 6 h	 I +  II	87																
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>76:24</td> </tr> <tr> <td>MeOH/acetone (1:1)</td> <td>60:40</td> </tr> <tr> <td>AcOEt/acetone (1:1)</td> <td>71:29</td> </tr> <tr> <td>CCl₄/acetone (1:1)</td> <td>76:24</td> </tr> <tr> <td>hexane/acetone (1:1)</td> <td>77:23</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>82:18</td> </tr> <tr> <td>hexane/acetone (9:1)</td> <td>82:18</td> </tr> </tbody> </table>	Solvent	I:II	acetone	76:24	MeOH/acetone (1:1)	60:40	AcOEt/acetone (1:1)	71:29	CCl ₄ /acetone (1:1)	76:24	hexane/acetone (1:1)	77:23	CCl ₄ /acetone (9:1)	82:18	hexane/acetone (9:1)	82:18	
	Solvent	I:II																	
	acetone	76:24																	
	MeOH/acetone (1:1)	60:40																	
AcOEt/acetone (1:1)	71:29																		
CCl ₄ /acetone (1:1)	76:24																		
hexane/acetone (1:1)	77:23																		
CCl ₄ /acetone (9:1)	82:18																		
hexane/acetone (9:1)	82:18																		
TFD, acetone- <i>d</i> ₆ /CDCl ₃ , 0.5 h	I + II (>95) I:II = 60:40	298																	
TFD, CCl ₄ , 0.5 h	I + II (57) I:II = 92:8	298																	
	DMD, acetone, 2 h	 I +  II (>95) I:II = 38:62	298																
	TFD, CCl ₄ /TFP, 0.5 h	I + II (>95) I:II = 24:76	298																
	DMD, acetone, 5 h	 I +  II (>95) I:II = 69:31	298																
	TFD, CCl ₄ /TFP, 0.5 h	I + II (>95) I:II = 80:20	298																
C ₇ 	DMD, solvent, rt, 60 min	 I +  II	67																
	<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>70</td> <td>90:10</td> </tr> <tr> <td>CH₂Cl₂/acetone (1:1)</td> <td>73</td> <td>94:6</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	acetone	70	90:10	CH ₂ Cl ₂ /acetone (1:1)	73	94:6									
Solvent	% Convn	I:II																	
acetone	70	90:10																	
CH ₂ Cl ₂ /acetone (1:1)	73	94:6																	

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)







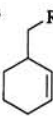
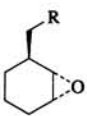
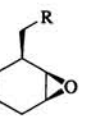
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																																																																																																										
	DMD, solvent, rt, 60 min	 I +  II	67																																																																																																																										
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>78</td> <td>51:49</td> </tr> <tr> <td>CH₂Cl₂/acetone (1:1)</td> <td>74</td> <td>57:43</td> </tr> </tbody> </table>		Solvent	% Convn	I:II	acetone	78	51:49	CH ₂ Cl ₂ /acetone (1:1)	74	57:43																																																																																																																	
Solvent	% Convn	I:II																																																																																																																											
acetone	78	51:49																																																																																																																											
CH ₂ Cl ₂ /acetone (1:1)	74	57:43																																																																																																																											
	DMD, solvent, rt, 60 min	 I +  II	67																																																																																																																										
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>82</td> <td>84:16</td> </tr> <tr> <td>CH₂Cl₂/acetone (9:1)</td> <td>100</td> <td>80:20</td> </tr> <tr> <td>CHCl₃/acetone (9:1)</td> <td>54</td> <td>87:13</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>73</td> <td>84:16</td> </tr> </tbody> </table>		Solvent	% Convn	I:II	acetone	82	84:16	CH ₂ Cl ₂ /acetone (9:1)	100	80:20	CHCl ₃ /acetone (9:1)	54	87:13	CCl ₄ /acetone (9:1)	73	84:16																																																																																																											
		Solvent		% Convn	I:II																																																																																																																								
		acetone		82	84:16																																																																																																																								
CH ₂ Cl ₂ /acetone (9:1)	100	80:20																																																																																																																											
CHCl ₃ /acetone (9:1)	54	87:13																																																																																																																											
CCl ₄ /acetone (9:1)	73	84:16																																																																																																																											
<table border="1"> <thead> <tr> <th>R</th> <th>Solvent</th> <th>Time</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>acetone</td> <td>60 min</td> <td>100</td> <td>38:62</td> </tr> <tr> <td>Br</td> <td>CH₂Cl₂/acetone (1:1)</td> <td>60 min</td> <td>100</td> <td>40:60</td> </tr> <tr> <td>Br</td> <td>MeOH/acetone (1:1)</td> <td>90 min</td> <td>100</td> <td>45:55</td> </tr> <tr> <td>Br</td> <td>CCl₄/acetone (9:1)</td> <td>5 h</td> <td>100</td> <td>27:73</td> </tr> <tr> <td>OH</td> <td>acetone</td> <td>60 min</td> <td>100</td> <td>44:56</td> </tr> <tr> <td>OH</td> <td>CH₂Cl₂/acetone (9:1)</td> <td>60 min</td> <td>100</td> <td>30:70</td> </tr> <tr> <td>OH</td> <td>CH₂Cl₂/acetone (95:5)</td> <td>60 min</td> <td>68</td> <td>28:72</td> </tr> <tr> <td>OH</td> <td>CHCl₃/acetone (9:1)</td> <td>60 min</td> <td>100</td> <td>37:63</td> </tr> <tr> <td>OH</td> <td>CCl₄/acetone (9:1)</td> <td>60 min</td> <td>92</td> <td>33:67</td> </tr> <tr> <td>OH</td> <td>CCl₄/acetone (95:5)</td> <td>60 min</td> <td>84</td> <td>26:74</td> </tr> <tr> <td>OH</td> <td>MeOH/acetone (9:1)</td> <td>120 min</td> <td>72</td> <td>55:45</td> </tr> <tr> <td>OAc</td> <td>acetone</td> <td>60 min</td> <td>100</td> <td>40:60</td> </tr> <tr> <td>OAc</td> <td>CH₂Cl₂/acetone (9:1)</td> <td>60 min</td> <td>100</td> <td>40:60</td> </tr> <tr> <td>CO₂Me</td> <td>acetone</td> <td>15 min</td> <td>100</td> <td>37:63</td> </tr> <tr> <td>CO₂Me</td> <td>CH₂Cl₂/acetone (9:1)</td> <td>60 min</td> <td>96</td> <td>39:61</td> </tr> <tr> <td>CO₂Me</td> <td>CCl₄/acetone (9:1)</td> <td>60 min</td> <td>91</td> <td>29:71</td> </tr> <tr> <td>CO₂Et</td> <td>acetone</td> <td>15 min</td> <td>100</td> <td>35:65</td> </tr> <tr> <td>CO₂Et</td> <td>CH₂Cl₂/acetone (9:1)</td> <td>60 min</td> <td>87</td> <td>38:62</td> </tr> <tr> <td>CO₂Et</td> <td>CCl₄/acetone (9:1)</td> <td>60 min</td> <td>89</td> <td>27:73</td> </tr> <tr> <td>CO₂Et</td> <td>CCl₄/acetone (95:5)</td> <td>60 min</td> <td>80</td> <td>26:74</td> </tr> <tr> <td>CO₂Et</td> <td>MeOH/acetone (9:1)</td> <td>60 min</td> <td>84</td> <td>41:59</td> </tr> <tr> <td>NHCOPh</td> <td>acetone</td> <td>15 min</td> <td>100</td> <td>36:64</td> </tr> <tr> <td>NHCOPh</td> <td>CCl₄/acetone (9:1)</td> <td>60 min</td> <td>100</td> <td>18:82</td> </tr> <tr> <td>NHCOPh</td> <td>CCl₄/acetone (95:5)</td> <td>60 min</td> <td>100</td> <td>13:87</td> </tr> </tbody> </table>	R	Solvent	Time	% Convn	I:II	Br	acetone	60 min	100	38:62	Br	CH ₂ Cl ₂ /acetone (1:1)	60 min	100	40:60	Br	MeOH/acetone (1:1)	90 min	100	45:55	Br	CCl ₄ /acetone (9:1)	5 h	100	27:73	OH	acetone	60 min	100	44:56	OH	CH ₂ Cl ₂ /acetone (9:1)	60 min	100	30:70	OH	CH ₂ Cl ₂ /acetone (95:5)	60 min	68	28:72	OH	CHCl ₃ /acetone (9:1)	60 min	100	37:63	OH	CCl ₄ /acetone (9:1)	60 min	92	33:67	OH	CCl ₄ /acetone (95:5)	60 min	84	26:74	OH	MeOH/acetone (9:1)	120 min	72	55:45	OAc	acetone	60 min	100	40:60	OAc	CH ₂ Cl ₂ /acetone (9:1)	60 min	100	40:60	CO ₂ Me	acetone	15 min	100	37:63	CO ₂ Me	CH ₂ Cl ₂ /acetone (9:1)	60 min	96	39:61	CO ₂ Me	CCl ₄ /acetone (9:1)	60 min	91	29:71	CO ₂ Et	acetone	15 min	100	35:65	CO ₂ Et	CH ₂ Cl ₂ /acetone (9:1)	60 min	87	38:62	CO ₂ Et	CCl ₄ /acetone (9:1)	60 min	89	27:73	CO ₂ Et	CCl ₄ /acetone (95:5)	60 min	80	26:74	CO ₂ Et	MeOH/acetone (9:1)	60 min	84	41:59	NHCOPh	acetone	15 min	100	36:64	NHCOPh	CCl ₄ /acetone (9:1)	60 min	100	18:82	NHCOPh	CCl ₄ /acetone (95:5)	60 min	100	13:87
R	Solvent	Time	% Convn	I:II																																																																																																																									
Br	acetone	60 min	100	38:62																																																																																																																									
Br	CH ₂ Cl ₂ /acetone (1:1)	60 min	100	40:60																																																																																																																									
Br	MeOH/acetone (1:1)	90 min	100	45:55																																																																																																																									
Br	CCl ₄ /acetone (9:1)	5 h	100	27:73																																																																																																																									
OH	acetone	60 min	100	44:56																																																																																																																									
OH	CH ₂ Cl ₂ /acetone (9:1)	60 min	100	30:70																																																																																																																									
OH	CH ₂ Cl ₂ /acetone (95:5)	60 min	68	28:72																																																																																																																									
OH	CHCl ₃ /acetone (9:1)	60 min	100	37:63																																																																																																																									
OH	CCl ₄ /acetone (9:1)	60 min	92	33:67																																																																																																																									
OH	CCl ₄ /acetone (95:5)	60 min	84	26:74																																																																																																																									
OH	MeOH/acetone (9:1)	120 min	72	55:45																																																																																																																									
OAc	acetone	60 min	100	40:60																																																																																																																									
OAc	CH ₂ Cl ₂ /acetone (9:1)	60 min	100	40:60																																																																																																																									
CO ₂ Me	acetone	15 min	100	37:63																																																																																																																									
CO ₂ Me	CH ₂ Cl ₂ /acetone (9:1)	60 min	96	39:61																																																																																																																									
CO ₂ Me	CCl ₄ /acetone (9:1)	60 min	91	29:71																																																																																																																									
CO ₂ Et	acetone	15 min	100	35:65																																																																																																																									
CO ₂ Et	CH ₂ Cl ₂ /acetone (9:1)	60 min	87	38:62																																																																																																																									
CO ₂ Et	CCl ₄ /acetone (9:1)	60 min	89	27:73																																																																																																																									
CO ₂ Et	CCl ₄ /acetone (95:5)	60 min	80	26:74																																																																																																																									
CO ₂ Et	MeOH/acetone (9:1)	60 min	84	41:59																																																																																																																									
NHCOPh	acetone	15 min	100	36:64																																																																																																																									
NHCOPh	CCl ₄ /acetone (9:1)	60 min	100	18:82																																																																																																																									
NHCOPh	CCl ₄ /acetone (95:5)	60 min	100	13:87																																																																																																																									
	DMD, solvent, rt	 I +  II	67																																																																																																																										

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)




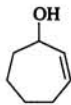
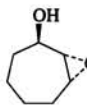
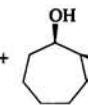
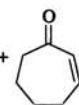




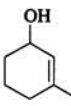
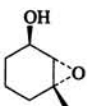
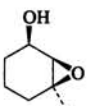
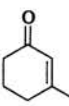







































Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomer Ratio (dr)	Refs.																																																		
C ₇ 	DMD, solvent, rt, 60 min	 I +  II	67																																																		
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>100</td> <td>48:52</td> </tr> <tr> <td>CH₂Cl₂/acetone (9:1)</td> <td>100</td> <td>53:47</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>100</td> <td>47:53</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	acetone	100	48:52	CH ₂ Cl ₂ /acetone (9:1)	100	53:47	CCl ₄ /acetone (9:1)	100	47:53																																							
Solvent	% Convn	I:II																																																			
acetone	100	48:52																																																			
CH ₂ Cl ₂ /acetone (9:1)	100	53:47																																																			
CCl ₄ /acetone (9:1)	100	47:53																																																			
	DMD, acetone, rt, 2 h	 I +  II +  III	83																																																		
		I:II = 67:33; (I + II):III = 62:38; I + II + III (—)																																																			
	DMD, acetone, 20°, 2 h	 I +  II +  III	75																																																		
		I:II = 75:25; (I + II):III = 81:19; I + II + III (92)																																																			
	DMD, acetone/CH ₂ Cl ₂ , rt, 3 h	 I +  II +  III	133																																																		
		I + II (88); III (10); I:II = 30:70; I + II + III (—)																																																			
	DMD, solvent, rt, 60 min	<table border="1"> <thead> <tr> <th>I + II + III</th> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> <th>(I+II):III</th> </tr> </thead> <tbody> <tr> <td></td> <td>acetone</td> <td>95</td> <td>65:35</td> <td>65:35</td> </tr> <tr> <td></td> <td>CH₂Cl₂/acetone (4:1)</td> <td>93</td> <td>39:61</td> <td>85:15</td> </tr> <tr> <td></td> <td>CH₂Cl₂/acetone (9:1)</td> <td>96</td> <td>35:65</td> <td>89:11</td> </tr> <tr> <td></td> <td>CH₂Cl₂/acetone (95:5)</td> <td>81</td> <td>13:87</td> <td>94:6</td> </tr> <tr> <td></td> <td>CH₂Cl₂/acetone (9:1)</td> <td>69</td> <td>82:18</td> <td>86:14</td> </tr> <tr> <td></td> <td><i>t</i>-BuOH/acetone (9:1)</td> <td>85</td> <td>73:27</td> <td>88:12</td> </tr> <tr> <td></td> <td>AcOH/acetone (9:1)</td> <td>100</td> <td>74:26</td> <td>89:11</td> </tr> <tr> <td></td> <td>CHCl₃/acetone (9:1)</td> <td>91</td> <td>17:83</td> <td>93:7</td> </tr> <tr> <td></td> <td>CCl₄/acetone (9:1)</td> <td>89</td> <td>21:79</td> <td>76:24</td> </tr> </tbody> </table>	I + II + III	Solvent	% Convn	I:II	(I+II):III		acetone	95	65:35	65:35		CH ₂ Cl ₂ /acetone (4:1)	93	39:61	85:15		CH ₂ Cl ₂ /acetone (9:1)	96	35:65	89:11		CH ₂ Cl ₂ /acetone (95:5)	81	13:87	94:6		CH ₂ Cl ₂ /acetone (9:1)	69	82:18	86:14		<i>t</i> -BuOH/acetone (9:1)	85	73:27	88:12		AcOH/acetone (9:1)	100	74:26	89:11		CHCl ₃ /acetone (9:1)	91	17:83	93:7		CCl ₄ /acetone (9:1)	89	21:79	76:24	67
I + II + III	Solvent	% Convn	I:II	(I+II):III																																																	
	acetone	95	65:35	65:35																																																	
	CH ₂ Cl ₂ /acetone (4:1)	93	39:61	85:15																																																	
	CH ₂ Cl ₂ /acetone (9:1)	96	35:65	89:11																																																	
	CH ₂ Cl ₂ /acetone (95:5)	81	13:87	94:6																																																	
	CH ₂ Cl ₂ /acetone (9:1)	69	82:18	86:14																																																	
	<i>t</i> -BuOH/acetone (9:1)	85	73:27	88:12																																																	
	AcOH/acetone (9:1)	100	74:26	89:11																																																	
	CHCl ₃ /acetone (9:1)	91	17:83	93:7																																																	
	CCl ₄ /acetone (9:1)	89	21:79	76:24																																																	
	Ketone, Oxone®, NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, rt	<table border="1"> <thead> <tr> <th>I + II</th> <th>Ketone</th> <th>I:II</th> <th>Ketone</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td></td> <td>MeCOMe</td> <td>1.4:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>EtCOEt</td> <td>—</td> <td></td> <td>3.7:1</td> </tr> <tr> <td></td> <td>ClCH₂COMe</td> <td>3.5:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>ClCH₂COCH₂Cl</td> <td>5.2:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>CF₃COMe</td> <td>9.1:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td></td> <td>2.0:1</td> <td></td> <td>4.4:1</td> </tr> <tr> <td></td> <td></td> <td>—</td> <td></td> <td>8.9:1</td> </tr> <tr> <td></td> <td></td> <td>3.9:1</td> <td></td> <td>2.9:1</td> </tr> <tr> <td></td> <td></td> <td>3.3:1</td> <td></td> <td>3.5:1</td> </tr> </tbody> </table>	I + II	Ketone	I:II	Ketone	I:II		MeCOMe	1.4:1				EtCOEt	—		3.7:1		ClCH ₂ COMe	3.5:1				ClCH ₂ COCH ₂ Cl	5.2:1				CF ₃ COMe	9.1:1					2.0:1		4.4:1			—		8.9:1			3.9:1		2.9:1			3.3:1		3.5:1	81
I + II	Ketone	I:II	Ketone	I:II																																																	
	MeCOMe	1.4:1																																																			
	EtCOEt	—		3.7:1																																																	
	ClCH ₂ COMe	3.5:1																																																			
	ClCH ₂ COCH ₂ Cl	5.2:1																																																			
	CF ₃ COMe	9.1:1																																																			
		2.0:1		4.4:1																																																	
		—		8.9:1																																																	
		3.9:1		2.9:1																																																	
		3.3:1		3.5:1																																																	

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

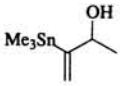
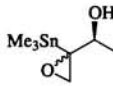
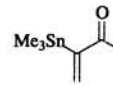

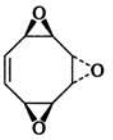

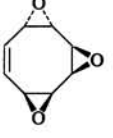

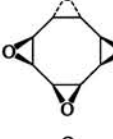

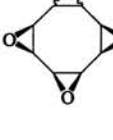

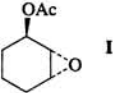
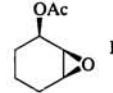
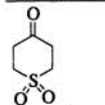
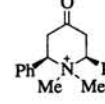
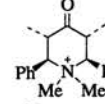
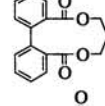
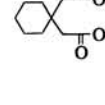




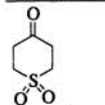
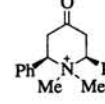
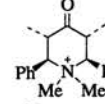
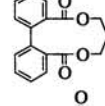
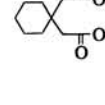




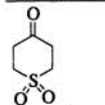
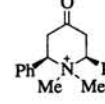
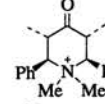
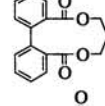
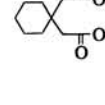




Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																								
	DMD, CH ₂ Cl ₂ /acetone, rt, 3.5 h	 (23), dr 80:20 +  (77)	74																																								
	DMD, acetone, -20°	 (—)	299																																								
	DMD, acetone, -20°	 (100)	299																																								
	DMD, acetone, -20°	 (100)	299																																								
	DMD, acetone, -20°	 (—)	299																																								
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, rt	 I +  II	81																																								
		<table border="0"> <thead> <tr> <th>Ketone</th> <th>I:II</th> <th>Ketone</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>MeCOMe</td> <td>2.2:1</td> <td></td> <td>2.0:1</td> </tr> <tr> <td>EtCOEt</td> <td>2.7:1</td> <td></td> <td>1.5:1</td> </tr> <tr> <td>ClCH₂COMe</td> <td>2.2:1</td> <td></td> <td>2.4:1</td> </tr> <tr> <td>ClCH₂COCH₂Cl</td> <td>1.7:1</td> <td></td> <td>1.6:1</td> </tr> <tr> <td>CF₃COMe</td> <td>1.9:1</td> <td></td> <td>1.4:1</td> </tr> <tr> <td></td> <td>2.3:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>2.8:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>2.7:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>2.1:1</td> <td></td> <td></td> </tr> </tbody> </table>	Ketone	I:II	Ketone	I:II	MeCOMe	2.2:1		2.0:1	EtCOEt	2.7:1		1.5:1	ClCH ₂ COMe	2.2:1		2.4:1	ClCH ₂ COCH ₂ Cl	1.7:1		1.6:1	CF ₃ COMe	1.9:1		1.4:1		2.3:1				2.8:1				2.7:1				2.1:1			
Ketone	I:II	Ketone	I:II																																								
MeCOMe	2.2:1		2.0:1																																								
EtCOEt	2.7:1		1.5:1																																								
ClCH ₂ COMe	2.2:1		2.4:1																																								
ClCH ₂ COCH ₂ Cl	1.7:1		1.6:1																																								
CF ₃ COMe	1.9:1		1.4:1																																								
	2.3:1																																										
	2.8:1																																										
	2.7:1																																										
	2.1:1																																										

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)











Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.												
	DMD, acetone, 20°, 4 h	I + II (>98) I:II = 72:28	75												
	DMD, acetone/CH ₂ Cl ₂ , rt, 2 h	I + II (95) I:II = 65:35	157												
	DMD, solvent, rt, 60 min	I + II													
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>86</td> <td>66:34</td> </tr> <tr> <td>CH₂Cl₂/acetone (1:1)</td> <td>84</td> <td>64:36</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>25</td> <td>65:35</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	acetone	86	66:34	CH ₂ Cl ₂ /acetone (1:1)	84	64:36	CCl ₄ /acetone (9:1)	25	65:35	300, 67
Solvent	% Convn	I:II													
acetone	86	66:34													
CH ₂ Cl ₂ /acetone (1:1)	84	64:36													
CCl ₄ /acetone (9:1)	25	65:35													
	DMD, acetone/CH ₂ Cl ₂ , Ar, 0 to 5°, 14 h	 (—)	187												
	DMD (2.5 equiv), acetone/CH ₂ Cl ₂ , Ar, 0 to 5°, 13 h	 (54) dr 72:28	187												
	DMD, solvent, rt, 60 min	 I +  II	67, 300												
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>97</td> <td>55:45</td> </tr> <tr> <td>CH₂Cl₂/acetone (1:1)</td> <td>95</td> <td>58:42</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>56</td> <td>68:32</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	acetone	97	55:45	CH ₂ Cl ₂ /acetone (1:1)	95	58:42	CCl ₄ /acetone (9:1)	56	68:32	
	Solvent	% Convn	I:II												
acetone	97	55:45													
CH ₂ Cl ₂ /acetone (1:1)	95	58:42													
CCl ₄ /acetone (9:1)	56	68:32													
	DMD, acetone, 20°, 4 h	 I +  II (95) I:II = 72:28	133												
	Methyl(isopropyl)dioxirane, 3-methyl-2-butanone, 20°, 4 h	I + II (24) I:II = 70:30	75												
	Diethyldioxirane, 3-pentanone, 20°, 4 h	I + II (95) I:II = 72:28	75												
	Cyclohexanone dioxirane, cyclohexanone, 20°, 4 h	I + II (85) I:II = 80:20	75												
	DMD, solvent, rt, 60 min	I + II (—)	<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>100</td> <td>73:27</td> </tr> <tr> <td>CH₂Cl₂/acetone (7:3)</td> <td>100</td> <td>77:23</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	acetone	100	73:27	CH ₂ Cl ₂ /acetone (7:3)	100	77:23	67		
Solvent	% Convn	I:II													
acetone	100	73:27													
CH ₂ Cl ₂ /acetone (7:3)	100	77:23													

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																					
Ketone, Oxone [®] , CH ₂ Cl ₂ / MeOH, buffer (pH 11.0), KOH, 18-crown-6, 0 to 5°	I + II (—)	<table border="1"> <thead> <tr> <th>Ketone</th> <th>Time</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>3.0 h (56)</td> <td>86:14</td> </tr> <tr> <td>cyclohexanone</td> <td>3.5 h (80)</td> <td>91:9</td> </tr> <tr> <td>2,6-dimethylcyclohexanone</td> <td>3.5 h (83)</td> <td>88:12</td> </tr> <tr> <td>2-phenylcyclohexanone</td> <td>4.0 h (68)</td> <td>93:7</td> </tr> <tr> <td>2-chlorocyclohexanone</td> <td>3.0 h (100)</td> <td>96:4</td> </tr> <tr> <td>camphor</td> <td>18.5 h (70)</td> <td>77:23</td> </tr> </tbody> </table>	Ketone	Time	I:II	acetone	3.0 h (56)	86:14	cyclohexanone	3.5 h (80)	91:9	2,6-dimethylcyclohexanone	3.5 h (83)	88:12	2-phenylcyclohexanone	4.0 h (68)	93:7	2-chlorocyclohexanone	3.0 h (100)	96:4	camphor	18.5 h (70)	77:23	297
			Ketone	Time	I:II																			
			acetone	3.0 h (56)	86:14																			
			cyclohexanone	3.5 h (80)	91:9																			
			2,6-dimethylcyclohexanone	3.5 h (83)	88:12																			
			2-phenylcyclohexanone	4.0 h (68)	93:7																			
			2-chlorocyclohexanone	3.0 h (100)	96:4																			
			camphor	18.5 h (70)	77:23																			
Ketone, oxygen donor, CH ₃ CN/phosphate buffer (pH 7.4)	I + II (—)	<table border="1"> <thead> <tr> <th>Ketone</th> <th>Oxidant</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>MeCOCO₂Me</td> <td>Oxone[®]</td> <td>42</td> <td>46:1</td> </tr> <tr> <td>MeCOCOMe</td> <td>Oxone[®]</td> <td>15</td> <td>100:0</td> </tr> <tr> <td>MeCOCO₂Me</td> <td>NaNO₃</td> <td>16</td> <td>4.8:1</td> </tr> <tr> <td>MeCOCOMe</td> <td>NaNO₃</td> <td>23</td> <td>100:0</td> </tr> </tbody> </table>	Ketone	Oxidant	% Convn	I:II	MeCOCO ₂ Me	Oxone [®]	42	46:1	MeCOCOMe	Oxone [®]	15	100:0	MeCOCO ₂ Me	NaNO ₃	16	4.8:1	MeCOCOMe	NaNO ₃	23	100:0	301	
			Ketone	Oxidant	% Convn	I:II																		
			MeCOCO ₂ Me	Oxone [®]	42	46:1																		
			MeCOCOMe	Oxone [®]	15	100:0																		
			MeCOCO ₂ Me	NaNO ₃	16	4.8:1																		
MeCOCOMe	NaNO ₃	23	100:0																					
DMD, acetone, 20°, 4 h	I + II (>95)	I:II = 72:28	75																					
Oxone [®] , acetone, NaHCO ₃ , MeOH/H ₂ O, 20°, 4 h	I + II (73)	I:II = 74:26	75																					
Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/ H ₂ O, Na ₂ EDTA, rt	I + II (—)		81																					

Ketone	I:II	Ketone	I:II
MeCOMe	3.7:1		4.7:1
EtCOEt	—		3.8:1
ClCH ₂ COMe	4.7:1		18.7:1
ClCH ₂ COCH ₂ Cl	5.4:1		4.7:1
CF ₃ COMe	8.4:1		6.3:1
	4.4:1		
	—		
	5.4:1		
	4.4:1		

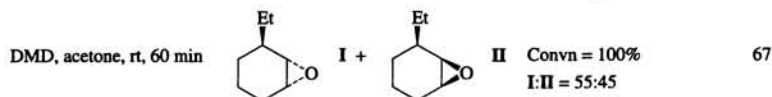


TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

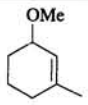
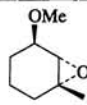
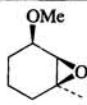
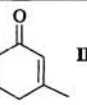
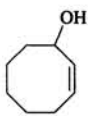
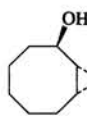
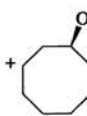
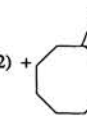
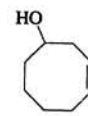
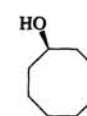
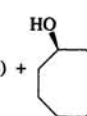
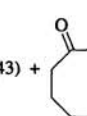
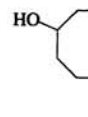
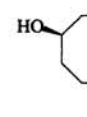
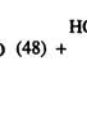
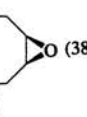
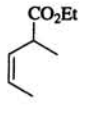
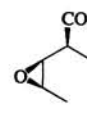
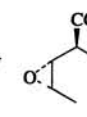
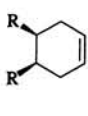
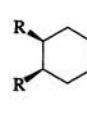
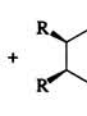
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																				
	DMD, solvent, rt, 60 min	 I +  II +  III	67																				
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> <th>(I+II):III</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>100</td> <td>95:5</td> <td>87:13</td> </tr> <tr> <td>CH₂Cl₂/acetone (4:1)</td> <td>75</td> <td>95:5</td> <td>92:8</td> </tr> <tr> <td>CH₂Cl₂/acetone (95:5)</td> <td>92</td> <td>95:5</td> <td>91:9</td> </tr> <tr> <td>CCl₄/acetone (95:5)</td> <td>86</td> <td>5:95</td> <td>80:20</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	(I+II):III	acetone	100	95:5	87:13	CH ₂ Cl ₂ /acetone (4:1)	75	95:5	92:8	CH ₂ Cl ₂ /acetone (95:5)	92	95:5	91:9	CCl ₄ /acetone (95:5)	86	5:95	80:20	
Solvent	% Convn	I:II	(I+II):III																				
acetone	100	95:5	87:13																				
CH ₂ Cl ₂ /acetone (4:1)	75	95:5	92:8																				
CH ₂ Cl ₂ /acetone (95:5)	92	95:5	91:9																				
CCl ₄ /acetone (95:5)	86	5:95	80:20																				
	DMD (0.9 equiv), acetone/ CH ₂ Cl ₂ , 20°, 0.2 h	 I (90) +  II (<2) +  III (<2) I:II = >98:<2	14																				
	DMD (2.2 equiv), acetone/ CH ₂ Cl ₂ , 20°, 168 h	I (58) + II (<3) + III (39) I:II = >95:<5	14																				
	Oxone [®] , acetone/CH ₂ Cl ₂ , phosphate buffer (pH 7.5), 18-crown-6, 6 to 8°, 4 h	I + II (91) I:II = 99:1	302																				
	DMD (0.9 equiv), acetone/ CH ₂ Cl ₂ , 20°, 0.2 h	 I (38) +  II (43) +  III (6) I:II = 47:53	14																				
	DMD (0.9 equiv), acetone/ CH ₂ Cl ₂ , 20°, 0.2 h	 I (48) +  II (38) +  III (3) I:II = 56:44	14																				
	DMD, acetone, 2 h	 I +  II (>95) I:II = 51:49	298																				
	TFP, Oxone [®] , MeCN/H ₂ O, Na ₂ EDTA, 0°, 2 to 3 h	 I +  II (—) <table border="1"> <thead> <tr> <th>R</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>MeO</td> <td>94:6</td> </tr> <tr> <td>MeO₂C</td> <td>72:28</td> </tr> <tr> <td>AcOCH₂</td> <td>90:10</td> </tr> <tr> <td>Et₃SiO</td> <td>98:2</td> </tr> <tr> <td>TBDMSO</td> <td>98:2</td> </tr> <tr> <td>PhCO₂</td> <td>81:19</td> </tr> <tr> <td>PhCO₂CH₂</td> <td>81:19</td> </tr> </tbody> </table>	R	I:II	MeO	94:6	MeO ₂ C	72:28	AcOCH ₂	90:10	Et ₃ SiO	98:2	TBDMSO	98:2	PhCO ₂	81:19	PhCO ₂ CH ₂	81:19	303				
R	I:II																						
MeO	94:6																						
MeO ₂ C	72:28																						
AcOCH ₂	90:10																						
Et ₃ SiO	98:2																						
TBDMSO	98:2																						
PhCO ₂	81:19																						
PhCO ₂ CH ₂	81:19																						

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

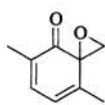
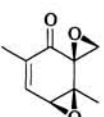
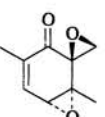
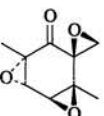
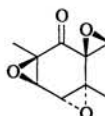
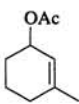
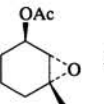
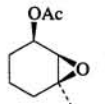



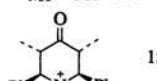
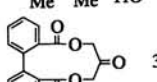
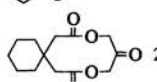






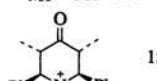
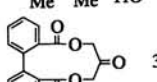
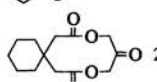






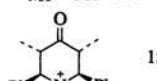
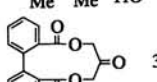
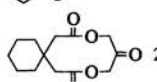




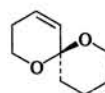
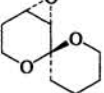
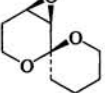
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																								
	TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, (pH 7-7.5), 0 to 1°, 15 min	 I (—) +  II (—) I:II = 67:33	304																																								
	TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, (pH 7-7.5), 0 to 1°, 9 h	 I (60) +  II (30) I:II = 67:33	304																																								
	DMD, acetone/CH ₂ Cl ₂ , rt, 1.5 h	 I +  II (90) I:II = 90:10	133																																								
	DMD, solvent, rt, 60 min	I + II (—) <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>94</td> <td>87:13</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>63</td> <td>88:12</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	acetone	94	87:13	CCl ₄ /acetone (9:1)	63	88:12	67																															
Solvent	% Convn	I:II																																									
acetone	94	87:13																																									
CCl ₄ /acetone (9:1)	63	88:12																																									
	Ketone, Oxone [®] , CH ₃ CN/ H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt	I + II (—)	81																																								
		<table border="1" style="width: 100%;"> <thead> <tr> <th>Ketone</th> <th>I:II</th> <th>Ketone</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>MeCOMe</td> <td>5.9:1</td> <td></td> <td>4.7:1</td> </tr> <tr> <td>EtCOEt</td> <td>8.5:1</td> <td></td> <td>3.4:1</td> </tr> <tr> <td>ClCH₂COMe</td> <td>4.8:1</td> <td></td> <td>15.1:1</td> </tr> <tr> <td>ClCH₂COCH₂Cl</td> <td>3.5:1</td> <td></td> <td>3.0:1</td> </tr> <tr> <td>CF₃COMe</td> <td>6.1:1</td> <td></td> <td>2.9:1</td> </tr> <tr> <td></td> <td>6.6:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>7.8:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>7.7:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>5.0:1</td> <td></td> <td></td> </tr> </tbody> </table>	Ketone	I:II	Ketone	I:II	MeCOMe	5.9:1		4.7:1	EtCOEt	8.5:1		3.4:1	ClCH ₂ COMe	4.8:1		15.1:1	ClCH ₂ COCH ₂ Cl	3.5:1		3.0:1	CF ₃ COMe	6.1:1		2.9:1		6.6:1				7.8:1				7.7:1				5.0:1			
		Ketone	I:II	Ketone	I:II																																						
		MeCOMe	5.9:1		4.7:1																																						
		EtCOEt	8.5:1		3.4:1																																						
		ClCH ₂ COMe	4.8:1		15.1:1																																						
		ClCH ₂ COCH ₂ Cl	3.5:1		3.0:1																																						
		CF ₃ COMe	6.1:1		2.9:1																																						
			6.6:1																																								
			7.8:1																																								
	7.7:1																																										
	5.0:1																																										
	DMD, acetone, rt, 16 h	 (76) +  (12)	305																																								

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

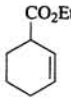
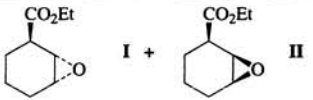
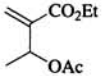
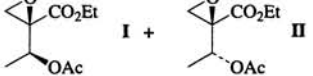
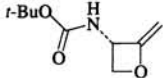
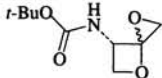
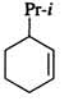
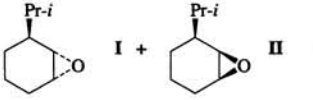
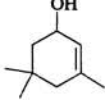
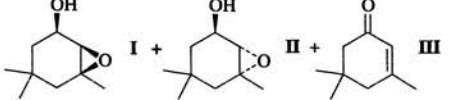
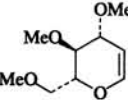
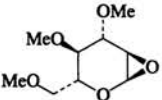
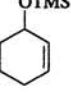
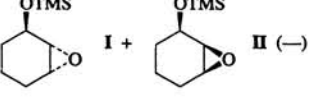
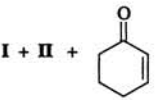
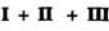
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																				
	DMD, solvent, rt, 60 min	 <table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>82</td> <td>66:34</td> </tr> <tr> <td>CH₂Cl₂/acetone (9:1)</td> <td>41</td> <td>62:38</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>22</td> <td>62:38</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	acetone	82	66:34	CH ₂ Cl ₂ /acetone (9:1)	41	62:38	CCl ₄ /acetone (9:1)	22	62:38	67								
Solvent	% Convn	I:II																					
acetone	82	66:34																					
CH ₂ Cl ₂ /acetone (9:1)	41	62:38																					
CCl ₄ /acetone (9:1)	22	62:38																					
	DMD, acetone, 20°, 3 d	 (98) I:II = 35:65	237																				
	DMD, CHCl ₃ /acetone	 (100) dr = 86:14	203																				
	DMD, acetone, rt, 2 h	 (59) I:II = 78:22	83																				
	DMD, solvent, ca. 20°	 <table border="1"> <thead> <tr> <th>Solvent</th> <th>Time</th> <th>% Convn</th> <th>I:II</th> <th>(I+II):III</th> </tr> </thead> <tbody> <tr> <td>MeOH/acetone (9:1)</td> <td>1.5 h</td> <td>66</td> <td>62:38</td> <td>92:8</td> </tr> <tr> <td>acetone</td> <td>0.5 h</td> <td>>95</td> <td>83:17</td> <td>77:23</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>12 h</td> <td>>95</td> <td>96:4</td> <td>92:8</td> </tr> </tbody> </table>	Solvent	Time	% Convn	I:II	(I+II):III	MeOH/acetone (9:1)	1.5 h	66	62:38	92:8	acetone	0.5 h	>95	83:17	77:23	CCl ₄ /acetone (9:1)	12 h	>95	96:4	92:8	87
Solvent	Time	% Convn	I:II	(I+II):III																			
MeOH/acetone (9:1)	1.5 h	66	62:38	92:8																			
acetone	0.5 h	>95	83:17	77:23																			
CCl ₄ /acetone (9:1)	12 h	>95	96:4	92:8																			
	DMD, acetone/CH ₂ Cl ₂ , 5°, 90 min	 (88)	306																				
	DMD, acetone, 20°, 2 to 8 h	 I + II (→) I:II = 88:12	75																				
	DMD, acetone, 20°, 12 h	 I + II + III (87) I:II = 88:12 (I + II):III = 90:10	157																				
	DMD, solvent, rt, 60 min	 I + II + III	67, 296																				
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> <th>(I+II):III</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>100</td> <td>87:13</td> <td>95:5</td> </tr> <tr> <td>CH₂Cl₂/acetone (1:1)</td> <td>95</td> <td>89:11</td> <td>94:6</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>60</td> <td>99:1</td> <td>90:10</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	(I+II):III	acetone	100	87:13	95:5	CH ₂ Cl ₂ /acetone (1:1)	95	89:11	94:6	CCl ₄ /acetone (9:1)	60	99:1	90:10					
Solvent	% Convn	I:II	(I+II):III																				
acetone	100	87:13	95:5																				
CH ₂ Cl ₂ /acetone (1:1)	95	89:11	94:6																				
CCl ₄ /acetone (9:1)	60	99:1	90:10																				

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																								
C ₉₋₁₈ 	DMD, THF/acetone, -78°	 <table border="1"> <thead> <tr> <th>n</th> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>H</td> <td>Me</td> <td>(92)</td> <td>—</td> </tr> <tr> <td>1</td> <td>H</td> <td>CH₂=CH</td> <td>(90)</td> <td>—</td> </tr> <tr> <td>1</td> <td>Me</td> <td>Me</td> <td>(79)</td> <td>—</td> </tr> <tr> <td>1</td> <td>Me</td> <td>CH₂=CH</td> <td>(87)</td> <td>100:0</td> </tr> <tr> <td>1</td> <td>Me</td> <td>Ph</td> <td>(—)</td> <td>67:33</td> </tr> <tr> <td>1</td> <td>H</td> <td>Bn</td> <td>(92)</td> <td>—</td> </tr> <tr> <td>2</td> <td>Me</td> <td>Bn</td> <td>(75)</td> <td>100:0</td> </tr> </tbody> </table>	n	R ¹	R ²	Yield (%)	I:II	1	H	Me	(92)	—	1	H	CH ₂ =CH	(90)	—	1	Me	Me	(79)	—	1	Me	CH ₂ =CH	(87)	100:0	1	Me	Ph	(—)	67:33	1	H	Bn	(92)	—	2	Me	Bn	(75)	100:0	307
n	R ¹	R ²	Yield (%)	I:II																																							
1	H	Me	(92)	—																																							
1	H	CH ₂ =CH	(90)	—																																							
1	Me	Me	(79)	—																																							
1	Me	CH ₂ =CH	(87)	100:0																																							
1	Me	Ph	(—)	67:33																																							
1	H	Bn	(92)	—																																							
2	Me	Bn	(75)	100:0																																							
C ₁₀ 	DMD, acetone, Ar, rt	(91)	308																																								
	DMD, acetone, 25°, 3 h	(36) + (49)	309																																								
C ₁₀₋₁₃ 	DMD, CHCl ₃ /acetone	 <table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(99)</td> <td>93:7</td> </tr> <tr> <td>Me</td> <td>(100)</td> <td>86:14</td> </tr> <tr> <td>CH₂=CHCH₂</td> <td>(97)</td> <td>75:25</td> </tr> </tbody> </table>	R	Yield (%)	dr	H	(99)	93:7	Me	(100)	86:14	CH ₂ =CHCH ₂	(97)	75:25	203																												
R	Yield (%)	dr																																									
H	(99)	93:7																																									
Me	(100)	86:14																																									
CH ₂ =CHCH ₂	(97)	75:25																																									
C ₁₀ 	DMD, acetone/CH ₂ Cl ₂ , Ar, 0°, 5 h	(35) + (40)	187																																								
	DMD (2.5 equiv), acetone/CH ₂ Cl ₂ , Ar, 0°, 5 h	(-100)	187																																								
	DMD, acetone/CH ₂ Cl ₂ , Ar, 0 to 5°, 14 h	(45)	187																																								
	DMD (2.5 equiv), acetone/CH ₂ Cl ₂ , Ar, 0 to 5°, 14 h	I (51)	187																																								
	DMD, acetone/CH ₂ Cl ₂ , Ar, 0°, 3 h	I (~100)	187																																								
	DMD, acetone, rt, 15 h (95% convn)	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I:(II+III)</th> <th>II: III</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>65:35</td> <td>45:55</td> </tr> <tr> <td>Me</td> <td>H</td> <td><5:>95</td> <td>80:20</td> </tr> </tbody> </table>	R ¹	R ²	I:(II+III)	II: III	H	Me	65:35	45:55	Me	H	<5:>95	80:20	310																												
R ¹	R ²	I:(II+III)	II: III																																								
H	Me	65:35	45:55																																								
Me	H	<5:>95	80:20																																								

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

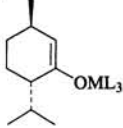
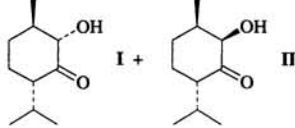
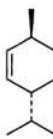
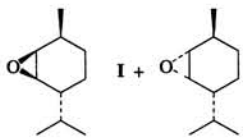

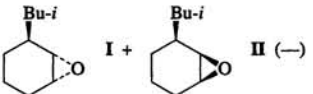

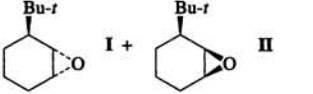
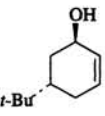
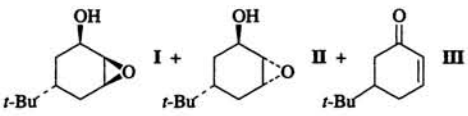
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																				
C ₁₀₋₂₀ 	1. DMD, THF/acetone, -78°, 1 min 2. NH ₄ F/H ₂ O, rt, 1 to 12 h	 <table border="1"> <thead> <tr> <th>M</th> <th>L₃</th> <th></th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Na</td> <td>—</td> <td>(63)</td> <td>67:33</td> </tr> <tr> <td>Si</td> <td>Me₃</td> <td>(97)</td> <td>76:24</td> </tr> <tr> <td>Ti</td> <td>Cp₂Cl</td> <td>(54)</td> <td>96:04</td> </tr> </tbody> </table>	M	L ₃		I:II	Na	—	(63)	67:33	Si	Me ₃	(97)	76:24	Ti	Cp ₂ Cl	(54)	96:04	97				
M	L ₃		I:II																				
Na	—	(63)	67:33																				
Si	Me ₃	(97)	76:24																				
Ti	Cp ₂ Cl	(54)	96:04																				
C ₁₀ 	DMD, acetone, 20°, 4 h DMD, acetone, -78°, 4 h Methyl(isopropyl)dioxirane, 3-methylbutanone, 20°, 24 h Diethyldioxirane, 3-pentanone, 20°, 24 h Cyclohexanone dioxirane, cyclohexanone, 20°, 24 h	 I + II (>95) I:II = 78:22 I + II (>95) I:II = 84:16 I + II (19) I:II = 81:19 I + II (58) I:II = 82:18 I + II (14) I:II = 80:20	75 75 75 75 75																				
	DMD, solvent, rt	 <table border="1"> <thead> <tr> <th>Solvent</th> <th>Time</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>60 min</td> <td>100</td> <td>55:45</td> </tr> <tr> <td>CH₂Cl₂/acetone (9:1)</td> <td>60 min</td> <td>100</td> <td>60:40</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>120 min</td> <td>100</td> <td>54:46</td> </tr> </tbody> </table>	Solvent	Time	% Convn	I:II	acetone	60 min	100	55:45	CH ₂ Cl ₂ /acetone (9:1)	60 min	100	60:40	CCl ₄ /acetone (9:1)	120 min	100	54:46	67				
Solvent	Time	% Convn	I:II																				
acetone	60 min	100	55:45																				
CH ₂ Cl ₂ /acetone (9:1)	60 min	100	60:40																				
CCl ₄ /acetone (9:1)	120 min	100	54:46																				
	DMD, solvent, rt, 60 min	 <table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>94</td> <td>95:5</td> </tr> <tr> <td>CH₂Cl₂/acetone (1:1)</td> <td>96</td> <td>96:4</td> </tr> </tbody> </table>	Solvent	% Convn	I:II	acetone	94	95:5	CH ₂ Cl ₂ /acetone (1:1)	96	96:4	67											
Solvent	% Convn	I:II																					
acetone	94	95:5																					
CH ₂ Cl ₂ /acetone (1:1)	96	96:4																					
	DMD, solvent, -20°	 <table border="1"> <thead> <tr> <th>Solvent</th> <th>Time</th> <th>% Convn</th> <th>I:II</th> <th>(I+II):III</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>10 h</td> <td>>95</td> <td>30:70</td> <td>58:42</td> </tr> <tr> <td>MeOH/acetone (9:1)</td> <td>2 h</td> <td>92</td> <td>29:71</td> <td>85:15</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>8 h</td> <td>>95</td> <td>58:42</td> <td>67:33</td> </tr> </tbody> </table>	Solvent	Time	% Convn	I:II	(I+II):III	acetone	10 h	>95	30:70	58:42	MeOH/acetone (9:1)	2 h	92	29:71	85:15	CCl ₄ /acetone (9:1)	8 h	>95	58:42	67:33	87
Solvent	Time	% Convn	I:II	(I+II):III																			
acetone	10 h	>95	30:70	58:42																			
MeOH/acetone (9:1)	2 h	92	29:71	85:15																			
CCl ₄ /acetone (9:1)	8 h	>95	58:42	67:33																			

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

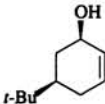
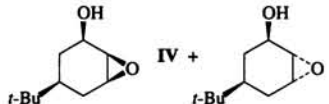
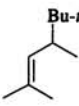
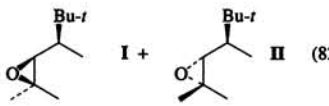

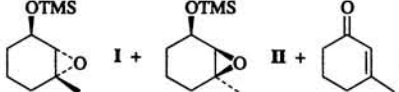
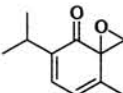
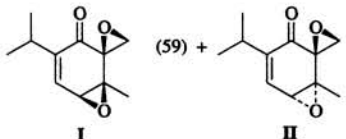
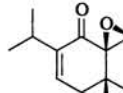
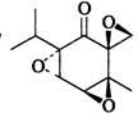
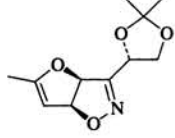
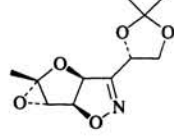
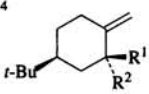
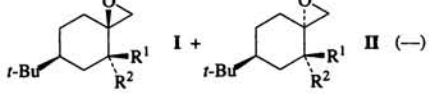
Substrate	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																	
	DMD, solvent, -20° 	87																																	
	<table border="1"> <thead> <tr> <th>Solvent</th> <th>Time</th> <th>% Convn</th> <th>IV:V (IV+V):III</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>4 h</td> <td>>95</td> <td>60:40 43:57</td> </tr> <tr> <td>MeOH/acetone (9:1)</td> <td>2 h</td> <td>60</td> <td>38:62 80:20</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>12 h</td> <td>>95</td> <td>82:18 57:43</td> </tr> </tbody> </table>	Solvent	Time	% Convn	IV:V (IV+V):III	acetone	4 h	>95	60:40 43:57	MeOH/acetone (9:1)	2 h	60	38:62 80:20	CCl ₄ /acetone (9:1)	12 h	>95	82:18 57:43																		
Solvent	Time	% Convn	IV:V (IV+V):III																																
acetone	4 h	>95	60:40 43:57																																
MeOH/acetone (9:1)	2 h	60	38:62 80:20																																
CCl ₄ /acetone (9:1)	12 h	>95	82:18 57:43																																
	DMD, acetone, 8 h 	298																																	
	DMD, solvent, rt, 60 min 	67																																	
	<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II (I+II):III</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>100</td> <td>95:5 97:3</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>86</td> <td>99:1 96:4</td> </tr> </tbody> </table>	Solvent	% Convn	I:II (I+II):III	acetone	100	95:5 97:3	CCl ₄ /acetone (9:1)	86	99:1 96:4																									
Solvent	% Convn	I:II (I+II):III																																	
acetone	100	95:5 97:3																																	
CCl ₄ /acetone (9:1)	86	99:1 96:4																																	
C ₁₁ 	TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/ H ₂ O, (pH 7-7.5), 0 to 1 $^{\circ}$, 20 min 	304																																	
	Isopropyl pyruvate, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O (pH 7-7.5), rt, 24 h 	304																																	
	DMD, acetone/CH ₂ Cl ₂ , 0 $^{\circ}$, 3 h 	313																																	
C ₁₁₋₁₄ 	DMD, acetone/CH ₂ Cl ₂ , 0 $^{\circ}$, 1 h 	82																																	
	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>31:69</td> </tr> <tr> <td>Me</td> <td>H</td> <td>23:77</td> </tr> <tr> <td>H</td> <td>Me</td> <td>55:45</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>17:83</td> </tr> <tr> <td>MeO</td> <td>Me</td> <td>31:69</td> </tr> <tr> <td>Me</td> <td>MeO</td> <td>62:38</td> </tr> <tr> <td>-(CH₂)₃O-</td> <td>-</td> <td>-</td> </tr> <tr> <td>-(CH₂)₃O-</td> <td>-</td> <td>-</td> </tr> <tr> <td>Me</td> <td>Et</td> <td>70:30</td> </tr> <tr> <td>Et</td> <td>Me</td> <td>29:71</td> </tr> </tbody> </table>	R ¹	R ²	I:II	H	H	31:69	Me	H	23:77	H	Me	55:45	Me	Me	17:83	MeO	Me	31:69	Me	MeO	62:38	-(CH ₂) ₃ O-	-	-	-(CH ₂) ₃ O-	-	-	Me	Et	70:30	Et	Me	29:71	
R ¹	R ²	I:II																																	
H	H	31:69																																	
Me	H	23:77																																	
H	Me	55:45																																	
Me	Me	17:83																																	
MeO	Me	31:69																																	
Me	MeO	62:38																																	
-(CH ₂) ₃ O-	-	-																																	
-(CH ₂) ₃ O-	-	-																																	
Me	Et	70:30																																	
Et	Me	29:71																																	

TABLE 4. DIASTERESELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

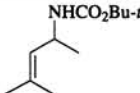


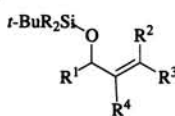




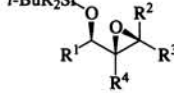
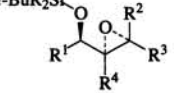



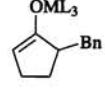


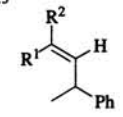
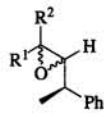
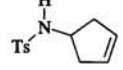
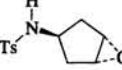
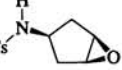
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																																																																																		
C ₁₁ 	DMD, acetone, 7 h	 I +  II (90) I:II = 62:38	298																																																																																																		
C ₁₁₋₂₂ 	Ketone, Oxone [®] , CH ₂ Cl ₂ /MeOH, buffer (pH 11), rt, 6 h  III  IV  V  VI	 I +  II <table border="1"> <thead> <tr> <th>R</th> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Ketone</th> <th>I:II</th> </tr> </thead> <tbody> <tr><td>Me</td><td>Me</td><td>H</td><td>Me</td><td>H</td><td>III (54)</td><td>43:57</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>Me</td><td>H</td><td>IV (84)</td><td>42:58</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>Me</td><td>H</td><td>V (50)</td><td>29:71</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>Me</td><td>H</td><td>VI (84)</td><td>22:78</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>Me</td><td>Me</td><td>V (24)</td><td>58:22</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>Me</td><td>Me</td><td>VI (13)</td><td>61:39</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>Me</td><td>H</td><td>IV (81)</td><td>32:68</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>Me</td><td>H</td><td>V (54)</td><td>30:70</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>Me</td><td>H</td><td>VI (99)</td><td>11:89</td></tr> <tr><td>Me</td><td>n-C₅H₁₁</td><td>H</td><td>H</td><td>H</td><td>V (21)</td><td>26:74</td></tr> <tr><td>Me</td><td>n-C₅H₁₁</td><td>H</td><td>H</td><td>H</td><td>VI (28)</td><td>25:75</td></tr> <tr><td>Ph</td><td>Me</td><td>Me</td><td>Me</td><td>H</td><td>V (28)</td><td>10:90</td></tr> <tr><td>Ph</td><td>Me</td><td>Me</td><td>Me</td><td>H</td><td>VI (94)</td><td>2:98</td></tr> </tbody> </table>	R	R ¹	R ²	R ³	R ⁴	Ketone	I:II	Me	Me	H	Me	H	III (54)	43:57	Me	Me	H	Me	H	IV (84)	42:58	Me	Me	H	Me	H	V (50)	29:71	Me	Me	H	Me	H	VI (84)	22:78	Me	Me	H	Me	Me	V (24)	58:22	Me	Me	H	Me	Me	VI (13)	61:39	Me	Me	Me	Me	H	IV (81)	32:68	Me	Me	Me	Me	H	V (54)	30:70	Me	Me	Me	Me	H	VI (99)	11:89	Me	n-C ₅ H ₁₁	H	H	H	V (21)	26:74	Me	n-C ₅ H ₁₁	H	H	H	VI (28)	25:75	Ph	Me	Me	Me	H	V (28)	10:90	Ph	Me	Me	Me	H	VI (94)	2:98	314
R	R ¹	R ²	R ³	R ⁴	Ketone	I:II																																																																																															
Me	Me	H	Me	H	III (54)	43:57																																																																																															
Me	Me	H	Me	H	IV (84)	42:58																																																																																															
Me	Me	H	Me	H	V (50)	29:71																																																																																															
Me	Me	H	Me	H	VI (84)	22:78																																																																																															
Me	Me	H	Me	Me	V (24)	58:22																																																																																															
Me	Me	H	Me	Me	VI (13)	61:39																																																																																															
Me	Me	Me	Me	H	IV (81)	32:68																																																																																															
Me	Me	Me	Me	H	V (54)	30:70																																																																																															
Me	Me	Me	Me	H	VI (99)	11:89																																																																																															
Me	n-C ₅ H ₁₁	H	H	H	V (21)	26:74																																																																																															
Me	n-C ₅ H ₁₁	H	H	H	VI (28)	25:75																																																																																															
Ph	Me	Me	Me	H	V (28)	10:90																																																																																															
Ph	Me	Me	Me	H	VI (94)	2:98																																																																																															
C ₁₂ 	DMD, solvent, rt, 60 min	 I +  II <table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr><td>acetone</td><td>100</td><td>82:18</td></tr> <tr><td>CCl₄/acetone (9:1)</td><td>70</td><td>85:15</td></tr> <tr><td>MeOH/acetone (1:1)</td><td>90</td><td>83:17</td></tr> </tbody> </table>	Solvent	% Convn	I:II	acetone	100	82:18	CCl ₄ /acetone (9:1)	70	85:15	MeOH/acetone (1:1)	90	83:17	67																																																																																						
Solvent	% Convn	I:II																																																																																																			
acetone	100	82:18																																																																																																			
CCl ₄ /acetone (9:1)	70	85:15																																																																																																			
MeOH/acetone (1:1)	90	83:17																																																																																																			
C ₁₂₋₂₂ 	1. DMD, THF/acetone, -78°, 1 min 2. NH ₄ F/H ₂ O, rt, 1 to 12 h	 I +  II <table border="1"> <thead> <tr> <th>M</th> <th>L₃</th> <th>I:II</th> </tr> </thead> <tbody> <tr><td>Na</td><td>—</td><td>(37) 53:47</td></tr> <tr><td>Si</td><td>Me₃</td><td>(96) 35:65</td></tr> <tr><td>Ti</td><td>Cp₂Cl</td><td>(50) 83:17</td></tr> </tbody> </table>	M	L ₃	I:II	Na	—	(37) 53:47	Si	Me ₃	(96) 35:65	Ti	Cp ₂ Cl	(50) 83:17	97																																																																																						
M	L ₃	I:II																																																																																																			
Na	—	(37) 53:47																																																																																																			
Si	Me ₃	(96) 35:65																																																																																																			
Ti	Cp ₂ Cl	(50) 83:17																																																																																																			
C ₁₂₋₁₃ 	DMD, acetone/CH ₂ Cl ₂ , -20°	 I <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time</th> <th>dr</th> </tr> </thead> <tbody> <tr><td>Me</td><td>CO₂H</td><td>20 h (96)</td><td>70:30</td></tr> <tr><td>Me</td><td>CO₂Me</td><td>16 h (98)</td><td>70:30</td></tr> <tr><td>CO₂Me</td><td>Me</td><td>20 h (99)</td><td>62:38</td></tr> </tbody> </table>	R ¹	R ²	Time	dr	Me	CO ₂ H	20 h (96)	70:30	Me	CO ₂ Me	16 h (98)	70:30	CO ₂ Me	Me	20 h (99)	62:38	53																																																																																		
R ¹	R ²	Time	dr																																																																																																		
Me	CO ₂ H	20 h (96)	70:30																																																																																																		
Me	CO ₂ Me	16 h (98)	70:30																																																																																																		
CO ₂ Me	Me	20 h (99)	62:38																																																																																																		
	TFP, Oxone [®] , MeCN/H ₂ O, Na ₂ EDTA, 0°, 2 to 3 h	 I +  II (—) I:II = 60:40	303																																																																																																		

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

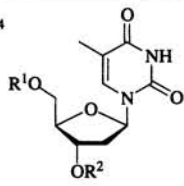
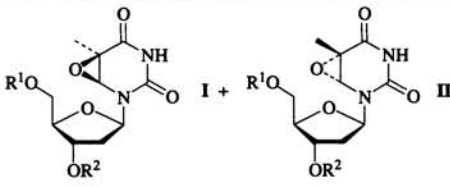
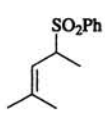
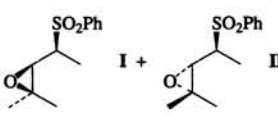
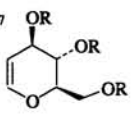
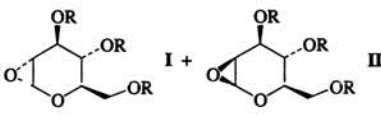
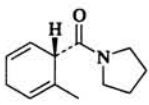
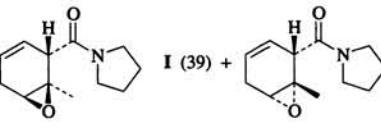



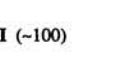
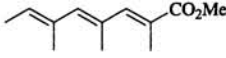
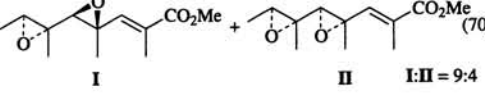
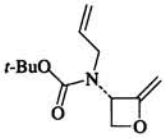
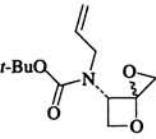
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																								
<p>C₁₂₋₁₄</p> 	DMD, catalyst, CH ₂ Cl ₂ , 25°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Catalyst</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Ac</td> <td>Mn(TDMPP)Cl^a</td> <td>(40)</td> <td>50:50</td> </tr> <tr> <td>H</td> <td>Ac</td> <td>Mn(Cl16TDMPP)Cl^b</td> <td>(57)</td> <td>90:10</td> </tr> <tr> <td>Ac</td> <td>H</td> <td>Mn(TDMPP)Cl^a</td> <td>(51)</td> <td>50:50</td> </tr> <tr> <td>Ac</td> <td>H</td> <td>Mn(Cl16TDMPP)Cl^b</td> <td>(55)</td> <td>17:83</td> </tr> <tr> <td>Ac</td> <td>H</td> <td>Mn(Cl8TDMPP)Cl^c</td> <td>(58)</td> <td>67:33</td> </tr> <tr> <td>Ac</td> <td>Ac</td> <td>Mn(TDMPP)Cl^a</td> <td>(53)</td> <td>50:50</td> </tr> <tr> <td>Ac</td> <td>Ac</td> <td>Mn(Cl16TDMPP)Cl^b</td> <td>(72)</td> <td>60:40</td> </tr> </tbody> </table>	R ¹	R ²	Catalyst	I	II	H	Ac	Mn(TDMPP)Cl ^a	(40)	50:50	H	Ac	Mn(Cl16TDMPP)Cl ^b	(57)	90:10	Ac	H	Mn(TDMPP)Cl ^a	(51)	50:50	Ac	H	Mn(Cl16TDMPP)Cl ^b	(55)	17:83	Ac	H	Mn(Cl8TDMPP)Cl ^c	(58)	67:33	Ac	Ac	Mn(TDMPP)Cl ^a	(53)	50:50	Ac	Ac	Mn(Cl16TDMPP)Cl ^b	(72)	60:40	315
R ¹	R ²	Catalyst	I	II																																							
H	Ac	Mn(TDMPP)Cl ^a	(40)	50:50																																							
H	Ac	Mn(Cl16TDMPP)Cl ^b	(57)	90:10																																							
Ac	H	Mn(TDMPP)Cl ^a	(51)	50:50																																							
Ac	H	Mn(Cl16TDMPP)Cl ^b	(55)	17:83																																							
Ac	H	Mn(Cl8TDMPP)Cl ^c	(58)	67:33																																							
Ac	Ac	Mn(TDMPP)Cl ^a	(53)	50:50																																							
Ac	Ac	Mn(Cl16TDMPP)Cl ^b	(72)	60:40																																							
<p>C₁₂</p> 	DMD, acetone, 8 h	 (87) I:II = >95:5	298																																								
<p>C₁₂₋₂₇</p> 	DMD, acetone/CH ₂ Cl ₂ , 0°, 1 h	 <table border="1"> <thead> <tr> <th>R</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Ac</td> <td>(—) mixture</td> </tr> <tr> <td>Bn</td> <td>(99) -95:5</td> </tr> <tr> <td>TBDMS</td> <td>(100) 100:0</td> </tr> </tbody> </table>	R	I:II	Ac	(—) mixture	Bn	(99) -95:5	TBDMS	(100) 100:0	91																																
R	I:II																																										
Ac	(—) mixture																																										
Bn	(99) -95:5																																										
TBDMS	(100) 100:0																																										
	Acetone, Oxone®, phosphate buffer (pH 7.2), 0°	 I (39) + II (27)	275																																								
	DMD (excess), acetone/CH ₂ Cl ₂ , Ar, 0° to rt, 5 h	 I (~100)	187																																								
	DMD, acetone/CH ₂ Cl ₂ , Ar, 0°, 3 h	 I (~100)	187																																								
	DMD, acetone, 25°, 18 h	 I II I:II = 9:4	86																																								
	DMD, CHCl ₃ /acetone	 (90) dr >95:<5	203																																								

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

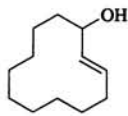
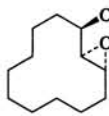
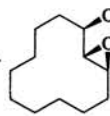
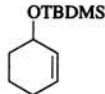
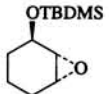
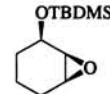
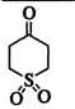

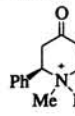
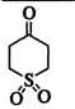

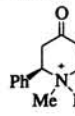
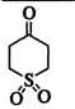

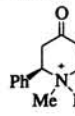

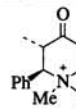

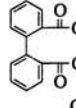

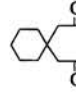

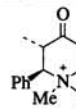

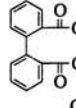

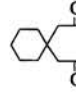

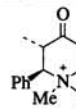

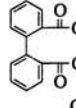

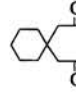
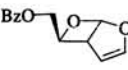
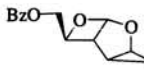
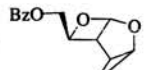
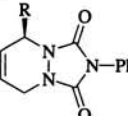
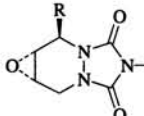
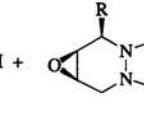
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																												
	Acetone, Oxone [®] , CH ₂ Cl ₂ , phosphate buffer (pH 7.5), 18-crown-6, 6 to 8 [°] , 4 h	 I +  II (86) I:II = 71:29	302																												
	Ketone, Oxone [®] , CH ₂ Cl ₂ /MeOH, buffer (pH 11.0), KOH, rt	 I +  II	297																												
		<table border="1"> <thead> <tr> <th>Ketone</th> <th>Time</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>3.5 h (40)</td> <td>87:13</td> </tr> <tr> <td>2-methylcyclohexanone</td> <td>1.5 h (77)</td> <td>90:10</td> </tr> <tr> <td>2,6-dimethylcyclohexanone</td> <td>3.0 h (65)</td> <td>93:7</td> </tr> </tbody> </table>	Ketone	Time	I:II	acetone	3.5 h (40)	87:13	2-methylcyclohexanone	1.5 h (77)	90:10	2,6-dimethylcyclohexanone	3.0 h (65)	93:7																	
Ketone	Time	I:II																													
acetone	3.5 h (40)	87:13																													
2-methylcyclohexanone	1.5 h (77)	90:10																													
2,6-dimethylcyclohexanone	3.0 h (65)	93:7																													
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, rt	I + II	81																												
		<table border="1"> <thead> <tr> <th>Ketone</th> <th>I:II</th> <th>Ketone</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>MeCOMe</td> <td>4.8:1</td> <td></td> <td>3.7:1</td> </tr> <tr> <td>EtCOEt</td> <td>6.3:1</td> <td></td> <td></td> </tr> <tr> <td>ClCH₂COMe</td> <td>4.2:1</td> <td></td> <td></td> </tr> <tr> <td>ClCH₂COCH₂Cl</td> <td>3.3:1</td> <td></td> <td></td> </tr> <tr> <td>CF₃COMe</td> <td>5.6:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>5.6:1</td> <td></td> <td>2.8:1</td> </tr> </tbody> </table>	Ketone	I:II	Ketone	I:II	MeCOMe	4.8:1		3.7:1	EtCOEt	6.3:1			ClCH ₂ COMe	4.2:1			ClCH ₂ COCH ₂ Cl	3.3:1			CF ₃ COMe	5.6:1				5.6:1		2.8:1	
Ketone	I:II	Ketone	I:II																												
MeCOMe	4.8:1		3.7:1																												
EtCOEt	6.3:1																														
ClCH ₂ COMe	4.2:1																														
ClCH ₂ COCH ₂ Cl	3.3:1																														
CF ₃ COMe	5.6:1																														
	5.6:1		2.8:1																												
		<table border="1"> <thead> <tr> <th>Ketone</th> <th>I:II</th> <th>Ketone</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td></td> <td>7.0:1</td> <td></td> <td>4.6:1</td> </tr> <tr> <td></td> <td>6.9:1</td> <td></td> <td>2.1:1</td> </tr> <tr> <td></td> <td>4.6:1</td> <td></td> <td>3.1:1</td> </tr> </tbody> </table>	Ketone	I:II	Ketone	I:II		7.0:1		4.6:1		6.9:1		2.1:1		4.6:1		3.1:1													
Ketone	I:II	Ketone	I:II																												
	7.0:1		4.6:1																												
	6.9:1		2.1:1																												
	4.6:1		3.1:1																												
C ₁₃ 	DMD, acetone	 I +  II (~100) I:II = 90:10	316																												
C ₁₃₋₁₅ 	DMD, acetone/solvent	 I +  II	317																												
		<table border="1"> <thead> <tr> <th>R</th> <th>Solvent</th> <th>Time</th> <th>Yield (%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>CH₂OH</td> <td>CHCl₃</td> <td>24 h</td> <td>(100)</td> <td>50:50</td> </tr> <tr> <td>CO₂Me</td> <td>CH₂Cl₂</td> <td>3 d</td> <td>(96)</td> <td>75:25</td> </tr> <tr> <td>CH₂OAc</td> <td>CH₂Cl₂</td> <td>3 d</td> <td>(85)</td> <td>50:50</td> </tr> </tbody> </table>	R	Solvent	Time	Yield (%)	I:II	CH ₂ OH	CHCl ₃	24 h	(100)	50:50	CO ₂ Me	CH ₂ Cl ₂	3 d	(96)	75:25	CH ₂ OAc	CH ₂ Cl ₂	3 d	(85)	50:50									
R	Solvent	Time	Yield (%)	I:II																											
CH ₂ OH	CHCl ₃	24 h	(100)	50:50																											
CO ₂ Me	CH ₂ Cl ₂	3 d	(96)	75:25																											
CH ₂ OAc	CH ₂ Cl ₂	3 d	(85)	50:50																											

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.															
	Ethylmethyldioxirane, butan-2-one, 24 h	R = CH ₂ OH, (66) I:II = 50:50	317															
	TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 20 h	R = CH ₂ OH, (79-100) I:II = 75:25	317															
	DMD, acetone, 56°	(58) dr 59:41	318															
	DMD, CHCl ₃ /acetone	(100) dr 33:33:17:17	203															
	DMD, solvent, rt, 60 min	I + II	67															
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>% Convn</th> <th>I : II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>100</td> <td>19:81</td> </tr> <tr> <td>CH₂Cl₂/acetone (9:1)</td> <td>100</td> <td>4:96</td> </tr> <tr> <td>CCl₄/acetone (9:1)</td> <td>100</td> <td>3:97</td> </tr> <tr> <td>MeOH/acetone (9:1)</td> <td>64</td> <td>26:74</td> </tr> </tbody> </table>	Solvent	% Convn	I : II	acetone	100	19:81	CH ₂ Cl ₂ /acetone (9:1)	100	4:96	CCl ₄ /acetone (9:1)	100	3:97	MeOH/acetone (9:1)	64	26:74	
Solvent	% Convn	I : II																
acetone	100	19:81																
CH ₂ Cl ₂ /acetone (9:1)	100	4:96																
CCl ₄ /acetone (9:1)	100	3:97																
MeOH/acetone (9:1)	64	26:74																
	TFP, Oxone [®] , MeCN/H ₂ O, Na ₂ EDTA, 0°, 2 to 3 h	I + II (—) I:II = 91:9	303															
C ₁₆₋₁₇ 	1. CH ₂ Cl ₂ /MgSO ₄ 2. DMD/acetone 3. rt, 12 h	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th></th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>Ac</td> <td>(47)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>PhCO</td> <td>(59)</td> </tr> </tbody> </table>	R ¹	R ²		Ph	Ac	(47)	<i>i</i> -Pr	PhCO	(59)	319						
R ¹	R ²																	
Ph	Ac	(47)																
<i>i</i> -Pr	PhCO	(59)																
C ₁₃ 	Acetone, Oxone [®] , phosphate buffer (pH 7.2), 0°	(76) + II (—) I:II = 87.5:12.5	84															
	Acetone, Oxone [®] , phosphate buffer (pH 7.2), 0°	(75)	84															
	DMD, acetone	I + II I:II = 60:40	86															
C ₁₃₋₁₉ 	DMD, acetone/CH ₂ Cl ₂ , 0°, 40 to 90 min	(—) R = Ph, <i>i</i> -Pr Ⓢ = solid support	93															

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

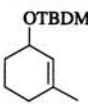
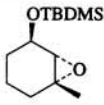
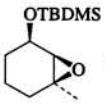



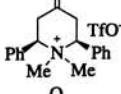

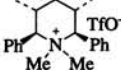

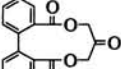

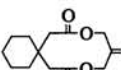



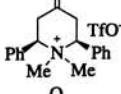

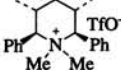

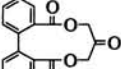

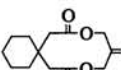



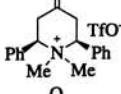

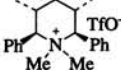

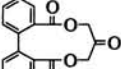

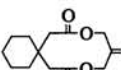
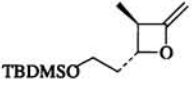

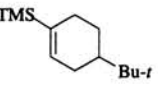
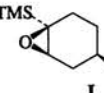
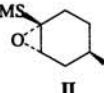
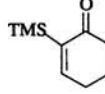
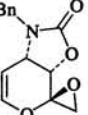
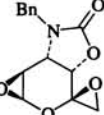
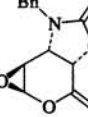
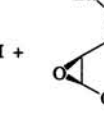
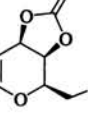
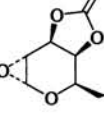
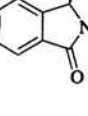
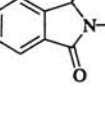
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																								
	Ketone, Oxone [®] , NaHCO ₃ , CH ₃ CN/ H ₂ O, Na ₂ EDTA, rt	OTBDMS  I +  II <table border="1"> <thead> <tr> <th>Ketone</th> <th>I:II</th> <th>Ketone</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>MeCOMe</td> <td>13.6:1</td> <td></td> <td></td> </tr> <tr> <td>EtCOEt</td> <td>14.1:1</td> <td></td> <td>6.3:1</td> </tr> <tr> <td>ClCH₂COMe</td> <td>7.4:1</td> <td></td> <td></td> </tr> <tr> <td>ClCH₂COCH₂Cl</td> <td>4.5:1</td> <td></td> <td></td> </tr> <tr> <td>CF₃COMe</td> <td>19.3:1</td> <td></td> <td></td> </tr> <tr> <td></td> <td>14.2:1</td> <td></td> <td>4.3:1</td> </tr> <tr> <td></td> <td>16.7:1</td> <td></td> <td>19.7:1</td> </tr> <tr> <td></td> <td>16.6:1</td> <td></td> <td>4.3:1</td> </tr> <tr> <td></td> <td>10.4:1</td> <td></td> <td>6.4:1</td> </tr> </tbody> </table>	Ketone	I:II	Ketone	I:II	MeCOMe	13.6:1			EtCOEt	14.1:1		6.3:1	ClCH ₂ COMe	7.4:1			ClCH ₂ COCH ₂ Cl	4.5:1			CF ₃ COMe	19.3:1				14.2:1		4.3:1		16.7:1		19.7:1		16.6:1		4.3:1		10.4:1		6.4:1	81
Ketone	I:II	Ketone	I:II																																								
MeCOMe	13.6:1																																										
EtCOEt	14.1:1		6.3:1																																								
ClCH ₂ COMe	7.4:1																																										
ClCH ₂ COCH ₂ Cl	4.5:1																																										
CF ₃ COMe	19.3:1																																										
	14.2:1		4.3:1																																								
	16.7:1		19.7:1																																								
	16.6:1		4.3:1																																								
	10.4:1		6.4:1																																								
	DMD, CHCl ₃ /acetone	 (93) dr 60:40	203																																								
	DMD, acetone, rt, 4 to 10 h	 (30) +  (50) +  (20) I:II = 38:62	74																																								
C ₁₄ 	DMD, CH ₂ Cl ₂ /acetone, rt	 I (—)	287																																								
	DMD, acetone/CH ₂ Cl ₂ , rt	 I + (—)	287																																								
	DMD, acetone/CH ₂ Cl ₂ , 0°, 1 h	 (—)	95																																								
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , rt, 4 h	 (—) dr 50:50	320																																								

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.												
	DMD, CH ₂ Cl ₂ , acetone, 0°, 80 min	(—)	94												
	DMD, acetone, Ar, rt, >16 h	(43)	308												
	DMD, acetone	I + II (50-60) I:II = 75:25	86												
	DMD, acetone, 25°, 18 h	I + II + other diastereomers (100) dr 45:33:11:11	86												
	DMD, acetone/CH ₂ Cl ₂ , 0°, 1 h	I + II (85) I:II = 40:60	82												
	1. DMD, THF/acetone, -78°, 1 min 2. NH ₄ F/H ₂ O, rt, 1 to 12 h	I + II	97												
		<table border="1"> <thead> <tr> <th>M</th> <th>L₃</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Na</td> <td>—</td> <td>(37) 90:10</td> </tr> <tr> <td>Si</td> <td>Me₃</td> <td>(85) >98:<2</td> </tr> <tr> <td>Ti</td> <td>Cp₂Cl</td> <td>(53) >98:<2</td> </tr> </tbody> </table>	M	L ₃	I:II	Na	—	(37) 90:10	Si	Me ₃	(85) >98:<2	Ti	Cp ₂ Cl	(53) >98:<2	
M	L ₃	I:II													
Na	—	(37) 90:10													
Si	Me ₃	(85) >98:<2													
Ti	Cp ₂ Cl	(53) >98:<2													
	DMD, acetone, 56°	(11) dr 50:50	318												
	DMD, acetone, 15 h	(88)	321												
	DMD, acetone, rt, 4 h	(63)	322												
	DMD, acetone, 45 min	(84)	323												

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

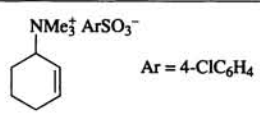
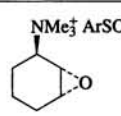
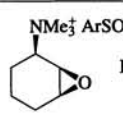
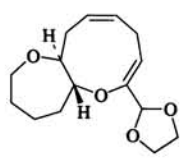
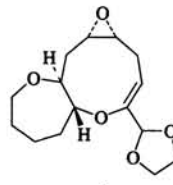
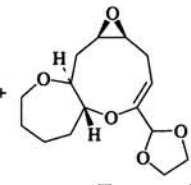
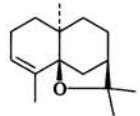
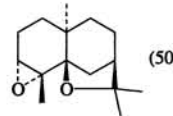
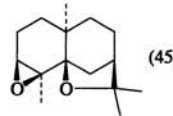
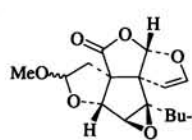
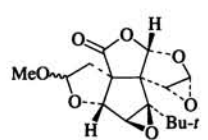
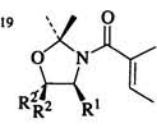
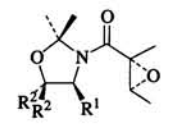
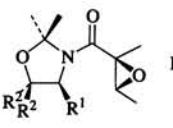
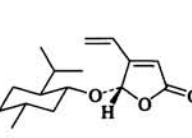
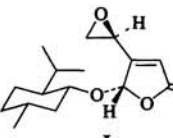
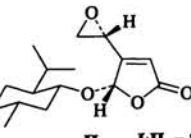
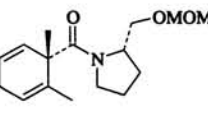
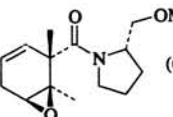
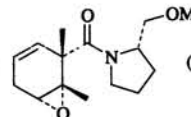
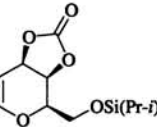
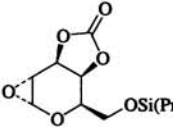
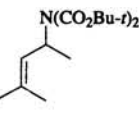
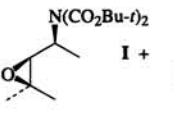
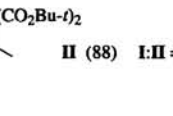
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																
 $\text{NMe}_3^+ \text{ArSO}_3^-$ $\text{Ar} = 4\text{-ClC}_6\text{H}_4$	DMD, acetone/ CH_3CN , 20° , 48 h, 100% convn	 I +  II (—) I:II = 80:20	324																
	DMD, acetone, 0° , 20 min	 I (89) +  II (—) I:II = 80:20	325																
	DMD, acetone, rt, 20 h	 I (50) +  II (45)	326																
C_{16} 	DMD, acetone, 18 h	 I (98)	321																
C_{16-19} 	DMD, acetone, 20° , 24 h	 I +  II	99																
		<table border="1"> <thead> <tr> <th>R^1</th> <th>R^2</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>>95</td> <td>83:17</td> </tr> <tr> <td>Bn</td> <td>H</td> <td>88</td> <td>91:09</td> </tr> <tr> <td>Bn</td> <td>Me</td> <td>95</td> <td>90:10</td> </tr> </tbody> </table>	R^1	R^2	% Convn	I:II	Ph	H	>95	83:17	Bn	H	88	91:09	Bn	Me	95	90:10	
R^1	R^2	% Convn	I:II																
Ph	H	>95	83:17																
Bn	H	88	91:09																
Bn	Me	95	90:10																
C_{16} 	DMD, acetone, rt, overnight	 I (69) +  II (—) I:II = 86:14	327																
	Acetone, Oxone [®] , phosphate buffer (pH 7.2), 0°	 I (68) +  II (—) I:II = 93:7	84																
	DMD, acetone/ CH_2Cl_2	 (~100)	328																
	DMD, acetone, 3 h	 I +  II (88) I:II = 75:25	298																

TABLE 4. DIASTERESELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

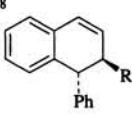
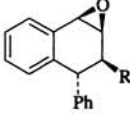
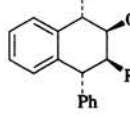
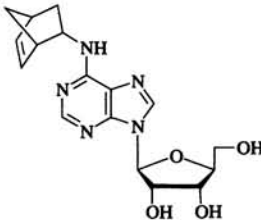
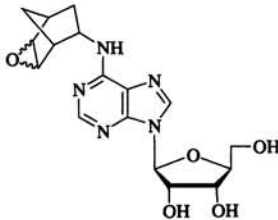
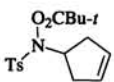
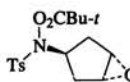
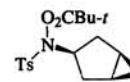
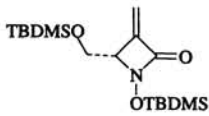
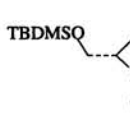
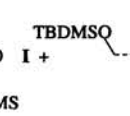
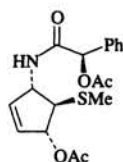
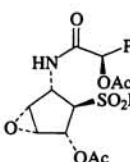
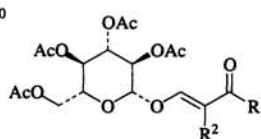
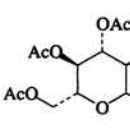
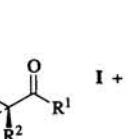
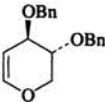
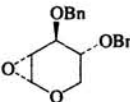
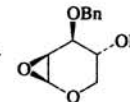
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																
C ₁₇₋₁₈ 	DMD, acetone/CH ₂ Cl ₂ , 0°, 2.5 h	 I +  II <table border="1"> <thead> <tr> <th>R</th> <th>Additive</th> <th>dr</th> <th>I (%)</th> <th>II (%)</th> </tr> </thead> <tbody> <tr> <td>CO₂H</td> <td>—</td> <td>>95:5</td> <td>(89)</td> <td>(0)</td> </tr> <tr> <td>CH₂OH</td> <td>—</td> <td>>95:5</td> <td>(94)</td> <td>(0)</td> </tr> <tr> <td>CO₂Me</td> <td>—</td> <td>>95:5</td> <td>(98)</td> <td>(0)</td> </tr> <tr> <td>CO₂Me</td> <td>HClO₄/H₂O</td> <td>>95:5</td> <td>(26)</td> <td>(67)</td> </tr> <tr> <td>CO₂Me</td> <td>H₂O</td> <td>—</td> <td>(0)</td> <td>(76)</td> </tr> </tbody> </table>	R	Additive	dr	I (%)	II (%)	CO ₂ H	—	>95:5	(89)	(0)	CH ₂ OH	—	>95:5	(94)	(0)	CO ₂ Me	—	>95:5	(98)	(0)	CO ₂ Me	HClO ₄ /H ₂ O	>95:5	(26)	(67)	CO ₂ Me	H ₂ O	—	(0)	(76)	329		
R	Additive	dr	I (%)	II (%)																															
CO ₂ H	—	>95:5	(89)	(0)																															
CH ₂ OH	—	>95:5	(94)	(0)																															
CO ₂ Me	—	>95:5	(98)	(0)																															
CO ₂ Me	HClO ₄ /H ₂ O	>95:5	(26)	(67)																															
CO ₂ Me	H ₂ O	—	(0)	(76)																															
	1. DMD, acetone/MeOH, 0°, 4 h 2. rt, 2 h	 (75)	61a																																
	TFP, Oxone®, MeCN/H ₂ O, Na ₂ EDTA, 0°, 2 to 3 h	 I +  II (—) I:II = 98:2	303																																
	DMD, acetone, rt, 3 d	 I +  II (93) I:II = 72:28	330																																
C ₁₈ 	DMD, acetone, Ar, rt	 (97)	308																																
C ₁₈₋₂₀ 	DMD, acetone	 I +  II <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I (%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>(—)</td> <td>69:31</td> </tr> <tr> <td>—O(CH₂)₂—</td> <td></td> <td>(70)</td> <td>86:14</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(73)</td> <td>90:10</td> </tr> <tr> <td>EtO</td> <td>H</td> <td>(—)</td> <td>67:33</td> </tr> <tr> <td>—(CH₂)₃—</td> <td></td> <td>(64)</td> <td>91:9</td> </tr> <tr> <td>Et</td> <td>Me</td> <td>(52)</td> <td>90:10</td> </tr> <tr> <td>EtO</td> <td>Me</td> <td>(74)</td> <td>91:9</td> </tr> </tbody> </table>	R ¹	R ²	I (%)	I:II	Me	H	(—)	69:31	—O(CH ₂) ₂ —		(70)	86:14	Me	Me	(73)	90:10	EtO	H	(—)	67:33	—(CH ₂) ₃ —		(64)	91:9	Et	Me	(52)	90:10	EtO	Me	(74)	91:9	331
R ¹	R ²	I (%)	I:II																																
Me	H	(—)	69:31																																
—O(CH ₂) ₂ —		(70)	86:14																																
Me	Me	(73)	90:10																																
EtO	H	(—)	67:33																																
—(CH ₂) ₃ —		(64)	91:9																																
Et	Me	(52)	90:10																																
EtO	Me	(74)	91:9																																
C ₁₉ 	DMD, acetone/CH ₂ Cl ₂	 I +  II (—) I:II = 80:20	328																																

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

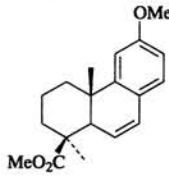
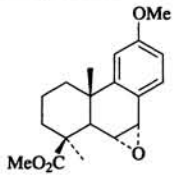
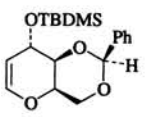
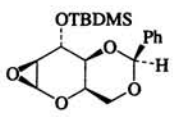
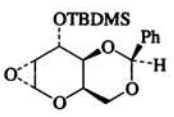
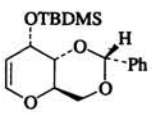
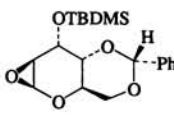
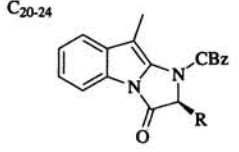
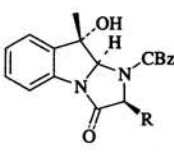
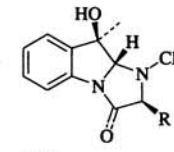

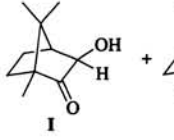
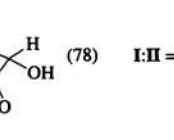

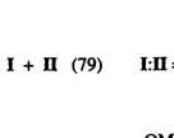
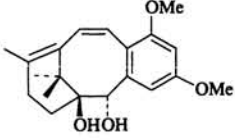
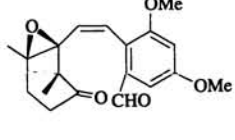
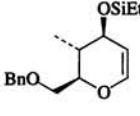
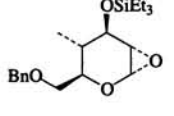
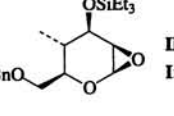
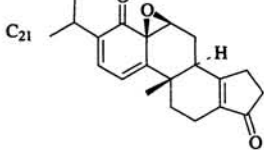
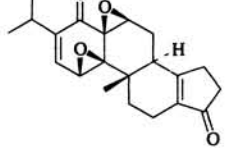
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.						
	DMD, acetone/CH ₃ CN, N ₂ , 0°, 36 min	 (99)	332						
	DMD, acetone/CH ₂ Cl ₂ , 0°, 1 h	 I +  II (90) I:II = -50:50	91						
	DMD, acetone/CH ₂ Cl ₂ , 0°, 1 h	 (98)	91						
	1. DMD, acetone/ MeOH, rt 2. NaBH ₄ , AcOH, 25°, 3 h	 I +  II <table border="1" data-bbox="1067 1033 1223 1125"> <thead> <tr> <th>R</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me (80)</td> <td>34:66</td> </tr> <tr> <td><i>i</i>-Bu (75)</td> <td>42:58</td> </tr> </tbody> </table>	R	I:II	Me (80)	34:66	<i>i</i> -Bu (75)	42:58	333
R	I:II								
Me (80)	34:66								
<i>i</i> -Bu (75)	42:58								
	1. DMD (1.6 equiv), acetone/THF, -78°, 108 s 2. NH ₄ F, H ₂ O, 20°, 2 to 3 h	 I +  II (78) I:II = 94:6	311						
	1. DMD (2 equiv), acetone/THF, -78°, 108 s 2. NH ₄ F, H ₂ O, 20°, 2 to 3 h	 I + II (79) I:II = 96:4	311						
	DMD, acetone/CH ₂ Cl ₂ , 0°	 (29)	96						
	DMD, acetone/CH ₂ Cl ₂ , 0°	 I +  II (>99) I:II >95:5	90						
	TFP, Oxone®, NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 25°, 4 h	 (70)	334						

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																														
	DMD, acetone/CH ₂ Cl ₂ , 0°, 30 min	I + II (100) I:II = 15:1	335																														
	DMD, acetone/CH ₂ Cl ₂ , 0°, 40 min	I + II (—) I:II = 9:1	336																														
C ₂₁₋₂₇ 	DMD, acetone/CH ₂ Cl ₂ , 0°, 40 min	I + II (—) R = Ph, <i>i</i> -Pr Ⓢ = solid support	93																														
C ₂₁ 	DMD, acetone, CH ₂ Cl ₂ , 20°, 20 h	I + II (90) I:II = 80:20	258																														
	TFP, Oxone®, NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 8°, 15 min	I + II (84) I:II = 75:25	35																														
C ₂₂₋₂₄ 	DMD, acetone/CH ₂ Cl ₂ , -20°	I + II <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time</th> </tr> </thead> <tbody> <tr><td>H</td><td>Br</td><td>408 h (82)</td></tr> <tr><td>H</td><td>Cl</td><td>408 h (86)</td></tr> <tr><td>H</td><td>H</td><td>240 h (79)</td></tr> <tr><td>H</td><td>CN</td><td>552 h (80)</td></tr> <tr><td>Me</td><td>H</td><td>312 h (75)</td></tr> <tr><td>H</td><td>Me</td><td>216 h (86)</td></tr> <tr><td>MeO</td><td>H</td><td>312 h (73)</td></tr> <tr><td>H</td><td>MeO</td><td>144 h (78)</td></tr> <tr><td>H</td><td>EtO</td><td>168 h (79)</td></tr> </tbody> </table>	R ¹	R ²	Time	H	Br	408 h (82)	H	Cl	408 h (86)	H	H	240 h (79)	H	CN	552 h (80)	Me	H	312 h (75)	H	Me	216 h (86)	MeO	H	312 h (73)	H	MeO	144 h (78)	H	EtO	168 h (79)	337
R ¹	R ²	Time																															
H	Br	408 h (82)																															
H	Cl	408 h (86)																															
H	H	240 h (79)																															
H	CN	552 h (80)																															
Me	H	312 h (75)																															
H	Me	216 h (86)																															
MeO	H	312 h (73)																															
H	MeO	144 h (78)																															
H	EtO	168 h (79)																															
	DMD, acetone/CH ₂ Cl ₂ , -20°	I + II <table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr><td>Br</td><td>432 h</td><td>(19)</td><td>(0)</td></tr> <tr><td>Cl</td><td>432 h</td><td>(15)</td><td>(0)</td></tr> <tr><td>H</td><td>336 h</td><td>(15)</td><td>(10)</td></tr> <tr><td>Me</td><td>228 h</td><td>(21)</td><td>(0)</td></tr> <tr><td>EtO</td><td>336 h</td><td>(0)</td><td>(14)</td></tr> </tbody> </table>	R	Time	I	II	Br	432 h	(19)	(0)	Cl	432 h	(15)	(0)	H	336 h	(15)	(10)	Me	228 h	(21)	(0)	EtO	336 h	(0)	(14)	337						
R	Time	I	II																														
Br	432 h	(19)	(0)																														
Cl	432 h	(15)	(0)																														
H	336 h	(15)	(10)																														
Me	228 h	(21)	(0)																														
EtO	336 h	(0)	(14)																														

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

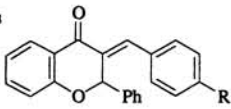
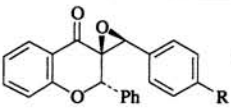
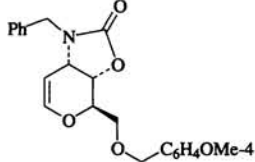
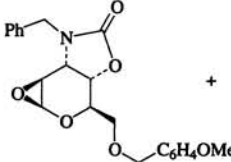
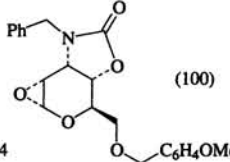
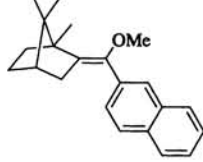
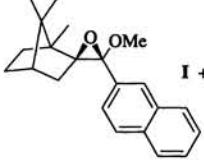
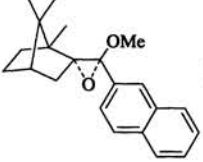
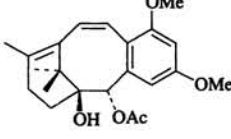
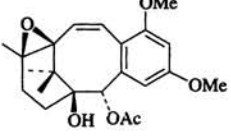
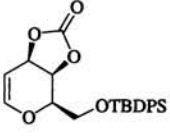
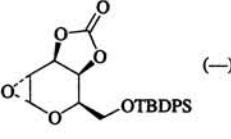
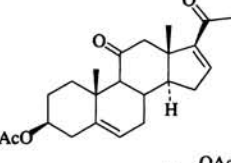
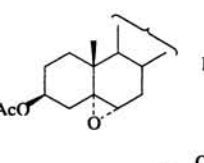
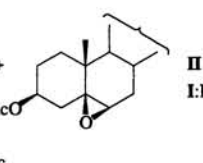
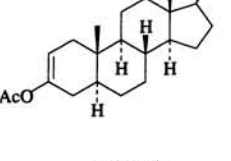
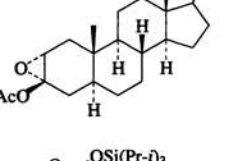
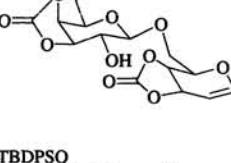
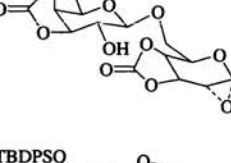

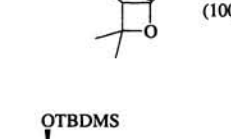
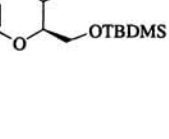
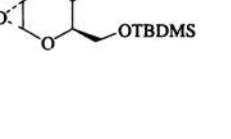
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.
C ₂₃₋₂₃ 	TFD, TFP/CH ₂ Cl ₂ , -20°, 5 to 8 h	 (—) R = Cl, H, Me	337
C ₂₃ 	DMD, acetone/CH ₂ Cl ₂ , 0°	 +  (100)	338
	TFD, TFP/CH ₂ Cl ₂ , -20°, 5 min	 I +  II (92) I:II = 50:50	222
	DMD, acetone/CH ₂ Cl ₂ , 0°	 (100)	96
C ₂₃ 	DMD, acetone/CH ₂ Cl ₂ , 0° to rt, 1 h	 (—)	339
	DMD, acetone, -40°, 12 h	 I +  II (88) I:II = 60:40	258
	DMD, acetone	 (90)	340
	DMD, CH ₂ Cl ₂ , acetone, 0°, 30 min	 (>48)	94
C ₂₄ 	DMD, CHCl ₃ /acetone	 (100) dr 52:48	203
	DMD, acetone/CH ₂ Cl ₂ , 0°, 1 h	 (98)	91

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

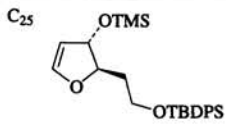
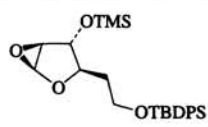
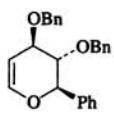
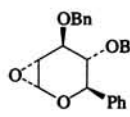
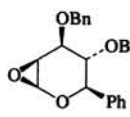
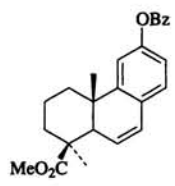
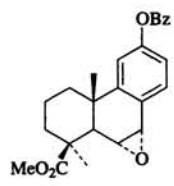
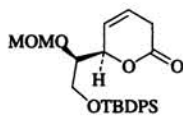
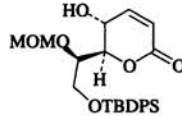
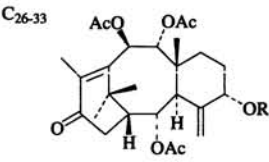
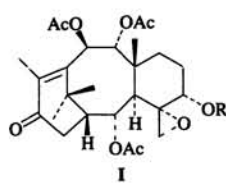
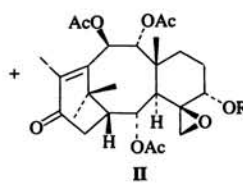
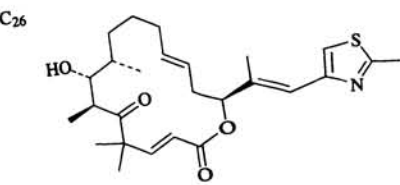
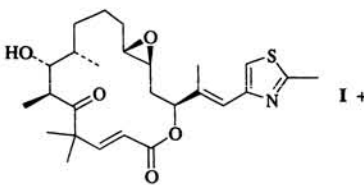
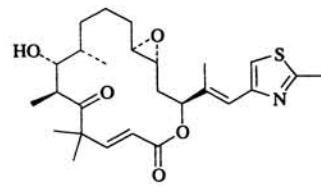
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																
	DMD, acetone/CH ₂ Cl ₂ , 0°, 30 min	 (—)	336																
	DMD, acetone	 I +  II (—) I:II = 5:1	341																
	DMD, acetone, N ₂ , rt, 30 min	 (65)	142																
	1. DMD, acetone, 3 h 2. Et ₃ N, CH ₂ Cl ₂ , 12 h	 (—)	342																
	DMD, acetone/CH ₂ Cl ₂ , rt, 36 h	 I +  II	343																
		<table border="1"> <thead> <tr> <th>R</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(66) 67:33</td> </tr> <tr> <td>CF₃CO</td> <td>(72) 50:50</td> </tr> <tr> <td>Ac</td> <td>(86) 67:33</td> </tr> <tr> <td>Piv</td> <td>(63) 33:67</td> </tr> <tr> <td>Et₃Si</td> <td>(86) 20:80</td> </tr> <tr> <td>TBDMS</td> <td>(69) 17:83</td> </tr> <tr> <td>PhCO</td> <td>(77) 67:33</td> </tr> </tbody> </table>	R	I:II	H	(66) 67:33	CF ₃ CO	(72) 50:50	Ac	(86) 67:33	Piv	(63) 33:67	Et ₃ Si	(86) 20:80	TBDMS	(69) 17:83	PhCO	(77) 67:33	
R	I:II																		
H	(66) 67:33																		
CF ₃ CO	(72) 50:50																		
Ac	(86) 67:33																		
Piv	(63) 33:67																		
Et ₃ Si	(86) 20:80																		
TBDMS	(69) 17:83																		
PhCO	(77) 67:33																		
	TFP, Oxone®, NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0°	 I +  II I(II) (45); II(I) (28)	344																

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

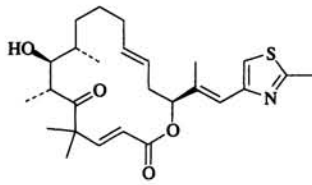
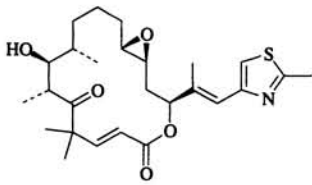
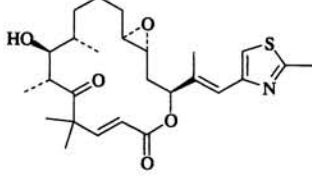
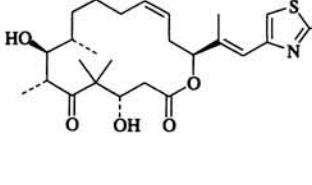
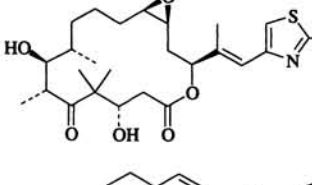
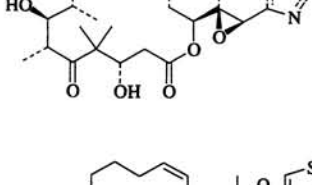
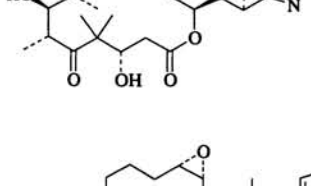
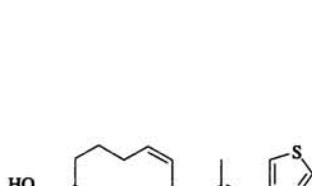
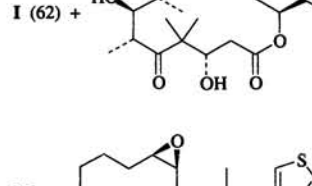
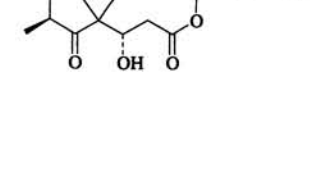
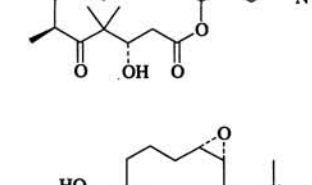
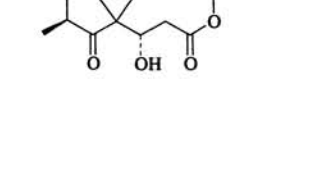
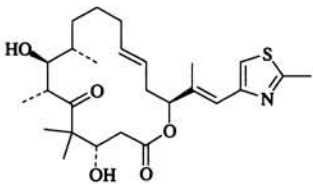
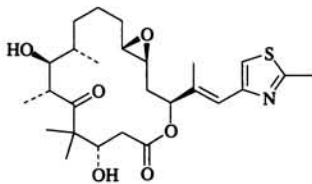
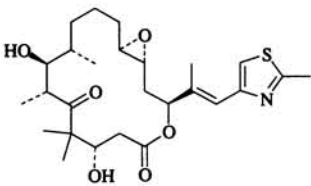
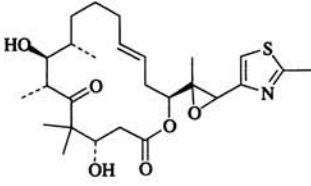
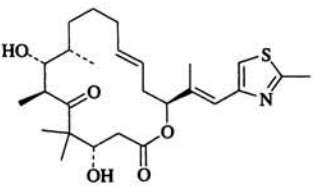
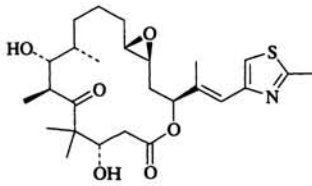
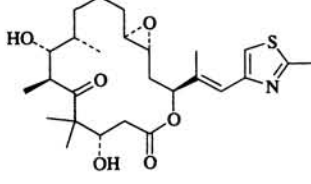
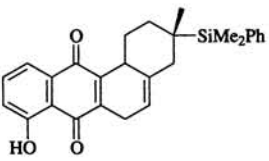
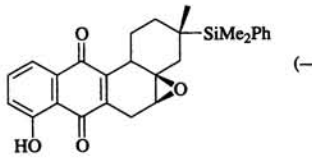
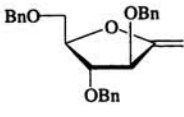
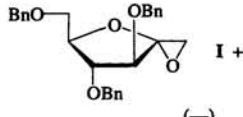
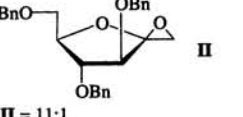
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.
	TFP, Oxone®, NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0°	 I +  II I(II) (60); II(I) (15)	344
	DMD, acetone/CH ₂ Cl ₂ , 0°	 I (50) +  II (5) +  III (5)	344
	TFP, Oxone®, NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0°	I (62) +  (13)	344
	TFP, Oxone®, NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0°	 I +  II I (II) (38) II (I) (29)	344

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.
	DMD, acetone/CH ₂ Cl ₂ , 0°	 I (10) +  II (10) +  III (40)	344
	TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0°	I (II) (45) + II (I) (35)	344
	TFP, Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0°	 I +  II I (II) (44) II (I) (21)	344
	DMD, acetone/CH ₂ Cl ₂ , 0°, 1 h	 (-)	345
	DMD, acetone/CH ₂ Cl ₂ , 0°	 I +  II (-) I:II = 11:1	346

C₂₇

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

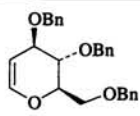
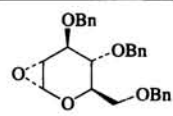
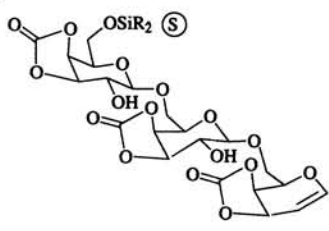
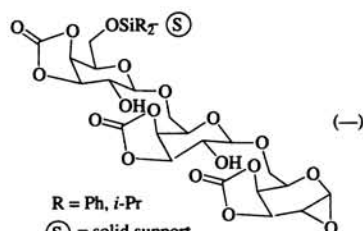
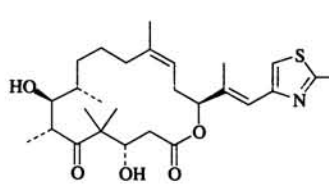
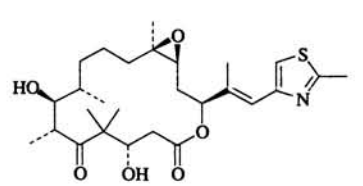
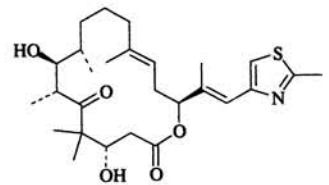
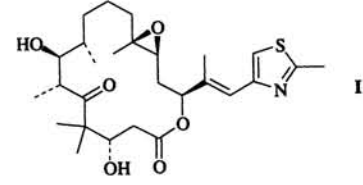
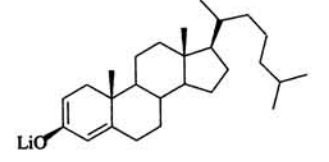
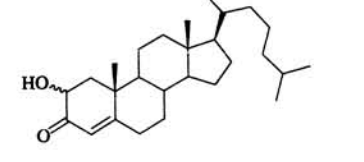
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.
	DMD, acetone/CH ₂ Cl ₂ , 0°, 6 min	 I (96)	347
	DMD, acetone/CH ₂ Cl ₂ , 0°, 10 min	I (—)	348
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 0°, 15 min	I (—)	349
C ₂₇₋₃₃ 	DMD, acetone/CH ₂ Cl ₂ , 0°, 40 min	 (—) R = Ph, <i>i</i> -Pr Ⓢ = solid support	93
C ₂₇ 	DMD, acetone/CH ₂ Cl ₂ , -50°	 I + II (75) I:II = 83:17	350
	TFP, Oxone®, NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0°	 I + II (86) I:II = 50:50	350
	DMD, acetone/THF, Ar, -78°, 10 min	 (60) dr 67:33	209

TABLE 4. DIASTERESELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

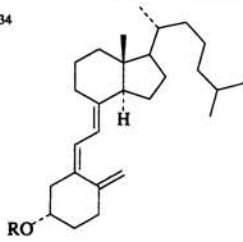
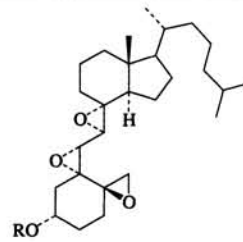
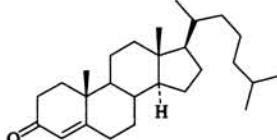
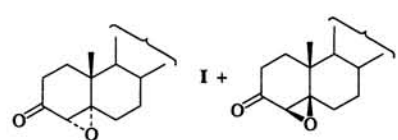
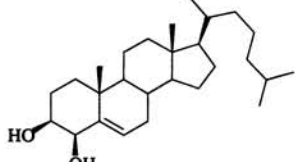
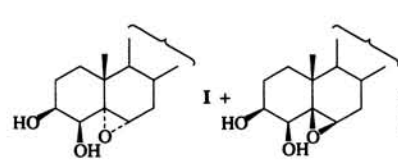
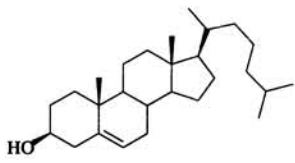
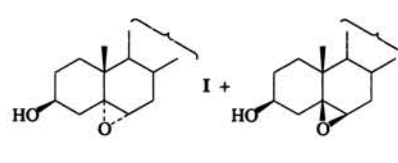
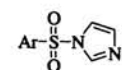
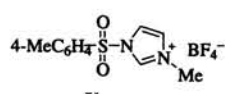
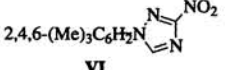
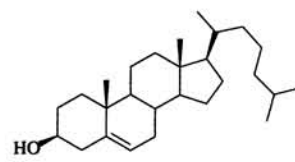
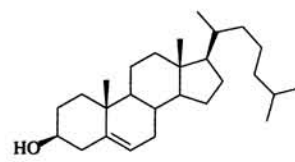
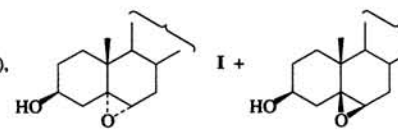
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																																															
<p>C₂₇₋₃₄</p> 	TFD, CH ₂ Cl ₂ /TFP, -40°, 1 h	 <table border="1" style="margin-left: 20px;"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(72)</td> </tr> <tr> <td>Ac</td> <td>(85)</td> </tr> <tr> <td>4-BrC₆H₄CO</td> <td>(83)</td> </tr> </tbody> </table>	R	Yield (%)	H	(72)	Ac	(85)	4-BrC ₆ H ₄ CO	(83)	351																																																							
R	Yield (%)																																																																	
H	(72)																																																																	
Ac	(85)																																																																	
4-BrC ₆ H ₄ CO	(83)																																																																	
<p>C₂₇</p> 	DMD, acetone, 20°, 20 h	 <p>I + II (80) I:II = 75:25</p>	258																																																															
	Oxone [®] , acetone/CH ₂ Cl ₂ , phosphate buffer (pH 7.5), 18-crown-6, 6 to 8°, 4 h	 <p>I + II (50) I:II = 22:78</p>	302																																																															
	Sulfonylazole, H ₂ O ₂ , acetone, THF, NaOH, 10°, ~3 h	 <p>I + II</p>	271																																																															
 <p>III: Ar = 4-MeC₆H₄ IV: Ar = 4-O₂NC₆H₄</p>  <p>V</p>  <p>VI</p>	<table border="1" style="margin-left: 20px;"> <thead> <tr> <th>Sulfonylazole</th> <th>Acetone (equiv)</th> <th>I+II (%)</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>III</td> <td>1</td> <td>(37)</td> <td>76:24</td> </tr> <tr> <td>III</td> <td>4</td> <td>(38)</td> <td>58:42</td> </tr> <tr> <td>III</td> <td>10</td> <td>(27)</td> <td>50:50</td> </tr> <tr> <td>III</td> <td>20</td> <td>(18)</td> <td>50:50</td> </tr> <tr> <td>III</td> <td>40</td> <td>(32)</td> <td>43:57</td> </tr> <tr> <td>III</td> <td>60</td> <td>(18)</td> <td>44:56</td> </tr> <tr> <td>III</td> <td>80</td> <td>(17)</td> <td>41:59</td> </tr> <tr> <td>III</td> <td>100</td> <td>(31)</td> <td>41:59</td> </tr> <tr> <td>IV</td> <td>1</td> <td>(54)</td> <td>75:25</td> </tr> <tr> <td>IV</td> <td>4</td> <td>(54)</td> <td>56:44</td> </tr> <tr> <td>IV</td> <td>20</td> <td>(52)</td> <td>45:55</td> </tr> <tr> <td>V</td> <td>20</td> <td>(92)</td> <td>82:18</td> </tr> <tr> <td>VI</td> <td>4</td> <td>(34)</td> <td>76:24</td> </tr> <tr> <td>VI</td> <td>20</td> <td>(18)</td> <td>70:30</td> </tr> <tr> <td>VI</td> <td>20</td> <td>(96)</td> <td>91:9</td> </tr> </tbody> </table>	Sulfonylazole	Acetone (equiv)	I+II (%)	I:II	III	1	(37)	76:24	III	4	(38)	58:42	III	10	(27)	50:50	III	20	(18)	50:50	III	40	(32)	43:57	III	60	(18)	44:56	III	80	(17)	41:59	III	100	(31)	41:59	IV	1	(54)	75:25	IV	4	(54)	56:44	IV	20	(52)	45:55	V	20	(92)	82:18	VI	4	(34)	76:24	VI	20	(18)	70:30	VI	20	(96)	91:9	
Sulfonylazole	Acetone (equiv)	I+II (%)	I:II																																																															
III	1	(37)	76:24																																																															
III	4	(38)	58:42																																																															
III	10	(27)	50:50																																																															
III	20	(18)	50:50																																																															
III	40	(32)	43:57																																																															
III	60	(18)	44:56																																																															
III	80	(17)	41:59																																																															
III	100	(31)	41:59																																																															
IV	1	(54)	75:25																																																															
IV	4	(54)	56:44																																																															
IV	20	(52)	45:55																																																															
V	20	(92)	82:18																																																															
VI	4	(34)	76:24																																																															
VI	20	(18)	70:30																																																															
VI	20	(96)	91:9																																																															
	Acetone, Oxone [®] , NaHCO ₃ , H ₂ O, 10°, 6 h	I + II (72) I:II = 44:56	271																																																															
	Ketone, Oxone [®] , CH ₂ Cl ₂ /phosphate buffer (pH 7.5), Bu ₄ NHSO ₄ , 0 to 5°	 <p>I + II</p> <table border="1" style="margin-left: 20px;"> <thead> <tr> <th>Ketone</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>acetone</td> <td>(90) 50:50</td> </tr> <tr> <td>cyclohexanone</td> <td>(59) 55:45</td> </tr> <tr> <td>2-methylcyclohexanone</td> <td>(70) 35:65</td> </tr> <tr> <td>2-hydroxy-2-methylcyclohexanone</td> <td>(37) 40:60</td> </tr> <tr> <td>ethyl pyruvate</td> <td>(83) 64:36</td> </tr> </tbody> </table>	Ketone	I:II	acetone	(90) 50:50	cyclohexanone	(59) 55:45	2-methylcyclohexanone	(70) 35:65	2-hydroxy-2-methylcyclohexanone	(37) 40:60	ethyl pyruvate	(83) 64:36	352																																																			
Ketone	I:II																																																																	
acetone	(90) 50:50																																																																	
cyclohexanone	(59) 55:45																																																																	
2-methylcyclohexanone	(70) 35:65																																																																	
2-hydroxy-2-methylcyclohexanone	(37) 40:60																																																																	
ethyl pyruvate	(83) 64:36																																																																	

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

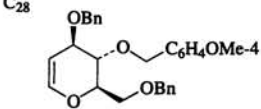
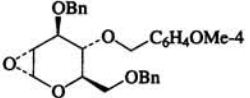
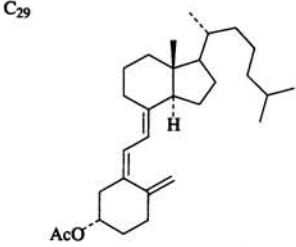
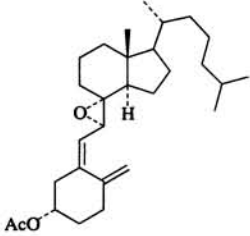
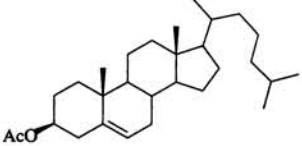
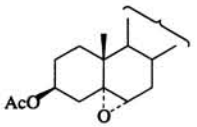
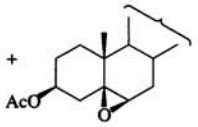
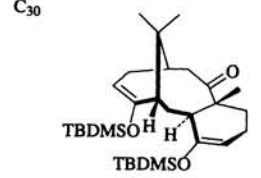
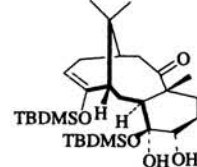
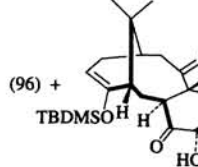
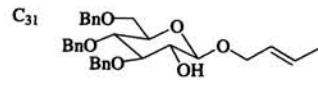
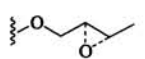
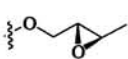
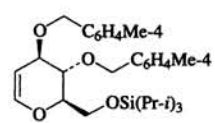
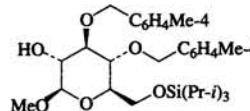

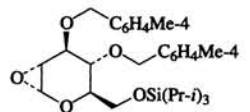
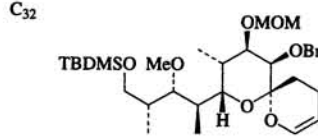
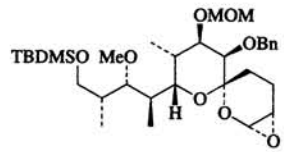
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.
C ₂₈ 	DMD, acetone	 (100)	353
C ₂₉ 	DMD, CH ₂ Cl ₂ /acetone, -40°, 2 h	 (60)	351
	Acetone, Oxone®, CH ₂ Cl ₂ /phosphate buffer (pH 7.5), Bu ₄ NHSO ₄ , 0 to 5°	 I +  II (86) I:II = 40:60	352
C ₃₀ 	1. DMD, acetone/CH ₂ Cl ₂ , -78 to -10°, 3 h 2. NaHCO ₃	 (96) +  II (3)	354, 355
C ₃₁ 	DMD, acetone/CH ₂ Cl ₂ , 0°, 6 h	 I +  II (80) I:II = 50:50	356
	1. DMD, acetone/CH ₂ Cl ₂ 2. MeOH, rt	 (76)	357
	DMD, acetone/CH ₂ Cl ₂ , 0°	 (---)	358
C ₃₂ 	DMD, acetone/CH ₂ Cl ₂ , 0°	 (100)	359

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

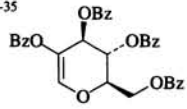
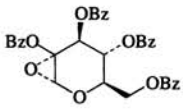
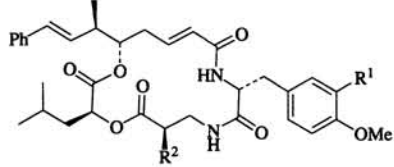
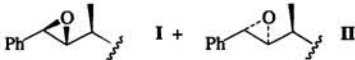
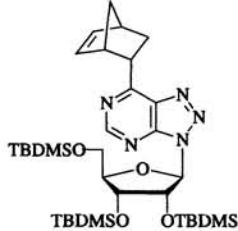
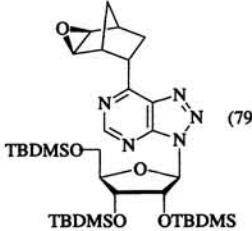
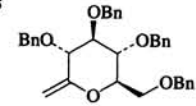
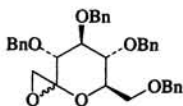

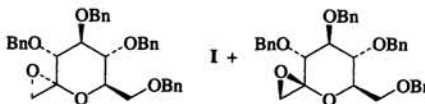
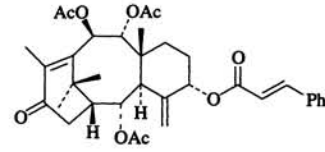
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.												
<p>C₃₄₋₃₅</p> 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -20°, 2 h	 (~100)	213												
	DMD, acetone/CH ₂ Cl ₂ , -30°, 24 h	 I + II <table border="1" data-bbox="954 826 1180 918"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(60)</td> <td>(20)</td> </tr> <tr> <td>Cl</td> <td>Me</td> <td>(55)</td> <td>(19)</td> </tr> </tbody> </table>	R ¹	R ²	I	II	H	H	(60)	(20)	Cl	Me	(55)	(19)	360
R ¹	R ²	I	II												
H	H	(60)	(20)												
Cl	Me	(55)	(19)												
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , -78 to -20°, 5.5 h	 (79)	361												
<p>C₃₅</p> 	DMD	 (—)	362												
	DMD, acetone/CH ₂ Cl ₂ , 0°	 I + II (—) <p>I:II = 60:40</p>	346												
	DMD, acetone/CH ₂ Cl ₂ , rt, 36 h	I (8) + II (—) <p>(77) I:II = 99:1</p>	343												

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.																																													
C ₃₇ 	DMD, acetone/solvent	 <table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>Time</th> <th>I</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>—</td> <td>rt</td> <td>24 h</td> <td>(56)</td> <td>80:20</td> </tr> <tr> <td>—</td> <td>4°</td> <td>72 h</td> <td>(57)</td> <td>84:16</td> </tr> <tr> <td>—</td> <td>-23°</td> <td>96 h</td> <td>(tr)</td> <td>87:13</td> </tr> <tr> <td>hexane</td> <td>rt</td> <td>24 h</td> <td>(16)</td> <td>58:42</td> </tr> <tr> <td>MeOH</td> <td>rt</td> <td>24 h</td> <td>(tr)</td> <td>—</td> </tr> <tr> <td>CH₂Cl₂</td> <td>rt</td> <td>24 h</td> <td>(30)</td> <td>71:29</td> </tr> <tr> <td>CHCl₃</td> <td>rt</td> <td>24 h</td> <td>(tr)</td> <td>—</td> </tr> <tr> <td>CCl₄</td> <td>rt</td> <td>24 h</td> <td>(58)</td> <td>80:20</td> </tr> </tbody> </table>	Solvent	Temp	Time	I	I:II	—	rt	24 h	(56)	80:20	—	4°	72 h	(57)	84:16	—	-23°	96 h	(tr)	87:13	hexane	rt	24 h	(16)	58:42	MeOH	rt	24 h	(tr)	—	CH ₂ Cl ₂	rt	24 h	(30)	71:29	CHCl ₃	rt	24 h	(tr)	—	CCl ₄	rt	24 h	(58)	80:20	363
Solvent	Temp	Time	I	I:II																																												
—	rt	24 h	(56)	80:20																																												
—	4°	72 h	(57)	84:16																																												
—	-23°	96 h	(tr)	87:13																																												
hexane	rt	24 h	(16)	58:42																																												
MeOH	rt	24 h	(tr)	—																																												
CH ₂ Cl ₂	rt	24 h	(30)	71:29																																												
CHCl ₃	rt	24 h	(tr)	—																																												
CCl ₄	rt	24 h	(58)	80:20																																												
	Ethylmethyldioxirane, 2-butanone, rt, 96 h	I (47) + II (—) I:II = 82:18	363																																													
	Ethylmethyldioxirane, 2-butanone, 4°, 96 h	I + II (tr) I:II = 72:28	363																																													
C ₄₀ 	DMD, acetone/CH ₂ Cl ₂ , 0° to rt, 1 h	(—)	339																																													
C ₄₀ OSi(Pr- <i>i</i>) ₂ (S) (S) = solid support	DMD, CH ₂ Cl ₂ /acetone, 0°	(—)	93																																													
C ₄₅ 	DMD, acetone/CH ₂ Cl ₂ , 0°	 (84) I:II = 1:5	364																																													
C ₄₈ 	DMD, acetone, 0°	(—)	365																																													
C ₅₀ 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 0°, 30 min	(>51)	366																																													

TABLE 4. DIASTEREOSELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

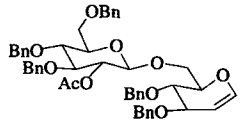
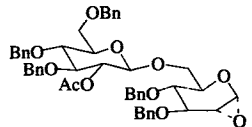
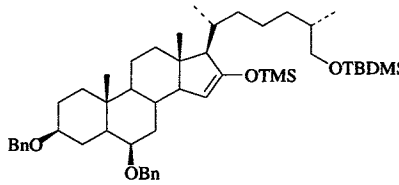
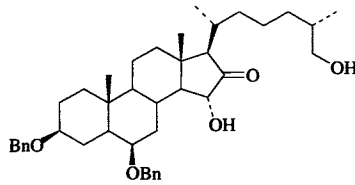
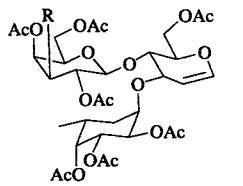
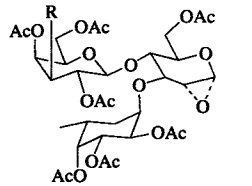
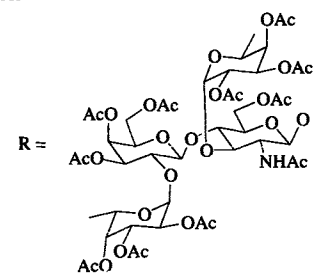
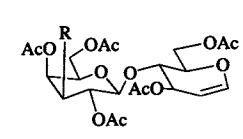
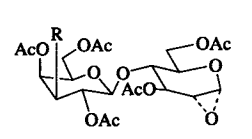
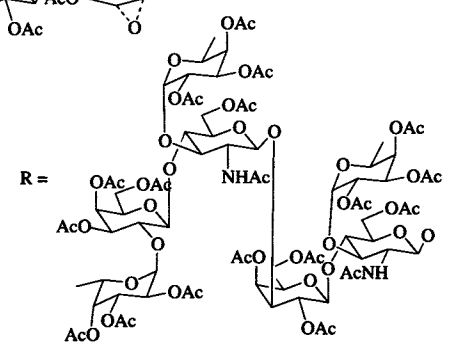
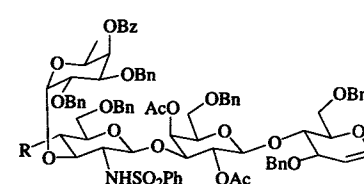
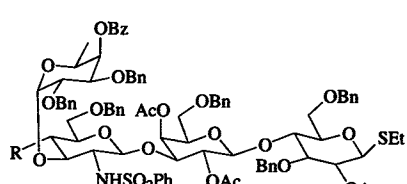
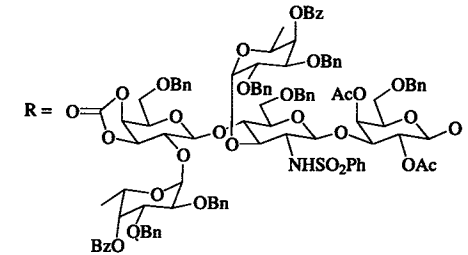
Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.
	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 0°, 30 min	 (>43)	366
	1. DMD, acetone/CH ₂ Cl ₂ , 0°, 1 h 2. Camphorsulfonic acid, acetone, 4°, 16 h	 (71)	367
<p>C₇₉</p> 	DMD, acetone/CH ₂ Cl ₂ , 0°, 45 min	 (-)	95
		<p>R =</p> 	
<p>C₁₀₂</p> 	DMD, acetone/CH ₂ Cl ₂ , N ₂ , 0°, 45 min	 (-)	95
		<p>R =</p> 	
<p>C₁₈₇</p> 	1. DMD, acetone/CH ₂ Cl ₂ , molecular sieves 4 Å, 45 min 2. EtSH, CF ₃ CO ₂ H, CH ₂ Cl ₂ , -78° to rt, 6 h 3. Ac ₂ O, CH ₂ Cl ₂ , pyridine, 24 h	 (60)	95
		<p>R =</p> 	

TABLE 4. DIASTERESELECTIVE EPOXIDATIONS OF OLEFINS BY DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%), Diastereomeric Ratio (dr)	Refs.
-----------	------------	--	-------

^aTDMPP is the dianion of 5,10,15,20-tetrakis(2,6-dimethoxyphenyl)porphyrin.

^bCl16TDMPP is the dianion of 2,3,7,8,12,13,17, 18-octachloro-5,10,15,20-tetrakis(3,5-dichloro-2,6-dimethoxyphenyl)porphyrin.

^cCl8TDMPP is the dianion of 5,10,15,20-tetrakis(3,5-dichloro-2,6-dimethoxyphenyl)porphyrin.

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES

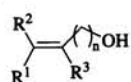
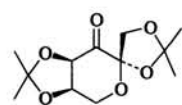
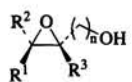
Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.																																																																											
<p>C₆₋₁₅</p> 		<p>Oxone[®], K₂CO₃, DMM/ CH₃CN, buffer (pH 9.3), Bu₄NHSO₄</p>	 I																																																																											
			<table border="1"> <thead> <tr> <th>n</th> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Temp</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>2</td> <td>H</td> <td>Et</td> <td>H</td> <td>-10°</td> <td>3 h (82)</td> <td>90</td> </tr> <tr> <td>1</td> <td>H</td> <td>Et</td> <td>Me</td> <td>-10°</td> <td>3 h (83)</td> <td>91</td> </tr> <tr> <td>1</td> <td>H</td> <td><i>n</i>-Pr</td> <td>H</td> <td>-10°</td> <td>3 h (68)</td> <td>91</td> </tr> <tr> <td>1</td> <td>H</td> <td>-(CH₂)₄-</td> <td>H</td> <td>-10°</td> <td>3 h (92)</td> <td>92</td> </tr> <tr> <td>1</td> <td>H</td> <td>Ph</td> <td>H</td> <td>-10°</td> <td>3 h (85)</td> <td>94</td> </tr> <tr> <td>2</td> <td>H</td> <td>Ph</td> <td>H</td> <td>0°</td> <td>2 h (90)</td> <td>91</td> </tr> <tr> <td>1</td> <td>H</td> <td>Bn</td> <td>H</td> <td>-10°</td> <td>2 h (45)</td> <td>91</td> </tr> <tr> <td>2</td> <td>H</td> <td><i>n</i>-C₆H₁₃</td> <td>H</td> <td>-10°</td> <td>2 h (86)</td> <td>90</td> </tr> <tr> <td>3</td> <td>H</td> <td>Bn</td> <td>H</td> <td>0°</td> <td>2 h (87)</td> <td>91</td> </tr> <tr> <td>1</td> <td>Ph</td> <td>Ph</td> <td>H</td> <td>0°</td> <td>2 h (87)</td> <td>94</td> </tr> </tbody> </table>	n	R ¹	R ²	R ³	Temp	Time	% ee	2	H	Et	H	-10°	3 h (82)	90	1	H	Et	Me	-10°	3 h (83)	91	1	H	<i>n</i> -Pr	H	-10°	3 h (68)	91	1	H	-(CH ₂) ₄ -	H	-10°	3 h (92)	92	1	H	Ph	H	-10°	3 h (85)	94	2	H	Ph	H	0°	2 h (90)	91	1	H	Bn	H	-10°	2 h (45)	91	2	H	<i>n</i> -C ₆ H ₁₃	H	-10°	2 h (86)	90	3	H	Bn	H	0°	2 h (87)	91	1	Ph	Ph	H	0°
n	R ¹	R ²	R ³	Temp	Time	% ee																																																																								
2	H	Et	H	-10°	3 h (82)	90																																																																								
1	H	Et	Me	-10°	3 h (83)	91																																																																								
1	H	<i>n</i> -Pr	H	-10°	3 h (68)	91																																																																								
1	H	-(CH ₂) ₄ -	H	-10°	3 h (92)	92																																																																								
1	H	Ph	H	-10°	3 h (85)	94																																																																								
2	H	Ph	H	0°	2 h (90)	91																																																																								
1	H	Bn	H	-10°	2 h (45)	91																																																																								
2	H	<i>n</i> -C ₆ H ₁₃	H	-10°	2 h (86)	90																																																																								
3	H	Bn	H	0°	2 h (87)	91																																																																								
1	Ph	Ph	H	0°	2 h (87)	94																																																																								
	"	<p>Oxone[®], K₂CO₃, DME, buffer (pH 9.3), Bu₄NHSO₄, -15°</p>	<p>I</p> <table border="1"> <thead> <tr> <th>n</th> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>H</td> <td>Et</td> <td>Me</td> <td>5 h (85)</td> <td>92</td> </tr> <tr> <td>1</td> <td>H</td> <td>-(CH₂)₄-</td> <td>H</td> <td>5 h (93)</td> <td>94</td> </tr> <tr> <td>1</td> <td>H</td> <td>Bn</td> <td>H</td> <td>7 h (43)</td> <td>92</td> </tr> <tr> <td>1</td> <td>H</td> <td>Ph</td> <td>Me</td> <td>5 h (75)</td> <td>74</td> </tr> <tr> <td>2</td> <td>H</td> <td><i>n</i>-C₆H₁₃</td> <td>H</td> <td>5 h (83)</td> <td>91</td> </tr> </tbody> </table>	n	R ¹	R ²	R ³	Time	% ee	1	H	Et	Me	5 h (85)	92	1	H	-(CH ₂) ₄ -	H	5 h (93)	94	1	H	Bn	H	7 h (43)	92	1	H	Ph	Me	5 h (75)	74	2	H	<i>n</i> -C ₆ H ₁₃	H	5 h (83)	91	149a																																						
n	R ¹	R ²	R ³	Time	% ee																																																																									
1	H	Et	Me	5 h (85)	92																																																																									
1	H	-(CH ₂) ₄ -	H	5 h (93)	94																																																																									
1	H	Bn	H	7 h (43)	92																																																																									
1	H	Ph	Me	5 h (75)	74																																																																									
2	H	<i>n</i> -C ₆ H ₁₃	H	5 h (83)	91																																																																									

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)


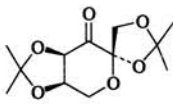







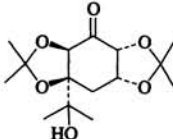

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee) Refs.																																																																															
C ₆₋₂₄ 		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, 0°, 2 h		117																																																																														
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Yield (%)</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td><i>n</i>-Pr</td> <td>H</td> <td>CH₂OH</td> <td>(60)</td> <td>78</td> </tr> <tr> <td>Et</td> <td>H</td> <td>(CH₂)₂OH</td> <td>(70)</td> <td>70</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CH₂Cl</td> <td>(61)</td> <td>93</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CH₂OH</td> <td>(81)</td> <td>88</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>(60)</td> <td>84</td> </tr> <tr> <td>Ph</td> <td>—(CH₂)₄—</td> <td></td> <td>(69)</td> <td>91</td> </tr> <tr> <td><i>n</i>-Pr</td> <td>H</td> <td>CH₂OTBDMS</td> <td>(80)</td> <td>93</td> </tr> <tr> <td>Et</td> <td>H</td> <td>(CH₂)₂OTBDMS</td> <td>(84)</td> <td>87</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Ph</td> <td>(73)</td> <td>95</td> </tr> <tr> <td><i>n</i>-C₆H₁₃</td> <td>H</td> <td><i>n</i>-C₆H₁₃</td> <td>(81)</td> <td>90</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Ph</td> <td>(73)</td> <td>92</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CH₂OTBDMS</td> <td>(74)</td> <td>93</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td><i>n</i>-C₁₀H₂₁</td> <td>(65)</td> <td>92</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Yield (%)	% ee	<i>n</i> -Pr	H	CH ₂ OH	(60)	78	Et	H	(CH ₂) ₂ OH	(70)	70	Ph	H	CH ₂ Cl	(61)	93	Ph	H	CH ₂ OH	(81)	88	Ph	H	Me	(60)	84	Ph	—(CH ₂) ₄ —		(69)	91	<i>n</i> -Pr	H	CH ₂ OTBDMS	(80)	93	Et	H	(CH ₂) ₂ OTBDMS	(84)	87	Ph	H	Ph	(73)	95	<i>n</i> -C ₆ H ₁₃	H	<i>n</i> -C ₆ H ₁₃	(81)	90	Ph	Me	Ph	(73)	92	Ph	H	CH ₂ OTBDMS	(74)	93	Ph	Ph	<i>n</i> -C ₁₀ H ₂₁	(65)	92									
			R ¹	R ²	R ³	Yield (%)	% ee																																																																											
			<i>n</i> -Pr	H	CH ₂ OH	(60)	78																																																																											
			Et	H	(CH ₂) ₂ OH	(70)	70																																																																											
			Ph	H	CH ₂ Cl	(61)	93																																																																											
			Ph	H	CH ₂ OH	(81)	88																																																																											
			Ph	H	Me	(60)	84																																																																											
			Ph	—(CH ₂) ₄ —		(69)	91																																																																											
			<i>n</i> -Pr	H	CH ₂ OTBDMS	(80)	93																																																																											
			Et	H	(CH ₂) ₂ OTBDMS	(84)	87																																																																											
			Ph	H	Ph	(73)	95																																																																											
			<i>n</i> -C ₆ H ₁₃	H	<i>n</i> -C ₆ H ₁₃	(81)	90																																																																											
			Ph	Me	Ph	(73)	92																																																																											
			Ph	H	CH ₂ OTBDMS	(74)	93																																																																											
Ph	Ph	<i>n</i> -C ₁₀ H ₂₁	(65)	92																																																																														
C ₇ 		Oxone [®] , CH ₂ Cl ₂ /buffer, Bu ₄ NHSO ₄ , 25°	 I (87) 6% ee	105																																																																														
			Oxone [®] , CH ₂ Cl ₂ /buffer, Bu ₄ NHSO ₄ , 5°	I (80) 12% ee	105																																																																													
				Oxone [®] , CH ₂ Cl ₂ /buffer, Bu ₄ NHSO ₄ , 5°	 (85) 5% ee	105																																																																												
C ₇₋₂₄ 		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer (pH 10.5)	 I	25																																																																														
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Yield (%)</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>—(CH₂)₄—</td> <td></td> <td>(77)</td> <td>81</td> </tr> <tr> <td>Me</td> <td>Me</td> <td><i>t</i>-Bu</td> <td>(35)</td> <td>91</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Me</td> <td>(89)</td> <td>97</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Ph</td> <td>(93)</td> <td>76</td> </tr> <tr> <td>Ph</td> <td>—(CH₂)₄—</td> <td></td> <td>(94)</td> <td>98</td> </tr> <tr> <td>EtO₂C(CH₂)₂</td> <td>Me</td> <td><i>c</i>-C₆H₁₁</td> <td>(77)</td> <td>81</td> </tr> <tr> <td>EtO₂C(CH₂)₂</td> <td>Me</td> <td><i>n</i>-C₆H₁₃</td> <td>(89)</td> <td>94</td> </tr> <tr> <td>Me</td> <td>Me</td> <td><i>n</i>-C₁₀H₂₁</td> <td>(97)</td> <td>87</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Ph</td> <td>(89)</td> <td>96</td> </tr> <tr> <td>Et</td> <td>Et</td> <td><i>n</i>-C₁₀H₂₁</td> <td>(94)</td> <td>89</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Yield (%)	% ee	Me	—(CH ₂) ₄ —		(77)	81	Me	Me	<i>t</i> -Bu	(35)	91	Ph	Me	Me	(89)	97	Me	Me	Ph	(93)	76	Ph	—(CH ₂) ₄ —		(94)	98	EtO ₂ C(CH ₂) ₂	Me	<i>c</i> -C ₆ H ₁₁	(77)	81	EtO ₂ C(CH ₂) ₂	Me	<i>n</i> -C ₆ H ₁₃	(89)	94	Me	Me	<i>n</i> -C ₁₀ H ₂₁	(97)	87	Ph	Me	Ph	(89)	96	Et	Et	<i>n</i> -C ₁₀ H ₂₁	(94)	89																								
			R ¹	R ²	R ³	Yield (%)	% ee																																																																											
			Me	—(CH ₂) ₄ —		(77)	81																																																																											
			Me	Me	<i>t</i> -Bu	(35)	91																																																																											
			Ph	Me	Me	(89)	97																																																																											
			Me	Me	Ph	(93)	76																																																																											
			Ph	—(CH ₂) ₄ —		(94)	98																																																																											
			EtO ₂ C(CH ₂) ₂	Me	<i>c</i> -C ₆ H ₁₁	(77)	81																																																																											
			EtO ₂ C(CH ₂) ₂	Me	<i>n</i> -C ₆ H ₁₃	(89)	94																																																																											
		Me	Me	<i>n</i> -C ₁₀ H ₂₁	(97)	87																																																																												
		Ph	Me	Ph	(89)	96																																																																												
		Et	Et	<i>n</i> -C ₁₀ H ₂₁	(94)	89																																																																												
		Oxone [®] , K ₂ CO ₃ , DME (DMM), K ₂ CO ₃ /AcOH buffer (pH 10.5)	I	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Temp</th> <th>Time</th> <th>Yield (%)</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>—(CH₂)₄—</td> <td></td> <td>-15°</td> <td>4 h</td> <td>(100)</td> <td>12</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>-15°</td> <td>4 h</td> <td>(79)</td> <td>69</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CH₂Cl</td> <td>0°</td> <td>6 h</td> <td>(95)</td> <td>82</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CH₂Cl</td> <td>-10°</td> <td>6 h</td> <td>(95)</td> <td>84</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>-15°</td> <td>4 h</td> <td>(94)</td> <td>80</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>MeCO</td> <td>0°</td> <td>8 h</td> <td>(75)</td> <td>82</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CO₂Me</td> <td>0°</td> <td>8 h</td> <td>(35)</td> <td>89</td> </tr> <tr> <td><i>n</i>-Bu</td> <td>—(CH₂)₄—</td> <td></td> <td>-15°</td> <td>4 h</td> <td>(96)</td> <td>13</td> </tr> <tr> <td>Ph</td> <td>—(CH₂)₄—</td> <td></td> <td>-10°</td> <td>4 h</td> <td>(94)</td> <td>85</td> </tr> <tr> <td>Ph</td> <td>H</td> <td><i>i</i>-PrCO</td> <td>0°</td> <td>8 h</td> <td>(70)</td> <td>89</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Temp	Time	Yield (%)	% ee	Me	—(CH ₂) ₄ —		-15°	4 h	(100)	12	Ph	H	H	-15°	4 h	(79)	69	Ph	H	CH ₂ Cl	0°	6 h	(95)	82	Ph	H	CH ₂ Cl	-10°	6 h	(95)	84	Ph	H	Me	-15°	4 h	(94)	80	Ph	H	MeCO	0°	8 h	(75)	82	Ph	H	CO ₂ Me	0°	8 h	(35)	89	<i>n</i> -Bu	—(CH ₂) ₄ —		-15°	4 h	(96)	13	Ph	—(CH ₂) ₄ —		-10°	4 h	(94)	85	Ph	H	<i>i</i> -PrCO	0°	8 h	(70)	89	115, 114
				R ¹	R ²	R ³	Temp	Time	Yield (%)	% ee																																																																								
				Me	—(CH ₂) ₄ —		-15°	4 h	(100)	12																																																																								
				Ph	H	H	-15°	4 h	(79)	69																																																																								
				Ph	H	CH ₂ Cl	0°	6 h	(95)	82																																																																								
				Ph	H	CH ₂ Cl	-10°	6 h	(95)	84																																																																								
				Ph	H	Me	-15°	4 h	(94)	80																																																																								
Ph	H			MeCO	0°	8 h	(75)	82																																																																										
Ph	H			CO ₂ Me	0°	8 h	(35)	89																																																																										
<i>n</i> -Bu	—(CH ₂) ₄ —				-15°	4 h	(96)	13																																																																										
Ph	—(CH ₂) ₄ —		-10°	4 h	(94)	85																																																																												
Ph	H	<i>i</i> -PrCO	0°	8 h	(70)	89																																																																												

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

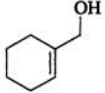
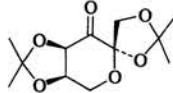
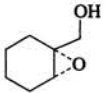
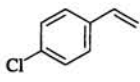
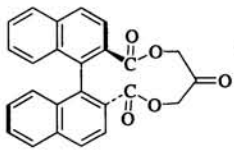
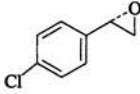

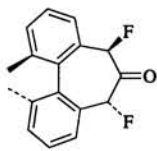


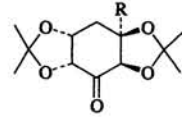

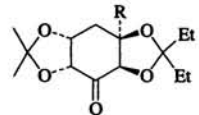

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee) Refs.																																																							
		Oxone [®] , CH ₃ CN/DMM, K ₂ CO ₃ /AcOH buffer, -10°	 (83) 92% ee 124, 123																																																							
C ₈ 		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 60 min	 (83) 18% ee 24																																																							
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/H ₂ O, 0°	 11																																																							
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>4-ClC₆H₄</td> <td>H</td> <td>H</td> <td>30 h (55)</td> <td>43</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>10 h (80)</td> <td>88</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CH₂OH</td> <td>7 h (93)</td> <td>89</td> </tr> <tr> <td>Ph</td> <td>—(CH₂)₄—</td> <td></td> <td>4 h (78)</td> <td>59</td> </tr> <tr> <td>Me</td> <td>H</td> <td>(CH₂)₃OBn</td> <td>11 h (72)</td> <td>68</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Ph</td> <td>72 h (46)</td> <td>94</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Time	% ee	4-ClC ₆ H ₄	H	H	30 h (55)	43	Ph	H	Me	10 h (80)	88	Ph	H	CH ₂ OH	7 h (93)	89	Ph	—(CH ₂) ₄ —		4 h (78)	59	Me	H	(CH ₂) ₃ OBn	11 h (72)	68	Ph	H	Ph	72 h (46)	94																				
R ¹	R ²	R ³	Time	% ee																																																						
4-ClC ₆ H ₄	H	H	30 h (55)	43																																																						
Ph	H	Me	10 h (80)	88																																																						
Ph	H	CH ₂ OH	7 h (93)	89																																																						
Ph	—(CH ₂) ₄ —		4 h (78)	59																																																						
Me	H	(CH ₂) ₃ OBn	11 h (72)	68																																																						
Ph	H	Ph	72 h (46)	94																																																						
		Oxone [®] , K ₂ CO ₃ , DME, K ₂ CO ₃ /AcOH buffer	 I 115, 114																																																							
			<table border="1"> <thead> <tr> <th>R</th> <th>Temp</th> <th>Time</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>-15°</td> <td>6 h</td> <td>13</td> <td>67</td> </tr> <tr> <td>CH₂F</td> <td>-15°</td> <td>4 h</td> <td>76</td> <td>67</td> </tr> <tr> <td>CO₂Me</td> <td>-10°</td> <td>4 h</td> <td>90</td> <td>67</td> </tr> <tr> <td>CH₂OAc</td> <td>-10°</td> <td>4 h</td> <td>96</td> <td>65</td> </tr> <tr> <td>CMe₂OH</td> <td>-15°</td> <td>4 h</td> <td>79</td> <td>69</td> </tr> <tr> <td>CMe₂OMe</td> <td>-15°</td> <td>4 h</td> <td>100</td> <td>70</td> </tr> <tr> <td>CH₂OTBDMS</td> <td>-10°</td> <td>4 h</td> <td>100</td> <td>66</td> </tr> <tr> <td>CH₂OBz</td> <td>-10°</td> <td>4 h</td> <td>99</td> <td>65</td> </tr> <tr> <td>CH₂OTs</td> <td>-10°</td> <td>4 h</td> <td>70</td> <td>67</td> </tr> <tr> <td>CPh₂OH</td> <td>-15°</td> <td>1 h</td> <td>7</td> <td>59</td> </tr> </tbody> </table>	R	Temp	Time	% Convn	% ee	H	-15°	6 h	13	67	CH ₂ F	-15°	4 h	76	67	CO ₂ Me	-10°	4 h	90	67	CH ₂ OAc	-10°	4 h	96	65	CMe ₂ OH	-15°	4 h	79	69	CMe ₂ OMe	-15°	4 h	100	70	CH ₂ OTBDMS	-10°	4 h	100	66	CH ₂ OBz	-10°	4 h	99	65	CH ₂ OTs	-10°	4 h	70	67	CPh ₂ OH	-15°	1 h	7	59
R	Temp	Time	% Convn	% ee																																																						
H	-15°	6 h	13	67																																																						
CH ₂ F	-15°	4 h	76	67																																																						
CO ₂ Me	-10°	4 h	90	67																																																						
CH ₂ OAc	-10°	4 h	96	65																																																						
CMe ₂ OH	-15°	4 h	79	69																																																						
CMe ₂ OMe	-15°	4 h	100	70																																																						
CH ₂ OTBDMS	-10°	4 h	100	66																																																						
CH ₂ OBz	-10°	4 h	99	65																																																						
CH ₂ OTs	-10°	4 h	70	67																																																						
CPh ₂ OH	-15°	1 h	7	59																																																						
		Oxone [®] , K ₂ CO ₃ , DME/ DMM, K ₂ CO ₃ /AcOH buffer, -15°, 4 h	 I <table border="1"> <thead> <tr> <th>R</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>CO₂Me</td> <td>94</td> <td>60</td> </tr> <tr> <td>CH₂OAc</td> <td>66</td> <td>67</td> </tr> <tr> <td>CMe₂OH</td> <td>31</td> <td>65</td> </tr> </tbody> </table> 115, 114	R	% Convn	% ee	CO ₂ Me	94	60	CH ₂ OAc	66	67	CMe ₂ OH	31	65																																											
R	% Convn	% ee																																																								
CO ₂ Me	94	60																																																								
CH ₂ OAc	66	67																																																								
CMe ₂ OH	31	65																																																								

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

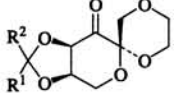
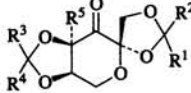
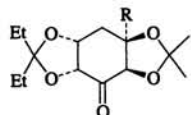
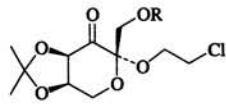
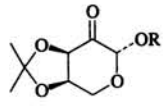
Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.							
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	R ¹	R ²	% Convn	% ee	119			
			Me	Me	38	38				
			—(CH ₂) ₄ —		39	37				
			Et	Et	42	42				
			—(CH ₂) ₅ —		42	36				
			<i>n</i> -Pr	<i>n</i> -Pr	29	43				
			Ph	Ph	30	20				
			Bn	Bn	6	21				
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	R ¹	R ²	R ³	R ⁴	R ⁵	% Convn	% ee	119
			Me	Me	Me	Me	F	8	32	
			Me	Me	Me	Me	H	100	15	
			Me	Me	Et	H	H	79	10	
			Me	Me	<i>i</i> -Pr	H	H	60	7	
			Me	Me	—(CH ₂) ₄ —		H	100	18	
			—(CH ₂) ₄ —		Me	Me	H	92	27	
			Me	Me	Et	Et	H	92	16	
			Et	Et	Me	Me	H	77	12	
			Me	Me	—(CH ₂) ₅ —		H	77	17	
			—(CH ₂) ₅ —		Me	Me	H	93	16	
			—(CH ₂) ₄ —		—(CH ₂) ₄ —		H	100	30	
			Et	Et	Et	Et	H	26	12	
			—(CH ₂) ₅ —		—(CH ₂) ₅ —		H	59	14	
			—(CH ₂) ₆ —		—(CH ₂) ₆ —		H	43	17	
			Me	Me	Bn	Bn	H	6	3 (S)	
	Oxone [®] , K ₂ CO ₃ , DME/ DMM, K ₂ CO ₃ /AcOH buffer, -15°, 4 h	I	R	% Convn	% ee	115, 114				
			CO ₂ Me	77	65					
			CH ₂ OAc	100	62					
			CMe ₂ OH	80	65					
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	R	% Convn	% ee	119				
			H	0	—					
			Ac	5	23					
			TBDMS	0	—					
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	R	% Convn	% ee	119				
			Me	14	27					
			(CH ₂) ₂ Cl	15	29					

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee) Refs.																																																																																				
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I (40) 10% ee 119																																																																																				
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I (41) 15% ee 119																																																																																				
C ₈₋₁₀ 		Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, -10°, 2 h	I <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>(64) 14</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>(81) 28</td> </tr> <tr> <td><i>i</i>-Pr₃SiCH₂</td> <td>H</td> <td>(92) 35</td> </tr> <tr> <td><i>n</i>-C₈H₁₇</td> <td>H</td> <td>(80) 27</td> </tr> </tbody> </table> 25	R ¹	R ²	% ee	Ph	H	(64) 14	Ph	Me	(81) 28	<i>i</i> -Pr ₃ SiCH ₂	H	(92) 35	<i>n</i> -C ₈ H ₁₇	H	(80) 27																																																																					
R ¹	R ²	% ee																																																																																					
Ph	H	(64) 14																																																																																					
Ph	Me	(81) 28																																																																																					
<i>i</i> -Pr ₃ SiCH ₂	H	(92) 35																																																																																					
<i>n</i> -C ₈ H ₁₇	H	(80) 27																																																																																					
	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, -10°, 2 h	I <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>(90) 24</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>(95) 20</td> </tr> <tr> <td><i>i</i>-Pr₃SiCH₂</td> <td>H</td> <td>(99) 31</td> </tr> <tr> <td><i>n</i>-C₈H₁₇</td> <td>H</td> <td>(92) 17</td> </tr> </tbody> </table> 25	R ¹	R ²	% ee	Ph	H	(90) 24	Ph	Me	(95) 20	<i>i</i> -Pr ₃ SiCH ₂	H	(99) 31	<i>n</i> -C ₈ H ₁₇	H	(92) 17																																																																					
R ¹	R ²	% ee																																																																																					
Ph	H	(90) 24																																																																																					
Ph	Me	(95) 20																																																																																					
<i>i</i> -Pr ₃ SiCH ₂	H	(99) 31																																																																																					
<i>n</i> -C ₈ H ₁₇	H	(92) 17																																																																																					
C ₈₋₂₀ 		Oxone [®] , K ₂ CO ₃ , DME (DMM), K ₂ CO ₃ / AcOH buffer	I <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Temp</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>-10°</td> <td>4 h</td> <td>(90) 65</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CH₂Cl</td> <td>0°</td> <td>5 h</td> <td>(94) 77</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>-15°</td> <td>4 h</td> <td>(92) 75</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>H</td> <td>-10°</td> <td>3 h</td> <td>(92) 52</td> </tr> <tr> <td><i>n</i>-C₈H₁₇</td> <td>H</td> <td>H</td> <td>-10°</td> <td>4 h</td> <td>(85) 15</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CO₂Et</td> <td>0°</td> <td>8 h</td> <td>(34) 86</td> </tr> <tr> <td>2-Naphthyl</td> <td>H</td> <td>H</td> <td>-10°</td> <td>4 h</td> <td>(89) 54</td> </tr> <tr> <td>Ph</td> <td>-(CH₂)₄-</td> <td>-(CH₂)₄-</td> <td>-10°</td> <td>4 h</td> <td>(95) 68</td> </tr> <tr> <td>(CH₂)₂CO₂Me</td> <td>Me</td> <td>C₆H₁₁</td> <td>-10°</td> <td>4 h</td> <td>(96) 43</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Ph</td> <td>-10°</td> <td>6 h</td> <td>(95) 90</td> </tr> <tr> <td><i>n</i>-C₆H₁₃</td> <td>H</td> <td><i>n</i>-C₆H₁₃</td> <td>-10°</td> <td>4 h</td> <td>(51) 42</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>PhCO</td> <td>0°</td> <td>6 h</td> <td>(80) 94</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>Ph</td> <td>0°</td> <td>5 h</td> <td>(86) 87</td> </tr> </tbody> </table> 115, 114	R ¹	R ²	R ³	Temp	Time	% ee	Ph	H	H	-10°	4 h	(90) 65	Ph	H	CH ₂ Cl	0°	5 h	(94) 77	Ph	H	Me	-15°	4 h	(92) 75	Ph	Me	H	-10°	3 h	(92) 52	<i>n</i> -C ₈ H ₁₇	H	H	-10°	4 h	(85) 15	Ph	H	CO ₂ Et	0°	8 h	(34) 86	2-Naphthyl	H	H	-10°	4 h	(89) 54	Ph	-(CH ₂) ₄ -	-(CH ₂) ₄ -	-10°	4 h	(95) 68	(CH ₂) ₂ CO ₂ Me	Me	C ₆ H ₁₁	-10°	4 h	(96) 43	Ph	H	Ph	-10°	6 h	(95) 90	<i>n</i> -C ₆ H ₁₃	H	<i>n</i> -C ₆ H ₁₃	-10°	4 h	(51) 42	Ph	H	PhCO	0°	6 h	(80) 94	Ph	Ph	Ph	0°	5 h	(86) 87
R ¹	R ²	R ³	Temp	Time	% ee																																																																																		
Ph	H	H	-10°	4 h	(90) 65																																																																																		
Ph	H	CH ₂ Cl	0°	5 h	(94) 77																																																																																		
Ph	H	Me	-15°	4 h	(92) 75																																																																																		
Ph	Me	H	-10°	3 h	(92) 52																																																																																		
<i>n</i> -C ₈ H ₁₇	H	H	-10°	4 h	(85) 15																																																																																		
Ph	H	CO ₂ Et	0°	8 h	(34) 86																																																																																		
2-Naphthyl	H	H	-10°	4 h	(89) 54																																																																																		
Ph	-(CH ₂) ₄ -	-(CH ₂) ₄ -	-10°	4 h	(95) 68																																																																																		
(CH ₂) ₂ CO ₂ Me	Me	C ₆ H ₁₁	-10°	4 h	(96) 43																																																																																		
Ph	H	Ph	-10°	6 h	(95) 90																																																																																		
<i>n</i> -C ₆ H ₁₃	H	<i>n</i> -C ₆ H ₁₃	-10°	4 h	(51) 42																																																																																		
Ph	H	PhCO	0°	6 h	(80) 94																																																																																		
Ph	Ph	Ph	0°	5 h	(86) 87																																																																																		
		Oxone [®] , NaHCO ₃ , MeCN, EDTA, H ₂ O	I <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td><2 h</td> <td>(33) 29</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CO₂Me</td> <td>24 h</td> <td>(33) 64</td> </tr> <tr> <td>Ph</td> <td>-(CH₂)₄-</td> <td>-(CH₂)₄-</td> <td><6 h</td> <td>(97) 69</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>Ph</td> <td><3 h</td> <td>(88) 76</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Ph</td> <td><4 h</td> <td>(100) 73</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>Ph</td> <td><4 h</td> <td>(100) 83</td> </tr> </tbody> </table> 108	R ¹	R ²	R ³	Time	% ee	Ph	H	H	<2 h	(33) 29	Ph	H	CO ₂ Me	24 h	(33) 64	Ph	-(CH ₂) ₄ -	-(CH ₂) ₄ -	<6 h	(97) 69	Ph	H	Ph	<3 h	(88) 76	Ph	Me	Ph	<4 h	(100) 73	Ph	Ph	Ph	<4 h	(100) 83																																																	
R ¹	R ²	R ³	Time	% ee																																																																																			
Ph	H	H	<2 h	(33) 29																																																																																			
Ph	H	CO ₂ Me	24 h	(33) 64																																																																																			
Ph	-(CH ₂) ₄ -	-(CH ₂) ₄ -	<6 h	(97) 69																																																																																			
Ph	H	Ph	<3 h	(88) 76																																																																																			
Ph	Me	Ph	<4 h	(100) 73																																																																																			
Ph	Ph	Ph	<4 h	(100) 83																																																																																			

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.																																																							
C ₈ 		Oxone®, K ₂ CO ₃ , CH ₃ CN/ DMM, K ₂ CO ₃ /AcOH buffer, -10°, 3 h	 (75) 94% ee 123, 124																																																							
C ₈₋₁₁ 		Oxone®, K ₂ CO ₃ , CH ₃ CN/ DMM, K ₂ CO ₃ /AcOH buffer	 <table border="1"> <thead> <tr> <th>R</th> <th>Temp</th> <th>Time</th> <th>% ee</th> <th>Refs.</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>-10°</td> <td>3 h</td> <td>(78) 93</td> <td>123,</td> </tr> <tr> <td>Me</td> <td>-10°</td> <td>3 h</td> <td>(88) 90</td> <td>124</td> </tr> <tr> <td>CO₂Et</td> <td>0°</td> <td>2 h</td> <td>(71) 93</td> <td></td> </tr> <tr> <td>TMS</td> <td>-10°</td> <td>3 h</td> <td>(86) 93</td> <td></td> </tr> </tbody> </table>	R	Temp	Time	% ee	Refs.	H	-10°	3 h	(78) 93	123,	Me	-10°	3 h	(88) 90	124	CO ₂ Et	0°	2 h	(71) 93		TMS	-10°	3 h	(86) 93																															
R	Temp	Time	% ee	Refs.																																																						
H	-10°	3 h	(78) 93	123,																																																						
Me	-10°	3 h	(88) 90	124																																																						
CO ₂ Et	0°	2 h	(71) 93																																																							
TMS	-10°	3 h	(86) 93																																																							
C ₈₋₁₄ 		Oxone®, CH ₃ CN (DMM), Na ₂ B ₄ O ₇ (or K ₂ CO ₃ / AcOH) buffer, 0°	 <table border="1"> <thead> <tr> <th>n</th> <th>R</th> <th>Time</th> <th>% ee</th> <th>Refs.</th> </tr> </thead> <tbody> <tr> <td>2</td> <td>Ac</td> <td>2.0 h</td> <td>(59) 74</td> <td>121</td> </tr> <tr> <td>1</td> <td>PhCO</td> <td>1.5 h</td> <td>(79) 80</td> <td></td> </tr> <tr> <td>2</td> <td>PhCO</td> <td>1.5 h</td> <td>(82) 93</td> <td></td> </tr> <tr> <td>3</td> <td>PhCO</td> <td>1.5 h</td> <td>(87) 91</td> <td></td> </tr> <tr> <td>4</td> <td>PhCO</td> <td>1.5 h</td> <td>(82) 95</td> <td></td> </tr> </tbody> </table>	n	R	Time	% ee	Refs.	2	Ac	2.0 h	(59) 74	121	1	PhCO	1.5 h	(79) 80		2	PhCO	1.5 h	(82) 93		3	PhCO	1.5 h	(87) 91		4	PhCO	1.5 h	(82) 95																										
n	R	Time	% ee	Refs.																																																						
2	Ac	2.0 h	(59) 74	121																																																						
1	PhCO	1.5 h	(79) 80																																																							
2	PhCO	1.5 h	(82) 93																																																							
3	PhCO	1.5 h	(87) 91																																																							
4	PhCO	1.5 h	(82) 95																																																							
C ₈ 		Oxone®, K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer (pH 10.5), EDTA, 0°, 4 h	 I (41) 96% ee II I + II (→) I:II = 7:1 122																																																							
		Oxone®, K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, -10°, 2 h	 I (50) 56% ee 25																																																							
		Oxone®, K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, -10°, 2 h	 I (43) 61% ee 25																																																							
		Oxone®, K ₂ CO ₃ , DME, K ₂ CO ₃ /AcOH buffer, -10°	 <table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>% Convn</th> <th>% ee</th> <th>Refs.</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>6 h</td> <td>9</td> <td>66</td> <td>115,</td> </tr> <tr> <td>CH₂F</td> <td>6 h</td> <td>66</td> <td>71</td> <td>114</td> </tr> <tr> <td>CO₂Me</td> <td>6 h</td> <td>56</td> <td>66</td> <td></td> </tr> <tr> <td>CH₂OAc</td> <td>6 h</td> <td>82</td> <td>68</td> <td></td> </tr> <tr> <td>CMe₂OH</td> <td>1 h</td> <td>55</td> <td>45</td> <td></td> </tr> <tr> <td>CMe₂OMe</td> <td>6 h</td> <td>47</td> <td>40</td> <td></td> </tr> <tr> <td>CH₂OTBDMS</td> <td>6 h</td> <td>70</td> <td>73</td> <td></td> </tr> <tr> <td>CH₂OBz</td> <td>6 h</td> <td>67</td> <td>71</td> <td></td> </tr> <tr> <td>CH₂OTs</td> <td>6 h</td> <td>62</td> <td>71</td> <td></td> </tr> <tr> <td>CPh₂OH</td> <td>6 h</td> <td>7</td> <td>88</td> <td></td> </tr> </tbody> </table>	R	Time	% Convn	% ee	Refs.	H	6 h	9	66	115,	CH ₂ F	6 h	66	71	114	CO ₂ Me	6 h	56	66		CH ₂ OAc	6 h	82	68		CMe ₂ OH	1 h	55	45		CMe ₂ OMe	6 h	47	40		CH ₂ OTBDMS	6 h	70	73		CH ₂ OBz	6 h	67	71		CH ₂ OTs	6 h	62	71		CPh ₂ OH	6 h	7	88	
R	Time	% Convn	% ee	Refs.																																																						
H	6 h	9	66	115,																																																						
CH ₂ F	6 h	66	71	114																																																						
CO ₂ Me	6 h	56	66																																																							
CH ₂ OAc	6 h	82	68																																																							
CMe ₂ OH	1 h	55	45																																																							
CMe ₂ OMe	6 h	47	40																																																							
CH ₂ OTBDMS	6 h	70	73																																																							
CH ₂ OBz	6 h	67	71																																																							
CH ₂ OTs	6 h	62	71																																																							
CPh ₂ OH	6 h	7	88																																																							
		Oxone®, K ₂ CO ₃ , DME, K ₂ CO ₃ /AcOH buffer, -10°, 6 h	 I (78) 68% ee 115, 114																																																							
		R = CH ₂ OAc																																																								

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

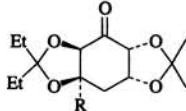
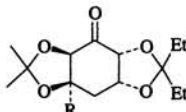
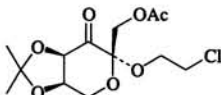
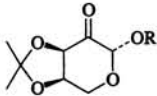
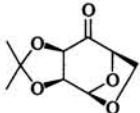
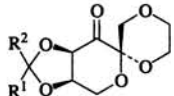
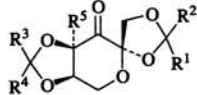
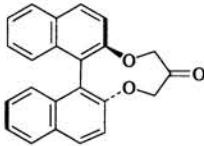
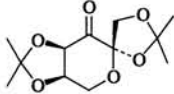
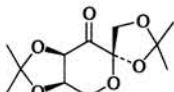
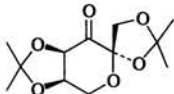
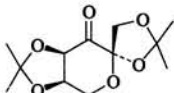
Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee) Refs.								
	Oxone [®] , K ₂ CO ₃ , DME, K ₂ CO ₃ /AcOH buffer,	-10°, 6 h	I	R	% Convn	% ee	115, 114				
				CO ₂ Me	41	65					
				CH ₂ OAc	73	62					
				CMe ₂ OH	47	44					
	Oxone [®] , K ₂ CO ₃ , DME, K ₂ CO ₃ /AcOH buffer,	-10°, 6 h	I	R	% Convn	% ee	115, 114				
				CO ₂ Me	59	61					
				CH ₂ OAc	75	63					
				CMe ₂ OH	61	42					
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h		I (8)	44% ee			119				
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h		I	R	% Convn	% ee	119				
				Me	13	42					
				(CH ₂) ₂ Cl	9	41					
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h		I (0)				119				
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h		I	R ¹	R ²	% Convn	% ee	119			
				Me	Me	30	60				
				—(CH ₂) ₄ —		29	57				
				Et	Et	24	49				
				—(CH ₂) ₅ —		31	52				
				<i>n</i> -Pr	<i>n</i> -Pr	13	46				
				Ph	Ph	8	4				
			Bn	Bn	8	39					
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h		I	R ¹	R ²	R ³	R ⁴	R ⁵	% Convn	% ee	119
				Me	Me	Me	Me	F	23	12	
				Me	Me	Me	Me	H	53	51	
				Me	Me	Et	H	H	55	42	
				Me	Me	<i>i</i> -Pr	H	H	55	43	
				Me	Me	—(CH ₂) ₄ —	H	H	56	48	
				—(CH ₂) ₄ —	Me	Me	H	H	57	49	
				Me	Me	Et	Et	H	19	43	
				Et	Et	Me	Me	H	24	55	
				Me	Me	—(CH ₂) ₅ —	H	H	46	46	
				—(CH ₂) ₅ —	Me	Me	H	H	50	52	
				—(CH ₂) ₄ —	—(CH ₂) ₄ —	H	H	73	47		
				Et	Et	Et	Et	H	17	47	
				—(CH ₂) ₅ —	—(CH ₂) ₅ —	H	H	43	44		
				—(CH ₂) ₆ —	—(CH ₂) ₆ —	H	H	6	51		
				Me	Me	Bn	Bn	H	0	—	

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.																																																																	
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	(46) 71% ee 119																																																																	
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, Na ₂ B ₄ O ₇ buffer (pH 10.5), EDTA, 0°, 1.5 h	(68) 90% ee 122																																																																	
		Oxone [®] , CH ₂ Cl ₂ /H ₂ O (pH 7.5), Bu ₄ NHSO ₄ , 2 to 5°, 48 h	(70) 20% ee 106																																																																	
		Oxone [®] , CH ₂ Cl ₂ /H ₂ O (pH 7.5), Bu ₄ NHSO ₄ , 2 to 5°, 48 h	(68) 18% ee 106																																																																	
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA	25																																																																	
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time</th> <th>Temp</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>CH₂Cl</td> <td>1.5 h</td> <td>0°</td> <td>(49) 96</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>2 h</td> <td>-10°</td> <td>(94) 96</td> </tr> <tr> <td>2-MeC₆H₄</td> <td>Me</td> <td>2 h</td> <td>-10°</td> <td>(91) 93</td> </tr> <tr> <td>2-MeC₆H₄</td> <td><i>i</i>-Pr</td> <td>2 h</td> <td>-10°</td> <td>(78) 96</td> </tr> <tr> <td><i>n</i>-Pr</td> <td>CH₂OTBDMS</td> <td>2 h</td> <td>-10°</td> <td>(83) 95</td> </tr> <tr> <td>Et</td> <td>(CH₂)₂OTBDMS</td> <td>2 h</td> <td>-10°</td> <td>(85) 93</td> </tr> <tr> <td>Bn</td> <td>(CH₂)₂CO₂Me</td> <td>1.5 h</td> <td>0°</td> <td>(68) 92</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>0.5 h</td> <td>20°</td> <td>(85) 98</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>1.5 h</td> <td>0°</td> <td>(78) 99</td> </tr> <tr> <td><i>n</i>-C₆H₁₃</td> <td><i>n</i>-C₆H₁₃</td> <td>2 h</td> <td>-10°</td> <td>(89) 95</td> </tr> <tr> <td>Ph</td> <td>CH₂OTBDMS</td> <td>1.5 h</td> <td>0°</td> <td>(71) 95</td> </tr> <tr> <td>Ph</td> <td>CH₂OTr</td> <td>1.5 h</td> <td>0°</td> <td>(55) 94</td> </tr> </tbody> </table>	R ¹	R ²	Time	Temp	% ee	Ph	CH ₂ Cl	1.5 h	0°	(49) 96	Ph	Me	2 h	-10°	(94) 96	2-MeC ₆ H ₄	Me	2 h	-10°	(91) 93	2-MeC ₆ H ₄	<i>i</i> -Pr	2 h	-10°	(78) 96	<i>n</i> -Pr	CH ₂ OTBDMS	2 h	-10°	(83) 95	Et	(CH ₂) ₂ OTBDMS	2 h	-10°	(85) 93	Bn	(CH ₂) ₂ CO ₂ Me	1.5 h	0°	(68) 92	Ph	Ph	0.5 h	20°	(85) 98	Ph	Ph	1.5 h	0°	(78) 99	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₆ H ₁₃	2 h	-10°	(89) 95	Ph	CH ₂ OTBDMS	1.5 h	0°	(71) 95	Ph	CH ₂ OTr	1.5 h	0°	(55) 94
R ¹	R ²	Time	Temp	% ee																																																																
Ph	CH ₂ Cl	1.5 h	0°	(49) 96																																																																
Ph	Me	2 h	-10°	(94) 96																																																																
2-MeC ₆ H ₄	Me	2 h	-10°	(91) 93																																																																
2-MeC ₆ H ₄	<i>i</i> -Pr	2 h	-10°	(78) 96																																																																
<i>n</i> -Pr	CH ₂ OTBDMS	2 h	-10°	(83) 95																																																																
Et	(CH ₂) ₂ OTBDMS	2 h	-10°	(85) 93																																																																
Bn	(CH ₂) ₂ CO ₂ Me	1.5 h	0°	(68) 92																																																																
Ph	Ph	0.5 h	20°	(85) 98																																																																
Ph	Ph	1.5 h	0°	(78) 99																																																																
<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₆ H ₁₃	2 h	-10°	(89) 95																																																																
Ph	CH ₂ OTBDMS	1.5 h	0°	(71) 95																																																																
Ph	CH ₂ OTr	1.5 h	0°	(55) 94																																																																
		Oxone [®] , CH ₂ Cl ₂ , buffer, Bu ₄ NHSO ₄ , 5°	I (60) 12% ee 105																																																																	
		Oxone [®] , CH ₂ Cl ₂ , buffer, Bu ₄ NHSO ₄ , 5°	I (85) 9.5% ee 105																																																																	
		Oxone [®] , CH ₂ Cl ₂ /H ₂ O (pH 7.5), Bu ₄ NHSO ₄ , 2 to 5°, 40 h	I (71) 13% ee 106																																																																	
		Oxone [®] , CH ₂ Cl ₂ /H ₂ O (pH 7.5), Bu ₄ NHSO ₄ , 2 to 5°, 42 h	I (61) 18% ee 106																																																																	

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.																								
		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 1 h	I (61) 29% ee 112																								
		H ₂ O ₂ , CH ₃ CN, K ₂ CO ₃ buffer, EDTA, 0°, 7 h	I (84) 92% ee 368																								
		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, 0°	I <table border="1"> <thead> <tr> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>1 h (31)</td> <td>>95</td> </tr> <tr> <td>2 h (39)</td> <td>>95</td> </tr> <tr> <td>4 h (40)</td> <td>89</td> </tr> <tr> <td>8 h (47)</td> <td>85</td> </tr> </tbody> </table>	Time	% ee	1 h (31)	>95	2 h (39)	>95	4 h (40)	89	8 h (47)	85														
Time	% ee																										
1 h (31)	>95																										
2 h (39)	>95																										
4 h (40)	89																										
8 h (47)	85																										
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA	I <table border="1"> <thead> <tr> <th>Temp</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>-11°</td> <td>99</td> <td>96</td> </tr> <tr> <td>-6°</td> <td>97</td> <td>95</td> </tr> <tr> <td>-2°</td> <td>98</td> <td>95</td> </tr> <tr> <td>2°</td> <td>99</td> <td>95</td> </tr> <tr> <td>8°</td> <td>99</td> <td>94</td> </tr> <tr> <td>20°</td> <td>99</td> <td>93</td> </tr> <tr> <td>30°</td> <td>97</td> <td>91</td> </tr> </tbody> </table>	Temp	% Convn	% ee	-11°	99	96	-6°	97	95	-2°	98	95	2°	99	95	8°	99	94	20°	99	93	30°	97	91
Temp	% Convn	% ee																									
-11°	99	96																									
-6°	97	95																									
-2°	98	95																									
2°	99	95																									
8°	99	94																									
20°	99	93																									
30°	97	91																									
		Oxone [®] , K ₂ CO ₃ , solvent, Na ₂ B ₄ O ₇ buffer, EDTA	I 25																								

Solvent	Time	Temp	% Convn	% ee
CH ₃ CN	20 min	20°	100	89
CH ₃ CN	1.5 h	0°	96	92
EtCN	1 h	20°	11	80
DMM	1 h	20°	36	91
DME	20 min	20°	100	89
DME	1.5 h	0°	92	89
DMF	20 min	20°	95	86
Dioxane	20 min	20°	100	86
Dioxane	1.5 h	0°	96	86
THF	1 h	20°	18	74
Et ₂ O	1 h	20°	0	—
CH ₂ Cl ₂	0.5 h	20°	<3	—
CH ₃ CN/DMM (2:1)	20 min	20°	100	90
CH ₃ CN/DMM (2:1)	1.5 h	0°	100	92
CH ₃ CN/DMM (1:1)	20 min	20°	98	91
CH ₃ CN/DMM (1:1)	1.5 h	0°	100	93
CH ₃ CN/DMM (1:2)	20 min	20°	94	92
CH ₃ CN/DMM (1:2)	1.5 h	0°	88	94
CH ₃ CN/DMM (1:4)	1.5 h	0°	77	94
DMM/DME (1:1)	25 min	20°	66	92
CH ₃ CN/DMM/DME (1:1:2)	20 min	20°	100	90
CH ₃ CN/DMM/DME (1:7:7)	20 min	20°	89	90
CH ₃ CN/THF (1:1)	25 min	20°	63	82
Et ₂ O/CH ₃ CN (1:1)	25 min	20°	28	84

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

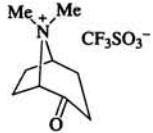
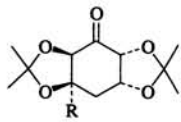
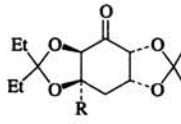
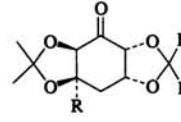
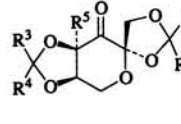
Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.																																																																																																																
	CF_3SO_3^-	Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 5 h	I 21% convn 107																																																																																																																
		Oxone [®] , K ₂ CO ₃ , DME, K ₂ CO ₃ /AcOH buffer, -15°	I																																																																																																																
			<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr><td>H</td><td>4 h</td><td>29</td><td>73</td></tr> <tr><td>CH₂F</td><td>4 h</td><td>78</td><td>73</td></tr> <tr><td>CO₂Me</td><td>4 h</td><td>61</td><td>75</td></tr> <tr><td>CH₂OAc</td><td>4 h</td><td>95</td><td>75</td></tr> <tr><td>CMe₂OH</td><td>4 h</td><td>97</td><td>80</td></tr> <tr><td>CMe₂OMe</td><td>4 h</td><td>95</td><td>80</td></tr> <tr><td>CH₂OTBDMS</td><td>4 h</td><td>77</td><td>73</td></tr> <tr><td>CH₂OBz</td><td>4 h</td><td>76</td><td>72</td></tr> <tr><td>CH₂OTs</td><td>4 h</td><td>60</td><td>72</td></tr> <tr><td>CPh₂OH</td><td>4 h</td><td>7</td><td>50</td></tr> </tbody> </table>	R	Time	% Convn	% ee	H	4 h	29	73	CH ₂ F	4 h	78	73	CO ₂ Me	4 h	61	75	CH ₂ OAc	4 h	95	75	CMe ₂ OH	4 h	97	80	CMe ₂ OMe	4 h	95	80	CH ₂ OTBDMS	4 h	77	73	CH ₂ OBz	4 h	76	72	CH ₂ OTs	4 h	60	72	CPh ₂ OH	4 h	7	50																																																																				
R	Time	% Convn	% ee																																																																																																																
H	4 h	29	73																																																																																																																
CH ₂ F	4 h	78	73																																																																																																																
CO ₂ Me	4 h	61	75																																																																																																																
CH ₂ OAc	4 h	95	75																																																																																																																
CMe ₂ OH	4 h	97	80																																																																																																																
CMe ₂ OMe	4 h	95	80																																																																																																																
CH ₂ OTBDMS	4 h	77	73																																																																																																																
CH ₂ OBz	4 h	76	72																																																																																																																
CH ₂ OTs	4 h	60	72																																																																																																																
CPh ₂ OH	4 h	7	50																																																																																																																
		Oxone [®] , K ₂ CO ₃ , DME, K ₂ CO ₃ /AcOH buffer, -15°, 4 h	I																																																																																																																
			<table border="1"> <thead> <tr> <th>R</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr><td>CO₂Me</td><td>43</td><td>74</td></tr> <tr><td>CH₂OAc</td><td>60</td><td>75</td></tr> <tr><td>CMe₂OH</td><td>35</td><td>76</td></tr> </tbody> </table>	R	% Convn	% ee	CO ₂ Me	43	74	CH ₂ OAc	60	75	CMe ₂ OH	35	76																																																																																																				
R	% Convn	% ee																																																																																																																	
CO ₂ Me	43	74																																																																																																																	
CH ₂ OAc	60	75																																																																																																																	
CMe ₂ OH	35	76																																																																																																																	
		Oxone [®] , K ₂ CO ₃ , DME, K ₂ CO ₃ /AcOH buffer, -15°, 4 h	I																																																																																																																
			<table border="1"> <thead> <tr> <th>R</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr><td>CO₂Me</td><td>78</td><td>77</td></tr> <tr><td>CH₂OAc</td><td>100</td><td>72</td></tr> <tr><td>CMe₂OH</td><td>100</td><td>79</td></tr> </tbody> </table>	R	% Convn	% ee	CO ₂ Me	78	77	CH ₂ OAc	100	72	CMe ₂ OH	100	79																																																																																																				
R	% Convn	% ee																																																																																																																	
CO ₂ Me	78	77																																																																																																																	
CH ₂ OAc	100	72																																																																																																																	
CMe ₂ OH	100	79																																																																																																																	
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I																																																																																																																
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>R⁵</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr><td>Me</td><td>Me</td><td>Me</td><td>Me</td><td>F</td><td>11</td><td>5</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>Me</td><td>H</td><td>93</td><td>92</td></tr> <tr><td>Me</td><td>Me</td><td>Et</td><td>H</td><td>H</td><td>79</td><td>91</td></tr> <tr><td>Me</td><td>Me</td><td><i>i</i>-Pr</td><td>H</td><td>H</td><td>64</td><td>89</td></tr> <tr><td>Me</td><td>Me</td><td>-(CH₂)₄-</td><td>H</td><td>H</td><td>95</td><td>93</td></tr> <tr><td>-(CH₂)₄-</td><td>Me</td><td>Me</td><td>H</td><td>H</td><td>100</td><td>93</td></tr> <tr><td>Me</td><td>Me</td><td>Et</td><td>Et</td><td>H</td><td>91</td><td>93</td></tr> <tr><td>Et</td><td>Et</td><td>Me</td><td>Me</td><td>H</td><td>81</td><td>90</td></tr> <tr><td>Me</td><td>Me</td><td>-(CH₂)₅-</td><td>H</td><td>H</td><td>100</td><td>89</td></tr> <tr><td>-(CH₂)₅-</td><td>Me</td><td>Me</td><td>H</td><td>H</td><td>100</td><td>91</td></tr> <tr><td>-(CH₂)₄-</td><td>-(CH₂)₄-</td><td>H</td><td>H</td><td>H</td><td>89</td><td>94</td></tr> <tr><td>Et</td><td>Et</td><td>Et</td><td>Et</td><td>H</td><td>32</td><td>86</td></tr> <tr><td>-(CH₂)₅-</td><td>-(CH₂)₅-</td><td>H</td><td>H</td><td>H</td><td>51</td><td>87</td></tr> <tr><td>-(CH₂)₆-</td><td>-(CH₂)₆-</td><td>H</td><td>H</td><td>H</td><td>37</td><td>91</td></tr> <tr><td>Me</td><td>Me</td><td>Bn</td><td>Bn</td><td>H</td><td>18</td><td>66</td></tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	R ⁵	% Convn	% ee	Me	Me	Me	Me	F	11	5	Me	Me	Me	Me	H	93	92	Me	Me	Et	H	H	79	91	Me	Me	<i>i</i> -Pr	H	H	64	89	Me	Me	-(CH ₂) ₄ -	H	H	95	93	-(CH ₂) ₄ -	Me	Me	H	H	100	93	Me	Me	Et	Et	H	91	93	Et	Et	Me	Me	H	81	90	Me	Me	-(CH ₂) ₅ -	H	H	100	89	-(CH ₂) ₅ -	Me	Me	H	H	100	91	-(CH ₂) ₄ -	-(CH ₂) ₄ -	H	H	H	89	94	Et	Et	Et	Et	H	32	86	-(CH ₂) ₅ -	-(CH ₂) ₅ -	H	H	H	51	87	-(CH ₂) ₆ -	-(CH ₂) ₆ -	H	H	H	37	91	Me	Me	Bn	Bn	H	18	66
R ¹	R ²	R ³	R ⁴	R ⁵	% Convn	% ee																																																																																																													
Me	Me	Me	Me	F	11	5																																																																																																													
Me	Me	Me	Me	H	93	92																																																																																																													
Me	Me	Et	H	H	79	91																																																																																																													
Me	Me	<i>i</i> -Pr	H	H	64	89																																																																																																													
Me	Me	-(CH ₂) ₄ -	H	H	95	93																																																																																																													
-(CH ₂) ₄ -	Me	Me	H	H	100	93																																																																																																													
Me	Me	Et	Et	H	91	93																																																																																																													
Et	Et	Me	Me	H	81	90																																																																																																													
Me	Me	-(CH ₂) ₅ -	H	H	100	89																																																																																																													
-(CH ₂) ₅ -	Me	Me	H	H	100	91																																																																																																													
-(CH ₂) ₄ -	-(CH ₂) ₄ -	H	H	H	89	94																																																																																																													
Et	Et	Et	Et	H	32	86																																																																																																													
-(CH ₂) ₅ -	-(CH ₂) ₅ -	H	H	H	51	87																																																																																																													
-(CH ₂) ₆ -	-(CH ₂) ₆ -	H	H	H	37	91																																																																																																													
Me	Me	Bn	Bn	H	18	66																																																																																																													

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

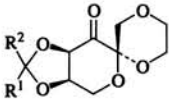
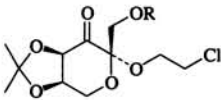
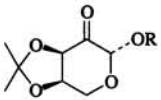
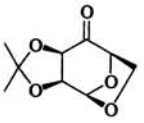
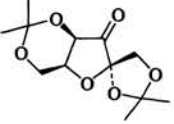
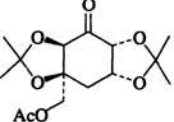
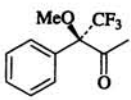
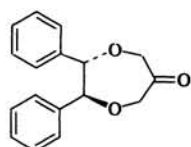
Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee) Refs.																																								
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Me</td> <td>44</td> <td>61</td> </tr> <tr> <td>—(CH₂)₄—</td> <td></td> <td>36</td> <td>61</td> </tr> <tr> <td>Et</td> <td>Et</td> <td>33</td> <td>61</td> </tr> <tr> <td>—(CH₂)₅—</td> <td></td> <td>52</td> <td>52</td> </tr> <tr> <td><i>n</i>-Pr</td> <td><i>n</i>-Pr</td> <td>28</td> <td>82</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>26</td> <td>48</td> </tr> <tr> <td>Bn</td> <td>Bn</td> <td>19</td> <td>56</td> </tr> </tbody> </table>	R ¹	R ²	% Convn	% ee	Me	Me	44	61	—(CH ₂) ₄ —		36	61	Et	Et	33	61	—(CH ₂) ₅ —		52	52	<i>n</i> -Pr	<i>n</i> -Pr	28	82	Ph	Ph	26	48	Bn	Bn	19	56								
R ¹	R ²	% Convn	% ee																																								
Me	Me	44	61																																								
—(CH ₂) ₄ —		36	61																																								
Et	Et	33	61																																								
—(CH ₂) ₅ —		52	52																																								
<i>n</i> -Pr	<i>n</i> -Pr	28	82																																								
Ph	Ph	26	48																																								
Bn	Bn	19	56																																								
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	<table border="1"> <thead> <tr> <th>R</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>8</td> <td>65</td> </tr> <tr> <td>Ac</td> <td>5</td> <td>66</td> </tr> <tr> <td>TBDMS</td> <td>10</td> <td>40</td> </tr> </tbody> </table>	R	% Convn	% ee	H	8	65	Ac	5	66	TBDMS	10	40																												
R	% Convn	% ee																																									
H	8	65																																									
Ac	5	66																																									
TBDMS	10	40																																									
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	<table border="1"> <thead> <tr> <th>R</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>15</td> <td>59</td> </tr> <tr> <td>(CH₂)₂Cl</td> <td>16</td> <td>67</td> </tr> </tbody> </table>	R	% Convn	% ee	Me	15	59	(CH ₂) ₂ Cl	16	67																															
R	% Convn	% ee																																									
Me	15	59																																									
(CH ₂) ₂ Cl	16	67																																									
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I (5)	41% ee																																								
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I (41)	62% ee																																								
	Oxone [®] , K ₂ CO ₃ , Solvent, Na ₂ B ₄ O ₇ buffer, EDTA	I	<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>Time</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>CH₃CN</td> <td>0°</td> <td>4 h</td> <td>58</td> <td>63</td> </tr> <tr> <td>DME</td> <td>0°</td> <td>4 h</td> <td>100</td> <td>70</td> </tr> <tr> <td>DME</td> <td>-10°</td> <td>4 h</td> <td>95</td> <td>73</td> </tr> <tr> <td>DMM</td> <td>0°</td> <td>4 h</td> <td>43</td> <td>66</td> </tr> <tr> <td>Dioxane</td> <td>0°</td> <td>4 h</td> <td>99</td> <td>67</td> </tr> <tr> <td>DMM/CH₃CN (2:1)</td> <td>0°</td> <td>4 h</td> <td>91</td> <td>67</td> </tr> <tr> <td>DMF</td> <td>0°</td> <td>3 h</td> <td>99</td> <td>64</td> </tr> </tbody> </table>	Solvent	Temp	Time	% Convn	% ee	CH ₃ CN	0°	4 h	58	63	DME	0°	4 h	100	70	DME	-10°	4 h	95	73	DMM	0°	4 h	43	66	Dioxane	0°	4 h	99	67	DMM/CH ₃ CN (2:1)	0°	4 h	91	67	DMF	0°	3 h	99	64
Solvent	Temp	Time	% Convn	% ee																																							
CH ₃ CN	0°	4 h	58	63																																							
DME	0°	4 h	100	70																																							
DME	-10°	4 h	95	73																																							
DMM	0°	4 h	43	66																																							
Dioxane	0°	4 h	99	67																																							
DMM/CH ₃ CN (2:1)	0°	4 h	91	67																																							
DMF	0°	3 h	99	64																																							
	Oxone [®] , CH ₂ Cl ₂ /H ₂ O (pH 7.5), Bu ₄ NHSO ₄ , 2 to 5°, 40 h	I (65)	17% ee																																								
	Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 1 h	I (61)	20% ee																																								

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

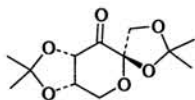
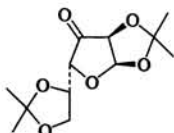
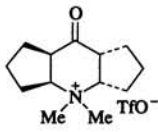

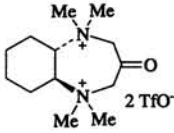
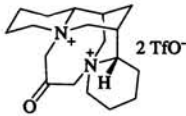
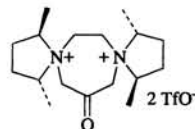
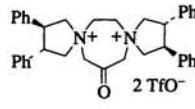
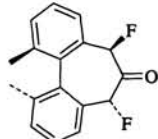
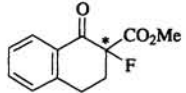

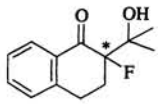
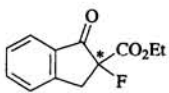
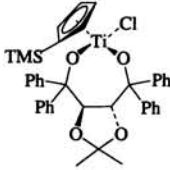
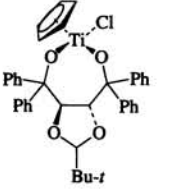
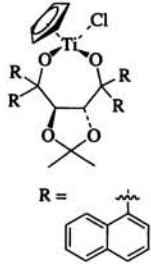

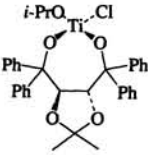

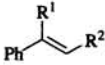
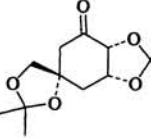

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer, -10°, 2 h	I (94) 96% ee 25
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I (4) 23% ee 119
		—	 11
		Oxone [®] , CH ₃ CN, buffer, 0°, 6 h	I (—) 9% ee 11
		Oxone [®] , CH ₃ CN, buffer, 0°, 2 h	I (—) 40% ee 11
		Oxone [®] , CH ₃ CN, buffer, 0°, 6 h	I (—) 8% ee 11
		Oxone [®] , CH ₃ CN, buffer, 0°, 3 h	I (—) 10% ee 11
		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 8 h	I (—) 71% ee 11
		Oxone [®] , phosphate buffer, CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 0°, 4.5 h	 I (±) (—) 369
		Oxone [®] , phosphate buffer, CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 0°, 4.5 h	I (—) 369
		Oxone [®] , phosphate buffer, CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 0°, 4.5 h	I (—) 369

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.
		Oxone [®] , phosphate buffer, CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 0°, 4.5 h	I (—) 369
C ₉₋₂₄ 		Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, EDTA, 0°, 1.5 h	 R ¹ R ² R ³ R ¹ R ² R ³ % ee Ph H Me (93) 92 Ph H CH ₂ OH (70) 90 <i>n</i> -Bu H <i>n</i> -Bu (70) 91 Bn H (CH ₂) ₂ CO ₂ Me (76) 91 Ph H Ph (75) 97 <i>n</i> -C ₆ H ₁₃ H <i>n</i> -C ₆ H ₁₃ (88) 93 Ph H CH ₂ OTBDMS (87) 94 Ph Ph <i>n</i> -C ₁₀ H ₂₁ (66) 94
C ₉₋₁₄ 		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, 0°, 5 h	 R % ee Me (85) 35 Ph (—) 58 107
C ₉ 		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 210 min	 (70) 18% ee 24
		H ₂ O ₂ , CH ₃ CN, K ₂ CO ₃ buffer, EDTA, 0°, 18 h	 (55) 89% ee 368
		Oxone [®] , K ₂ CO ₃ , DMM/ CH ₃ CN, buffer (pH 9.3), Bu ₄ NHSO ₄ , -10°, 3 h	 (82) 94% ee 149a
		1. LDA, THF, Ar, -78°, 30 min 2. -78°, 3 h 3. DMD, acetone, -78°, 1 min	 I (40) 13% ee 98
	"	1. LDA, THF, Ar, -78°, 30 min 2. -78 to 0°, 3 h 3. DMD, acetone, -78°, 1 min	I (64) 40% ee 98

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.
		1. LDA, THF, Ar, -78°, 30 min 2. -78 to 0°, 3 h 3. DMD, acetone, -78°, 1 min	I (39) 38% ee 98
		1. LDA, THF, Ar, -78°, 30 min 2. -78°, 3 h 3. DMD, acetone, -78°, 1 min	I (36) 13% ee 98
	 <p>R = </p>	1. LDA, THF, Ar, -78°, 30 min 2. -78 to 0°, 3 h 3. DMD, acetone/Et ₂ O, -78°, 1 min	I (18) 63% ee 98
		1. LDA, THF, Ar, -78°, 30 min 2. -78 to 0°, 3 h 3. DMD, acetone, -78°, 1 min	 (24) 5% ee 98
		Oxone®, NaHCO ₃ , solvent, H ₂ O, EDTA	 I (95) 116

Equiv	Solvent	Temp	Time	R ¹	R ²	% Convn	% ee
1	CH ₃ CN	0°	6.5 h	H	CH ₂ OH	26	18
1	CH ₃ CN	20°	5 h	H	Ph	26	62
1	CH ₃ CN	0°	5 h	H	Ph	20	78
1	CH ₃ CN	-10°	6 h	H	Ph	5	75
3	CH ₃ CN	0°	6.5 h	H	Ph	35	85
1	DME	20°	5 h	H	Ph	42	37
1	DME	-10°	6 h	H	Ph	<5	38
1	DMM	0°	5 h	H	Ph	<5	77
1	CH ₂ Cl ₂	0°	5 h	H	Ph	0	—
1	CH ₃ CN	20°	5 h	H	CH ₂ OTBDMS	23	57
3	CH ₃ CN	0°	6.5 h	H	CH ₂ OTBDMS	29	87
3	CH ₃ CN	0°	5 h	Me	Ph	47	70
3	CH ₃ CN	0°	2.5 h	Ph	Ph	36	85
3	CH ₃ CN	-10°	6 h	Ph	Ph	22	84

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.																																																															
		Oxone [®] , solvent, buffer (pH), Na ₂ EDTA, rt	I (95) 113																																																															
		<table border="1"> <thead> <tr> <th>Solvent</th> <th>pH</th> <th>Time</th> <th>R¹</th> <th>R²</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Dioxane</td> <td>8.0</td> <td>240 h</td> <td>H</td> <td>CH₂OH</td> <td>40</td> <td>14</td> </tr> <tr> <td>Dioxane</td> <td>10.5</td> <td>5 h</td> <td>H</td> <td>CH₂OH</td> <td>51</td> <td>80</td> </tr> <tr> <td>CH₃CN</td> <td>8.0</td> <td>72 h</td> <td>H</td> <td>Ph</td> <td>39</td> <td>1</td> </tr> <tr> <td>Dioxane</td> <td>8.0</td> <td>168 h</td> <td>H</td> <td>Ph</td> <td>54</td> <td>33</td> </tr> <tr> <td>Dioxane</td> <td>10.5</td> <td>5 h</td> <td>H</td> <td>Ph</td> <td>67</td> <td>65</td> </tr> <tr> <td>Dioxane</td> <td>10.5</td> <td>5 h</td> <td>H</td> <td>CH₂OTBDMS</td> <td>78</td> <td>77</td> </tr> <tr> <td>Dioxane</td> <td>8.0</td> <td>84 h</td> <td>Ph</td> <td>Ph</td> <td>55</td> <td>66</td> </tr> <tr> <td>Dioxane</td> <td>10.5</td> <td>5 h</td> <td>Ph</td> <td>Ph</td> <td>70</td> <td>81</td> </tr> </tbody> </table>	Solvent	pH	Time	R ¹	R ²	% Convn	% ee	Dioxane	8.0	240 h	H	CH ₂ OH	40	14	Dioxane	10.5	5 h	H	CH ₂ OH	51	80	CH ₃ CN	8.0	72 h	H	Ph	39	1	Dioxane	8.0	168 h	H	Ph	54	33	Dioxane	10.5	5 h	H	Ph	67	65	Dioxane	10.5	5 h	H	CH ₂ OTBDMS	78	77	Dioxane	8.0	84 h	Ph	Ph	55	66	Dioxane	10.5	5 h	Ph	Ph	70	81	
Solvent	pH	Time	R ¹	R ²	% Convn	% ee																																																												
Dioxane	8.0	240 h	H	CH ₂ OH	40	14																																																												
Dioxane	10.5	5 h	H	CH ₂ OH	51	80																																																												
CH ₃ CN	8.0	72 h	H	Ph	39	1																																																												
Dioxane	8.0	168 h	H	Ph	54	33																																																												
Dioxane	10.5	5 h	H	Ph	67	65																																																												
Dioxane	10.5	5 h	H	CH ₂ OTBDMS	78	77																																																												
Dioxane	8.0	84 h	Ph	Ph	55	66																																																												
Dioxane	10.5	5 h	Ph	Ph	70	81																																																												
C ₉₋₁₃		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, K ₂ CO ₃ /AcOH buffer, -10°, 4 h	<table border="1"> <thead> <tr> <th>R</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>CH₂OMe (35)</td> <td>89</td> </tr> <tr> <td>TMS (71)</td> <td>89</td> </tr> <tr> <td>TBDMS (69)</td> <td>89</td> </tr> </tbody> </table>	R	% ee	CH ₂ OMe (35)	89	TMS (71)	89	TBDMS (69)	89	123, 124																																																						
R	% ee																																																																	
CH ₂ OMe (35)	89																																																																	
TMS (71)	89																																																																	
TBDMS (69)	89																																																																	
C ₉		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, Na ₂ B ₄ O ₇ buffer, Bu ₄ NHSO ₄ , Na ₂ EDTA, -10°, 2 h	 (41) 97% ee	25																																																														
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	 (65) 89% ee	122																																																														
C ₁₀		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 80 min	 (85) <5% ee	24																																																														
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, -10°, 2 h	 I (85) 32% ee	25																																																														
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, -10°, 2 h	 I (92) 12% ee	25																																																														
		Oxone [®] , K ₂ CO ₃ , DME, K ₂ CO ₃ /AcOH buffer, -10°, 4 h	 (93) 21% ee	114, 115																																																														
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	<table border="1"> <thead> <tr> <th>R</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>6</td> <td>68</td> </tr> <tr> <td>Ac</td> <td>11</td> <td>67</td> </tr> <tr> <td>TBDMS</td> <td>8</td> <td>17</td> </tr> </tbody> </table>	R	% Convn	% ee	H	6	68	Ac	11	67	TBDMS	8	17	119																																																		
R	% Convn	% ee																																																																
H	6	68																																																																
Ac	11	67																																																																
TBDMS	8	17																																																																

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.						
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	R ¹ Me -(CH ₂) ₄ - Et -(CH ₂) ₅ - <i>n</i> -Pr Ph Bn	R ² Me Et <i>n</i> -Pr Ph Bn	% Convn 65 81 63 80 43 36 17	% ee 84 76 76 74 73 21 29	119		
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	R Me (CH ₂) ₂ Cl		% Convn 17 18	% ee 30 29	119		
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	(5)		35%	ee	119		
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I					119		
			R ¹	R ²	R ³	R ⁴	R ⁵	% Convn	% ee
			Me	Me	Me	Me	F	23	12
			Me	Me	Me	Me	H	100	72
			Me	Me	Et	H	H	100	65
			Me	Me	<i>i</i> -Pr	H	H	83	61
			Me	Me	-(CH ₂) ₄ -	H	H	100	69
			-(CH ₂) ₄ -	Me	Me	H	H	100	72
			Me	Me	Et	Et	H	98	57
			Et	Et	Me	Me	H	77	71
			Me	Me	-(CH ₂) ₅ -	H	H	100	63
			-(CH ₂) ₅ -	Me	Me	H	H	100	72
			-(CH ₂) ₄ -	-(CH ₂) ₄ -	H	H	H	100	68
			Et	Et	Et	Et	H	40	57
			-(CH ₂) ₅ -	-(CH ₂) ₅ -	H	H	H	80	58
			-(CH ₂) ₆ -	-(CH ₂) ₆ -	H	H	H	37	66
			Me	Me	Bn	Bn	H	15	29
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h		Ph		(57)	20%	ee		119
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h				(82)	95%	ee		122
	Oxone [®] , NaHCO ₃ , CH ₃ CN, EDTA, 0°				I				149a
					II				

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.																																								
C ₁₁₋₁₇ 		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, K ₂ CO ₃ /AcOH buffer, -10°	 R Time % ee H 3 h (35) 93 TMS 2 h (83) 97 TBDMS 2 h (93) 97																																								
C ₁₁ 	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	 (61) 94% ee																																								
	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	 (89) 94% ee																																								
	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, -10°, 2 h	 (92) 92% ee																																								
C ₁₂₋₂₅ 		DMD, acetone/CH ₂ Cl ₂ , -20°, 20 to 24 h	 296, 102																																								
			<table border="1"> <thead> <tr> <th>mol %</th> <th>Additive</th> <th>R¹</th> <th>R²</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>5</td> <td>—</td> <td>H</td> <td>CN</td> <td>(67) 21</td> </tr> <tr> <td>10</td> <td>—</td> <td>H</td> <td>CN</td> <td>(53) 70</td> </tr> <tr> <td>10</td> <td><i>N</i>-methylimidazole</td> <td>H</td> <td>CN</td> <td>(68) 82</td> </tr> <tr> <td>15</td> <td>—</td> <td>H</td> <td>CN</td> <td>(62) 85</td> </tr> <tr> <td>20</td> <td>—</td> <td>4-BrC₆H₄SO₃</td> <td>4-BrC₆H₄SO₃</td> <td>(85) 83</td> </tr> <tr> <td>16</td> <td>—</td> <td>PhSO₃</td> <td>PhSO₃</td> <td>(64) 84</td> </tr> <tr> <td>14</td> <td>—</td> <td>TsO</td> <td>TsO</td> <td>(68) 84</td> </tr> </tbody> </table>	mol %	Additive	R ¹	R ²	% ee	5	—	H	CN	(67) 21	10	—	H	CN	(53) 70	10	<i>N</i> -methylimidazole	H	CN	(68) 82	15	—	H	CN	(62) 85	20	—	4-BrC ₆ H ₄ SO ₃	4-BrC ₆ H ₄ SO ₃	(85) 83	16	—	PhSO ₃	PhSO ₃	(64) 84	14	—	TsO	TsO	(68) 84
mol %	Additive	R ¹	R ²	% ee																																							
5	—	H	CN	(67) 21																																							
10	—	H	CN	(53) 70																																							
10	<i>N</i> -methylimidazole	H	CN	(68) 82																																							
15	—	H	CN	(62) 85																																							
20	—	4-BrC ₆ H ₄ SO ₃	4-BrC ₆ H ₄ SO ₃	(85) 83																																							
16	—	PhSO ₃	PhSO ₃	(64) 84																																							
14	—	TsO	TsO	(68) 84																																							
		DMD, acetone/CH ₂ Cl ₂ , -20°, 20 to 24 h	 296, 102																																								
			<table border="1"> <thead> <tr> <th>mol %</th> <th>Additive</th> <th>R¹</th> <th>R²</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>5</td> <td>—</td> <td>H</td> <td>CN</td> <td>(55) 15</td> </tr> <tr> <td>10</td> <td>—</td> <td>H</td> <td>CN</td> <td>(56) 81</td> </tr> <tr> <td>10</td> <td><i>N</i>-methylimidazole</td> <td>H</td> <td>CN</td> <td>(62) 84</td> </tr> <tr> <td>15</td> <td>—</td> <td>H</td> <td>CN</td> <td>(78) 93</td> </tr> <tr> <td>20</td> <td>—</td> <td>4-BrC₆H₄SO₃</td> <td>4-BrC₆H₄SO₃</td> <td>(73) 84</td> </tr> <tr> <td>16</td> <td>—</td> <td>PhSO₃</td> <td>PhSO₃</td> <td>(61) 88</td> </tr> <tr> <td>17</td> <td>—</td> <td>TsO</td> <td>TsO</td> <td>(69) 86</td> </tr> </tbody> </table>	mol %	Additive	R ¹	R ²	% ee	5	—	H	CN	(55) 15	10	—	H	CN	(56) 81	10	<i>N</i> -methylimidazole	H	CN	(62) 84	15	—	H	CN	(78) 93	20	—	4-BrC ₆ H ₄ SO ₃	4-BrC ₆ H ₄ SO ₃	(73) 84	16	—	PhSO ₃	PhSO ₃	(61) 88	17	—	TsO	TsO	(69) 86
mol %	Additive	R ¹	R ²	% ee																																							
5	—	H	CN	(55) 15																																							
10	—	H	CN	(56) 81																																							
10	<i>N</i> -methylimidazole	H	CN	(62) 84																																							
15	—	H	CN	(78) 93																																							
20	—	4-BrC ₆ H ₄ SO ₃	4-BrC ₆ H ₄ SO ₃	(73) 84																																							
16	—	PhSO ₃	PhSO ₃	(61) 88																																							
17	—	TsO	TsO	(69) 86																																							
		H ₂ O ₂ , CH ₃ CN, K ₂ CO ₃ buffer, EDTA, 0°, 7 h	 (90) 95% ee																																								

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee) Refs.																																																															
	—	—	(—) 58% ee 11																																																															
	Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 90 min	<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>4 h (81)</td> <td>64</td> </tr> <tr> <td>Cl</td> <td>1.5 h (75)</td> <td>65</td> </tr> <tr> <td>H</td> <td>1.5 h (83)</td> <td>33</td> </tr> <tr> <td>CH₂OMe</td> <td>1.5 h (80)</td> <td>67</td> </tr> <tr> <td>1,3-dioxolan-2-yl</td> <td>1.3 h (90)</td> <td>71</td> </tr> </tbody> </table>	R	Time	% ee	Br	4 h (81)	64	Cl	1.5 h (75)	65	H	1.5 h (83)	33	CH ₂ OMe	1.5 h (80)	67	1,3-dioxolan-2-yl	1.3 h (90)	71	24, 110, 111																																													
R	Time	% ee																																																																
Br	4 h (81)	64																																																																
Cl	1.5 h (75)	65																																																																
H	1.5 h (83)	33																																																																
CH ₂ OMe	1.5 h (80)	67																																																																
1,3-dioxolan-2-yl	1.3 h (90)	71																																																																
	Oxone [®] , K ₂ CO ₃ , DMM/CH ₃ CN, buffer (pH 9.3), Bu ₄ NHSO ₄ , 0°, 2 h	(88) 91% ee 149a																																																																
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	I (54) 95% ee + 122 II (—) I:II = 12:1																																																																
	Oxone [®] , CH ₃ CN, buffer (pH), Na ₂ EDTA, 0°	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>pH</th> <th>Time</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Ph</td> <td>Me</td> <td>8</td> <td>1.5 h</td> <td>46</td> <td>54</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Me</td> <td>8</td> <td>1.5 h</td> <td>35</td> <td>18</td> </tr> <tr> <td>Et</td> <td>Ph</td> <td>Me</td> <td>8</td> <td>1.5 h</td> <td>33</td> <td>67</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td><i>t</i>-Bu</td> <td>8</td> <td>3.0 h</td> <td>92</td> <td>82</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td><i>t</i>-Bu</td> <td>10.5</td> <td>1.5 h</td> <td><10</td> <td>42</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>Me</td> <td>8</td> <td>1.5 h</td> <td>36</td> <td>61</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>Me</td> <td>8</td> <td>18 h</td> <td>53</td> <td>53</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>Me</td> <td>10.5</td> <td>1.5 h</td> <td>38</td> <td>22</td> </tr> </tbody> </table>	R ¹	R ²	R ³	pH	Time	% Convn	% ee	Me	Ph	Me	8	1.5 h	46	54	Ph	Me	Me	8	1.5 h	35	18	Et	Ph	Me	8	1.5 h	33	67	Me	Ph	<i>t</i> -Bu	8	3.0 h	92	82	Me	Ph	<i>t</i> -Bu	10.5	1.5 h	<10	42	Ph	Ph	Me	8	1.5 h	36	61	Ph	Ph	Me	8	18 h	53	53	Ph	Ph	Me	10.5	1.5 h	38	22	26
R ¹	R ²	R ³	pH	Time	% Convn	% ee																																																												
Me	Ph	Me	8	1.5 h	46	54																																																												
Ph	Me	Me	8	1.5 h	35	18																																																												
Et	Ph	Me	8	1.5 h	33	67																																																												
Me	Ph	<i>t</i> -Bu	8	3.0 h	92	82																																																												
Me	Ph	<i>t</i> -Bu	10.5	1.5 h	<10	42																																																												
Ph	Ph	Me	8	1.5 h	36	61																																																												
Ph	Ph	Me	8	18 h	53	53																																																												
Ph	Ph	Me	10.5	1.5 h	38	22																																																												
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, DMM, K ₂ CO ₃ /AcOH buffer, -10°	<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>3 h (60)</td> <td>93</td> </tr> <tr> <td>TMS</td> <td>3 h (83)</td> <td>97</td> </tr> <tr> <td>TBDMS</td> <td>2 h (93)</td> <td>97</td> </tr> </tbody> </table>	R	Time	% ee	Me	3 h (60)	93	TMS	3 h (83)	97	TBDMS	2 h (93)	97	124, 123																																																			
R	Time	% ee																																																																
Me	3 h (60)	93																																																																
TMS	3 h (83)	97																																																																
TBDMS	2 h (93)	97																																																																
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	I (68) 96% ee + 122 II (13) 91% ee I:II = 4.6:1																																																																

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

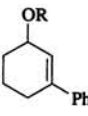
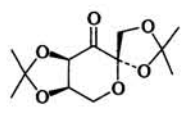
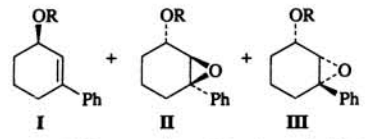
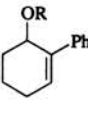
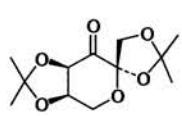
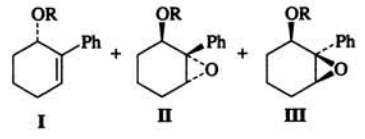
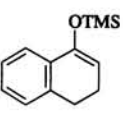
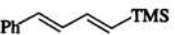
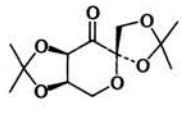
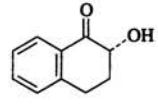
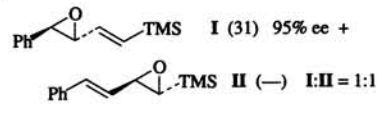
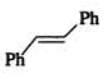
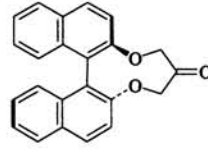
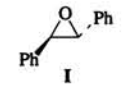
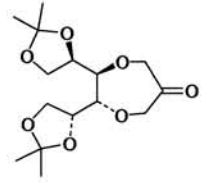
Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee) Refs.																							
C ₁₃₋₁₈ 		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer, EDTA, -10°, 1.5 h		125																						
			<table border="1"> <thead> <tr> <th>R</th> <th>% Convn</th> <th>% ee of I</th> <th>% ee of II</th> <th>II:III</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>61</td> <td>95</td> <td>—</td> <td>6:1</td> </tr> <tr> <td>TBDMS</td> <td>70</td> <td>99</td> <td>81</td> <td>4:1</td> </tr> </tbody> </table>	R	% Convn	% ee of I	% ee of II	II:III	Me	61	95	—	6:1	TBDMS	70	99	81	4:1								
R	% Convn	% ee of I	% ee of II	II:III																						
Me	61	95	—	6:1																						
TBDMS	70	99	81	4:1																						
C ₁₃₋₁₅ 		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer, EDTA, 2.5 h		125																						
			<table border="1"> <thead> <tr> <th>R</th> <th>Temp</th> <th>% Convn</th> <th>% ee of II</th> <th>II:III</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>-10°</td> <td>65</td> <td>85</td> <td>6:1</td> </tr> <tr> <td>COMe</td> <td>0°</td> <td>54</td> <td>88</td> <td>12:1</td> </tr> <tr> <td>CO₂Et</td> <td>-10°</td> <td>51</td> <td>97</td> <td>>20:1</td> </tr> <tr> <td>TMS</td> <td>-10°</td> <td>49</td> <td>95</td> <td>>20:1</td> </tr> </tbody> </table>	R	Temp	% Convn	% ee of II	II:III	Me	-10°	65	85	6:1	COMe	0°	54	88	12:1	CO ₂ Et	-10°	51	97	>20:1	TMS	-10°	49
R	Temp	% Convn	% ee of II	II:III																						
Me	-10°	65	85	6:1																						
COMe	0°	54	88	12:1																						
CO ₂ Et	-10°	51	97	>20:1																						
TMS	-10°	49	95	>20:1																						
C ₁₃  		Oxone [®] , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1 h	 (70) 83% ee	121																						
			Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h		122																					
C ₁₄ 		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA	 <table border="1"> <thead> <tr> <th>Temp</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>rt</td> <td>1 h (90)</td> <td>20</td> </tr> <tr> <td>0°</td> <td>5 h (79)</td> <td>26</td> </tr> </tbody> </table>	Temp	Time	% ee	rt	1 h (90)	20	0°	5 h (79)	26	112													
			Temp	Time	% ee																					
			rt	1 h (90)	20																					
			0°	5 h (79)	26																					
			Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, rt, 72 h	I (43) 27% ee	113																					
Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, rt, 1.5 h	I (55) 30% ee	113																								
Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, rt, 0.4 h	I (39) 39% ee	113																								
	Oxone [®] , K ₂ CO ₃ , DME/ DMM, K ₂ CO ₃ /AcOH buffer, -10°, 6 h	<table border="1"> <thead> <tr> <th>R</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>CO₂Me (65)</td> <td>94</td> </tr> <tr> <td>CH₂OAc (77)</td> <td>92</td> </tr> <tr> <td>CMe₂OH (57)</td> <td>95</td> </tr> </tbody> </table>	R	% ee	CO ₂ Me (65)	94	CH ₂ OAc (77)	92	CMe ₂ OH (57)	95	115, 114															
R	% ee																									
CO ₂ Me (65)	94																									
CH ₂ OAc (77)	92																									
CMe ₂ OH (57)	95																									

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

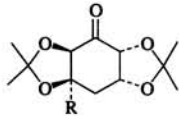
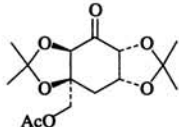
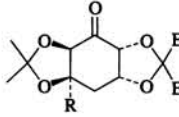
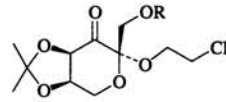
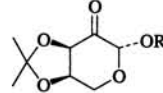
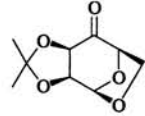
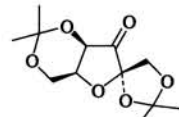
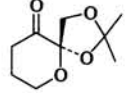
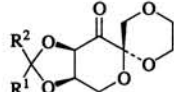
Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee) Refs.				
	Oxone [®] , K ₂ CO ₃ , DME/ DMM, K ₂ CO ₃ /AcOH buffer, -10°, 6 h	I	R		% ee		
			H	(11)	93	115,	
			CH ₂ F	(71)	89	114	
			CO ₂ Me	(66)	95		
			CH ₂ OAc	(95)	90		
			CMe ₂ OH	(91)	96		
			CMe ₂ OMe	(94)	96		
			CH ₂ OTBDMS	(77)	90		
			CH ₂ OBz	(91)	90		
			CH ₂ OTs	(74)	90		
	Oxone [®] , DME, buffer (pH), 0°	I	pH	% Convn	% ee		
			8.5	15	64	115,	
			9.5	32	67	114	
			10.5	44	67		
			11.7-12.3	50	66		
	Oxone [®] , K ₂ CO ₃ , DME/ DMM, K ₂ CO ₃ /AcOH buffer, -10°, 6 h	I	R		% ee		
			CO ₂ Me	(58)	93	115,	
			CH ₂ OAc	(75)	92	114	
			CMe ₂ OH	(57)	94		
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	R	% Convn	% ee		
			H	2	—		
			Ac	6	96	119	
			TBDMS	0	—		
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	R	% Convn	% ee		
			Me	10	88	119	
			(CH ₂) ₂ Cl	10	90		
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I (27)		74%	ee	119	
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I (14)		75%	ee	119	
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I (—)		78%	ee	119	
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I	R ¹	R ²	% Convn	% ee	
			Me	Me	34	90	119
			—(CH ₂) ₄ —		34	91	
			Et	Et	25	85	
			—(CH ₂) ₅ —		35	78	
			Ph	Ph	10	67	
			Bn	Bn	10	82	

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

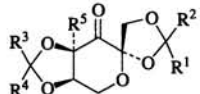
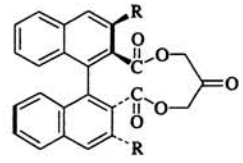
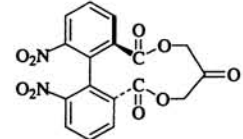
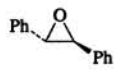
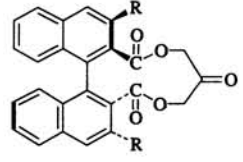









Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.																																																																																																																
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I 119																																																																																																																
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>R⁵</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr><td>Me</td><td>Me</td><td>Me</td><td>Me</td><td>F</td><td>3</td><td>11</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>Me</td><td>H</td><td>75</td><td>97</td></tr> <tr><td>Me</td><td>Me</td><td>Et</td><td>H</td><td>H</td><td>38</td><td>96</td></tr> <tr><td>Me</td><td>Me</td><td><i>i</i>-Pr</td><td>H</td><td>H</td><td>39</td><td>95</td></tr> <tr><td>Me</td><td>Me</td><td>—(CH₂)₄—</td><td>H</td><td>H</td><td>52</td><td>98</td></tr> <tr><td>—(CH₂)₄—</td><td>Me</td><td>Me</td><td>H</td><td>H</td><td>66</td><td>98</td></tr> <tr><td>Me</td><td>Me</td><td>Et</td><td>Et</td><td>H</td><td>38</td><td>94</td></tr> <tr><td>Et</td><td>Et</td><td>Me</td><td>Me</td><td>H</td><td>36</td><td>98</td></tr> <tr><td>Me</td><td>Me</td><td>—(CH₂)₃—</td><td>H</td><td>H</td><td>59</td><td>92</td></tr> <tr><td>—(CH₂)₅—</td><td>Me</td><td>Me</td><td>H</td><td>H</td><td>59</td><td>98</td></tr> <tr><td>—(CH₂)₄—</td><td>—(CH₂)₄—</td><td>H</td><td>H</td><td>H</td><td>57</td><td>99</td></tr> <tr><td>Et</td><td>Et</td><td>Et</td><td>Et</td><td>H</td><td>16</td><td>96</td></tr> <tr><td>—(CH₂)₅—</td><td>—(CH₂)₃—</td><td>H</td><td>H</td><td>H</td><td>41</td><td>98</td></tr> <tr><td>—(CH₂)₆—</td><td>—(CH₂)₆—</td><td>H</td><td>H</td><td>H</td><td>30</td><td>98</td></tr> <tr><td>Me</td><td>Me</td><td>Bn</td><td>Bn</td><td>H</td><td>7</td><td>93</td></tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	R ⁵	% Convn	% ee	Me	Me	Me	Me	F	3	11	Me	Me	Me	Me	H	75	97	Me	Me	Et	H	H	38	96	Me	Me	<i>i</i> -Pr	H	H	39	95	Me	Me	—(CH ₂) ₄ —	H	H	52	98	—(CH ₂) ₄ —	Me	Me	H	H	66	98	Me	Me	Et	Et	H	38	94	Et	Et	Me	Me	H	36	98	Me	Me	—(CH ₂) ₃ —	H	H	59	92	—(CH ₂) ₅ —	Me	Me	H	H	59	98	—(CH ₂) ₄ —	—(CH ₂) ₄ —	H	H	H	57	99	Et	Et	Et	Et	H	16	96	—(CH ₂) ₅ —	—(CH ₂) ₃ —	H	H	H	41	98	—(CH ₂) ₆ —	—(CH ₂) ₆ —	H	H	H	30	98	Me	Me	Bn	Bn	H	7	93
R ¹	R ²	R ³	R ⁴	R ⁵	% Convn	% ee																																																																																																													
Me	Me	Me	Me	F	3	11																																																																																																													
Me	Me	Me	Me	H	75	97																																																																																																													
Me	Me	Et	H	H	38	96																																																																																																													
Me	Me	<i>i</i> -Pr	H	H	39	95																																																																																																													
Me	Me	—(CH ₂) ₄ —	H	H	52	98																																																																																																													
—(CH ₂) ₄ —	Me	Me	H	H	66	98																																																																																																													
Me	Me	Et	Et	H	38	94																																																																																																													
Et	Et	Me	Me	H	36	98																																																																																																													
Me	Me	—(CH ₂) ₃ —	H	H	59	92																																																																																																													
—(CH ₂) ₅ —	Me	Me	H	H	59	98																																																																																																													
—(CH ₂) ₄ —	—(CH ₂) ₄ —	H	H	H	57	99																																																																																																													
Et	Et	Et	Et	H	16	96																																																																																																													
—(CH ₂) ₅ —	—(CH ₂) ₃ —	H	H	H	41	98																																																																																																													
—(CH ₂) ₆ —	—(CH ₂) ₆ —	H	H	H	30	98																																																																																																													
Me	Me	Bn	Bn	H	7	93																																																																																																													
		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt	<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr><td>Me</td><td>1 h</td><td>93</td></tr> <tr><td>TMS</td><td>20 h</td><td>(—) 44</td></tr> </tbody> </table> I 24	R	Time	% ee	Me	1 h	93	TMS	20 h	(—) 44																																																																																																							
R	Time	% ee																																																																																																																	
Me	1 h	93																																																																																																																	
TMS	20 h	(—) 44																																																																																																																	
		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 35 min	 I (94) 50% ee 24																																																																																																																
		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt	<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr><td>Br</td><td>3 h</td><td>(92) 75</td></tr> <tr><td>Cl</td><td>2 h</td><td>(95) 76</td></tr> <tr><td>I</td><td>22 h</td><td>(45) 32</td></tr> <tr><td>H</td><td>1 h</td><td>(91) 47</td></tr> <tr><td>CH₂OMe</td><td>1.8 h</td><td>(92) 66</td></tr> <tr><td>Ph</td><td>24 h</td><td>(22) 55</td></tr> </tbody> </table> I 24	R	Time	% ee	Br	3 h	(92) 75	Cl	2 h	(95) 76	I	22 h	(45) 32	H	1 h	(91) 47	CH ₂ OMe	1.8 h	(92) 66	Ph	24 h	(22) 55																																																																																											
R	Time	% ee																																																																																																																	
Br	3 h	(92) 75																																																																																																																	
Cl	2 h	(95) 76																																																																																																																	
I	22 h	(45) 32																																																																																																																	
H	1 h	(91) 47																																																																																																																	
CH ₂ OMe	1.8 h	(92) 66																																																																																																																	
Ph	24 h	(22) 55																																																																																																																	
			<table border="1"> <tbody> <tr> <td></td> <td>20 h</td> <td>(90) 77</td> </tr> <tr> <td></td> <td>20 h</td> <td>(93) 84</td> </tr> <tr> <td></td> <td>20 h</td> <td>(91) 75</td> </tr> </tbody> </table>		20 h	(90) 77		20 h	(93) 84		20 h	(91) 75																																																																																																							
	20 h	(90) 77																																																																																																																	
	20 h	(93) 84																																																																																																																	
	20 h	(91) 75																																																																																																																	

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.
		Oxone®, NaHCO ₃ , DME/H ₂ O, 25°, 22 h	I (—) R % ee F 87 Cl 85 H 42 OH 81 OEt 72 109
		Oxone®, NaHCO ₃ , DME/H ₂ O, 25°	I (—) 32% ee 109
		Oxone®, NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 1 h	I Temp Time % ee rt 1 h (73) 30 0° 5 h (72) 59 112
		Oxone®, K ₂ CO ₃ , CH ₃ CN/DMM, Na ₂ B ₄ O ₇ buffer, 0°, 1.5 h	I (81) 98% ee 25
		Oxone®, phosphate buffer, CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 0°, 4.5 h	I (±) (—) 369
		Oxone®, phosphate buffer, CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 0°, 4.5 h	I (±) (—) 369
		Oxone®, NaHCO ₃ , DME/H ₂ O, 25°	(—) R Time % ee Cl 4 h 74 F 4 h 78 H 1 h 86 Me 4 h 89 MeO 0.5 h 85 AcO 1 h 74 109
		Oxone®, NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt	I R Time % ee H 20 min (99) 47 Me 40 min (99) 50 Et 40 min (96) 60 <i>i</i> -Pr 40 min (98) 71 <i>t</i> -Bu 40 min (95) 76 Ph 480 min (82) 87 24

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

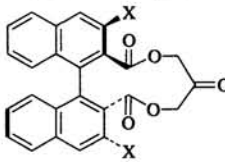
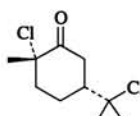
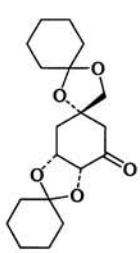
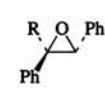
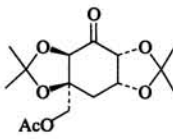
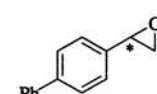
Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.																																																																																																																																		
		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA	I (—) 24																																																																																																																																		
			<table border="1"> <thead> <tr> <th>X</th> <th>R</th> <th>Time</th> <th>Temp</th> <th>% ee</th> </tr> </thead> <tbody> <tr><td>Cl</td><td>H</td><td>2-3 h</td><td>rt</td><td>(>90)</td></tr> <tr><td>Br</td><td>H</td><td>2-3 h</td><td>rt</td><td>(>90)</td></tr> <tr><td>Br</td><td>H</td><td>25 h</td><td>0-1°</td><td>(83)</td></tr> <tr><td>1,3-dioxolan-2-yl</td><td>H</td><td>40 min</td><td>rt</td><td>(>90)</td></tr> <tr><td>1,3-dioxolan-2-yl</td><td>H</td><td>20 h</td><td>0-1°</td><td>(>90)</td></tr> <tr><td>Cl</td><td>Me</td><td>2-3 h</td><td>rt</td><td>(>90)</td></tr> <tr><td>Br</td><td>Me</td><td>2-3 h</td><td>rt</td><td>(>90)</td></tr> <tr><td>Br</td><td>Me</td><td>20 h</td><td>0-1°</td><td>(>90)</td></tr> <tr><td>1,3-dioxolan-2-yl</td><td>Me</td><td>40 min</td><td>rt</td><td>(>90)</td></tr> <tr><td>1,3-dioxolan-2-yl</td><td>Me</td><td>20 h</td><td>0-1°</td><td>(>90)</td></tr> <tr><td>Cl</td><td>Et</td><td>2-3 h</td><td>rt</td><td>(>90)</td></tr> <tr><td>Br</td><td>Et</td><td>2-3 h</td><td>rt</td><td>(>90)</td></tr> <tr><td>Br</td><td>Et</td><td>24 h</td><td>0-1°</td><td>(51)</td></tr> <tr><td>1,3-dioxolan-2-yl</td><td>Et</td><td>40 min</td><td>rt</td><td>(>90)</td></tr> <tr><td>1,3-dioxolan-2-yl</td><td>Et</td><td>20 h</td><td>0-1°</td><td>(>90)</td></tr> <tr><td>Cl</td><td><i>i</i>-Pr</td><td>2-3 h</td><td>rt</td><td>(>90)</td></tr> <tr><td>Br</td><td><i>i</i>-Pr</td><td>2-3 h</td><td>rt</td><td>(>90)</td></tr> <tr><td>Br</td><td><i>i</i>-Pr</td><td>21 h</td><td>0-1°</td><td>(50)</td></tr> <tr><td>1,3-dioxolan-2-yl</td><td><i>i</i>-Pr</td><td>40 min</td><td>rt</td><td>(>90)</td></tr> <tr><td>1,3-dioxolan-2-yl</td><td><i>i</i>-Pr</td><td>20 h</td><td>0-1°</td><td>(>90)</td></tr> <tr><td>Cl</td><td><i>t</i>-Bu</td><td>2-3 h</td><td>rt</td><td>(>90)</td></tr> <tr><td>Br</td><td><i>t</i>-Bu</td><td>2-3 h</td><td>rt</td><td>(>90)</td></tr> <tr><td>Br</td><td><i>t</i>-Bu</td><td>18 h</td><td>0-1°</td><td>(22)</td></tr> <tr><td>1,3-dioxolan-2-yl</td><td><i>t</i>-Bu</td><td>40 min</td><td>rt</td><td>(>90)</td></tr> <tr><td>1,3-dioxolan-2-yl</td><td><i>t</i>-Bu</td><td>20 h</td><td>0-1°</td><td>(>90)</td></tr> </tbody> </table>	X	R	Time	Temp	% ee	Cl	H	2-3 h	rt	(>90)	Br	H	2-3 h	rt	(>90)	Br	H	25 h	0-1°	(83)	1,3-dioxolan-2-yl	H	40 min	rt	(>90)	1,3-dioxolan-2-yl	H	20 h	0-1°	(>90)	Cl	Me	2-3 h	rt	(>90)	Br	Me	2-3 h	rt	(>90)	Br	Me	20 h	0-1°	(>90)	1,3-dioxolan-2-yl	Me	40 min	rt	(>90)	1,3-dioxolan-2-yl	Me	20 h	0-1°	(>90)	Cl	Et	2-3 h	rt	(>90)	Br	Et	2-3 h	rt	(>90)	Br	Et	24 h	0-1°	(51)	1,3-dioxolan-2-yl	Et	40 min	rt	(>90)	1,3-dioxolan-2-yl	Et	20 h	0-1°	(>90)	Cl	<i>i</i> -Pr	2-3 h	rt	(>90)	Br	<i>i</i> -Pr	2-3 h	rt	(>90)	Br	<i>i</i> -Pr	21 h	0-1°	(50)	1,3-dioxolan-2-yl	<i>i</i> -Pr	40 min	rt	(>90)	1,3-dioxolan-2-yl	<i>i</i> -Pr	20 h	0-1°	(>90)	Cl	<i>t</i> -Bu	2-3 h	rt	(>90)	Br	<i>t</i> -Bu	2-3 h	rt	(>90)	Br	<i>t</i> -Bu	18 h	0-1°	(22)	1,3-dioxolan-2-yl	<i>t</i> -Bu	40 min	rt	(>90)	1,3-dioxolan-2-yl	<i>t</i> -Bu	20 h	0-1°	(>90)
X	R	Time	Temp	% ee																																																																																																																																	
Cl	H	2-3 h	rt	(>90)																																																																																																																																	
Br	H	2-3 h	rt	(>90)																																																																																																																																	
Br	H	25 h	0-1°	(83)																																																																																																																																	
1,3-dioxolan-2-yl	H	40 min	rt	(>90)																																																																																																																																	
1,3-dioxolan-2-yl	H	20 h	0-1°	(>90)																																																																																																																																	
Cl	Me	2-3 h	rt	(>90)																																																																																																																																	
Br	Me	2-3 h	rt	(>90)																																																																																																																																	
Br	Me	20 h	0-1°	(>90)																																																																																																																																	
1,3-dioxolan-2-yl	Me	40 min	rt	(>90)																																																																																																																																	
1,3-dioxolan-2-yl	Me	20 h	0-1°	(>90)																																																																																																																																	
Cl	Et	2-3 h	rt	(>90)																																																																																																																																	
Br	Et	2-3 h	rt	(>90)																																																																																																																																	
Br	Et	24 h	0-1°	(51)																																																																																																																																	
1,3-dioxolan-2-yl	Et	40 min	rt	(>90)																																																																																																																																	
1,3-dioxolan-2-yl	Et	20 h	0-1°	(>90)																																																																																																																																	
Cl	<i>i</i> -Pr	2-3 h	rt	(>90)																																																																																																																																	
Br	<i>i</i> -Pr	2-3 h	rt	(>90)																																																																																																																																	
Br	<i>i</i> -Pr	21 h	0-1°	(50)																																																																																																																																	
1,3-dioxolan-2-yl	<i>i</i> -Pr	40 min	rt	(>90)																																																																																																																																	
1,3-dioxolan-2-yl	<i>i</i> -Pr	20 h	0-1°	(>90)																																																																																																																																	
Cl	<i>t</i> -Bu	2-3 h	rt	(>90)																																																																																																																																	
Br	<i>t</i> -Bu	2-3 h	rt	(>90)																																																																																																																																	
Br	<i>t</i> -Bu	18 h	0-1°	(22)																																																																																																																																	
1,3-dioxolan-2-yl	<i>t</i> -Bu	40 min	rt	(>90)																																																																																																																																	
1,3-dioxolan-2-yl	<i>t</i> -Bu	20 h	0-1°	(>90)																																																																																																																																	
		Oxone [®] , NaHCO ₃ , DME/H ₂ O, 25°	I (—)																																																																																																																																		
			<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr><td>Br</td><td>4 h</td><td>75</td></tr> <tr><td>F</td><td>4 h</td><td>79</td></tr> <tr><td>H</td><td>1 h</td><td>86</td></tr> <tr><td>Me</td><td>4 h</td><td>87</td></tr> <tr><td>AcO</td><td>4 h</td><td>72</td></tr> <tr><td><i>t</i>-Bu</td><td>4 h</td><td>87</td></tr> </tbody> </table>	R	Time	% ee	Br	4 h	75	F	4 h	79	H	1 h	86	Me	4 h	87	AcO	4 h	72	<i>t</i> -Bu	4 h	87																																																																																																													
R	Time	% ee																																																																																																																																			
Br	4 h	75																																																																																																																																			
F	4 h	79																																																																																																																																			
H	1 h	86																																																																																																																																			
Me	4 h	87																																																																																																																																			
AcO	4 h	72																																																																																																																																			
<i>t</i> -Bu	4 h	87																																																																																																																																			
C ₁₄₋₂₀ 	Oxone [®] , NaHCO ₃ , solvent, H ₂ O, EDTA, 20°		116																																																																																																																																		
			<table border="1"> <thead> <tr> <th>R</th> <th>Solvent</th> <th>Time</th> <th>% Convn</th> <th>% ee</th> </tr> </thead> <tbody> <tr><td>H</td><td>CH₃CN</td><td>24 h</td><td>12</td><td>32</td></tr> <tr><td>H</td><td>dioxane</td><td>3 h</td><td>31</td><td>25</td></tr> <tr><td>H</td><td>CH₃CN/DMM (2:1)</td><td>24 h</td><td><5</td><td>45</td></tr> <tr><td>Ph</td><td>dioxane</td><td>3 h</td><td>32</td><td>25</td></tr> </tbody> </table>	R	Solvent	Time	% Convn	% ee	H	CH ₃ CN	24 h	12	32	H	dioxane	3 h	31	25	H	CH ₃ CN/DMM (2:1)	24 h	<5	45	Ph	dioxane	3 h	32	25																																																																																																									
R	Solvent	Time	% Convn	% ee																																																																																																																																	
H	CH ₃ CN	24 h	12	32																																																																																																																																	
H	dioxane	3 h	31	25																																																																																																																																	
H	CH ₃ CN/DMM (2:1)	24 h	<5	45																																																																																																																																	
Ph	dioxane	3 h	32	25																																																																																																																																	
C ₁₄ 	Oxone [®] , K ₂ CO ₃ , DME, K ₂ CO ₃ /AcOH buffer, -10°, 4 h		(54) 65% ee 115, 114																																																																																																																																		

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee) Refs.																												
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, K ₂ CO ₃ /AcOH buffer, 0°, 2 h	 (64) 94% ee 124, 123																												
	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	 I (77) 94% ee + 122 II (—) I:II = 14:1																												
C ₁₄₋₂₁ 	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, K ₂ CO ₃ /AcOH buffer, -10°, 3 h	 n % ee 1 (97) 77 124, 4 (98) 96 123 8 (99) 86																												
C ₁₄ 	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	 (68) 95% ee 122																												
C ₁₄₋₁₅ 	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer, EDTA, -10°, 2.5 h	 I + II + 125 III																												
			<table border="1"> <thead> <tr> <th>R</th> <th>% Convn</th> <th>% ee of I</th> <th>% ee of II</th> <th>II:III</th> </tr> </thead> <tbody> <tr> <td><i>i</i>-Pr</td> <td>59</td> <td>93</td> <td>85</td> <td>8:1</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>54</td> <td>99</td> <td>84</td> <td>>20:1</td> </tr> <tr> <td>OTMS</td> <td>61</td> <td>91</td> <td>76</td> <td>4:1</td> </tr> </tbody> </table>	R	% Convn	% ee of I	% ee of II	II:III	<i>i</i> -Pr	59	93	85	8:1	<i>t</i> -Bu	54	99	84	>20:1	OTMS	61	91	76	4:1								
R	% Convn	% ee of I	% ee of II	II:III																											
<i>i</i> -Pr	59	93	85	8:1																											
<i>t</i> -Bu	54	99	84	>20:1																											
OTMS	61	91	76	4:1																											
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	 (81) 96% ee 122																												
	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	 (79) 95% ee 122																												
C ₁₅₋₁₇ 		DMD, acetone/CH ₂ Cl ₂ , -20°, 10 d R = <i>t</i> -Bu	 103, 104 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(34) 56</td> </tr> <tr> <td>MeO</td> <td>H</td> <td>H</td> <td>(36) 39</td> </tr> <tr> <td>Ms</td> <td>H</td> <td>H</td> <td>(27) 48</td> </tr> <tr> <td>MeO</td> <td>MeO</td> <td>H</td> <td>(32) 86</td> </tr> <tr> <td>MeO</td> <td>H</td> <td>MeO</td> <td>(29) 22</td> </tr> <tr> <td>Ms'</td> <td>MeO</td> <td>H</td> <td>(23) 90</td> </tr> </tbody> </table>	R ¹	R ²	R ³	% ee	H	H	H	(34) 56	MeO	H	H	(36) 39	Ms	H	H	(27) 48	MeO	MeO	H	(32) 86	MeO	H	MeO	(29) 22	Ms'	MeO	H	(23) 90
R ¹	R ²	R ³	% ee																												
H	H	H	(34) 56																												
MeO	H	H	(36) 39																												
Ms	H	H	(27) 48																												
MeO	MeO	H	(32) 86																												
MeO	H	MeO	(29) 22																												
Ms'	MeO	H	(23) 90																												

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.																													
	 R = <i>t</i> -Bu	DMD, acetone/CH ₂ Cl ₂ , -20°, 10 d	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(31) 52</td> </tr> <tr> <td>MeO</td> <td>H</td> <td>H</td> <td>(27) 37</td> </tr> <tr> <td>Ms</td> <td>H</td> <td>H</td> <td>(22) 21</td> </tr> <tr> <td>MeO</td> <td>MeO</td> <td>H</td> <td>(31) 82</td> </tr> <tr> <td>MeO</td> <td>H</td> <td>MeO</td> <td>(39) 52</td> </tr> <tr> <td>Ms</td> <td>MeO</td> <td>H</td> <td>(25) 72</td> </tr> </tbody> </table>	R ¹	R ²	R ³	% ee	H	H	H	(31) 52	MeO	H	H	(27) 37	Ms	H	H	(22) 21	MeO	MeO	H	(31) 82	MeO	H	MeO	(39) 52	Ms	MeO	H	(25) 72	103, 104
R ¹	R ²	R ³	% ee																													
H	H	H	(31) 52																													
MeO	H	H	(27) 37																													
Ms	H	H	(22) 21																													
MeO	MeO	H	(31) 82																													
MeO	H	MeO	(39) 52																													
Ms	MeO	H	(25) 72																													
C ₁₅		H ₂ O ₂ , CH ₃ CN, K ₂ CO ₃ buffer, EDTA, 0°, 7 h	 (75) 93% ee	368																												
	"	H ₂ O ₂ , CH ₃ CN, K ₂ CO ₃ buffer, EDTA, 0°, 15 h	 (74) 93% ee	368																												
	"	Oxone [®] , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 2 h	 (80) 90% ee	121																												
	"	Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, Na ₂ EDTA, 0°, 3.0 h	 I (→) 52% ee	26																												
	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, Na ₂ EDTA, 0°, 1.5 h	I (→) 43% ee	26																												
C ₁₆	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	 I (77) 97% ee + II (→) I:II = 22:1	122																												
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	 I (65) 97% ee + II (→) I:II = 26:1	122																												
		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, 0°, 2 h	 I (74) 95% ee	117																												
	"	Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, 0°	 I II	149a																												
			<table border="1"> <thead> <tr> <th>pH</th> <th>Time</th> <th>% Convn</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>7.0-7.5</td> <td>2 h</td> <td>5</td> <td>4.3:1</td> </tr> <tr> <td>8.0</td> <td>1.5 h</td> <td>10</td> <td>4.4:1</td> </tr> <tr> <td>10.6</td> <td>1.5 h</td> <td>41</td> <td>4.5:1</td> </tr> </tbody> </table>	pH	Time	% Convn	I:II	7.0-7.5	2 h	5	4.3:1	8.0	1.5 h	10	4.4:1	10.6	1.5 h	41	4.5:1													
pH	Time	% Convn	I:II																													
7.0-7.5	2 h	5	4.3:1																													
8.0	1.5 h	10	4.4:1																													
10.6	1.5 h	41	4.5:1																													

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.												
		Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer, Bu ₄ NHSO ₄ , Na ₂ EDTA, -10°, 2 h	I (98) 95% ee 25												
	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, buffer (pH 10.5), EDTA, 0°, 1.5 h	 (81) 95% ee 122												
C₁₇ 	"	Oxone [®] , CH ₃ CN, DMM, Na ₂ B ₄ O ₇ buffer, EDTA, 0°, 1.5 h	 (92) 88% ee 121												
	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, DMM, Na ₂ B ₄ O ₇ buffer, EDTA, 0°, 2.5 h	 (-) 81% ee + I (-) + 125 II (-) I:II = 1.7:1												
	"	Oxone [®] , K ₂ CO ₃ , CH ₃ CN/ DMM, Na ₂ B ₄ O ₇ buffer, EDTA, 2.5 h	 I + II + 125 III												
			<table border="1"> <thead> <tr> <th>Temp</th> <th>% Convn</th> <th>% ee of I</th> <th>II:III</th> </tr> </thead> <tbody> <tr> <td>-10°</td> <td>49</td> <td>75</td> <td>13:1</td> </tr> <tr> <td>20°</td> <td>66</td> <td>96</td> <td>8:1</td> </tr> </tbody> </table>	Temp	% Convn	% ee of I	II:III	-10°	49	75	13:1	20°	66	96	8:1
Temp	% Convn	% ee of I	II:III												
-10°	49	75	13:1												
20°	66	96	8:1												
C₁₈ 		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt	 (>90) 24 <table border="1"> <thead> <tr> <th>X</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>2-3 h</td> <td>74</td> </tr> <tr> <td>1,3-dioxolan-2-yl</td> <td>40 min</td> <td>73</td> </tr> </tbody> </table>	X	Time	% ee	Br	2-3 h	74	1,3-dioxolan-2-yl	40 min	73			
X	Time	% ee													
Br	2-3 h	74													
1,3-dioxolan-2-yl	40 min	73													
C₁₉ 		Oxone [®] , CH ₂ Cl ₂ /H ₂ O (pH 7.5), Bu ₄ NHSO ₄ , 2 to 5°, 17 h	 (68) 16% ee 106												
		Oxone [®] , CH ₂ Cl ₂ /H ₂ O (pH 7.5), Bu ₄ NHSO ₄ , 2 to 5°, 17 h	 (68) 16% ee 106												

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)


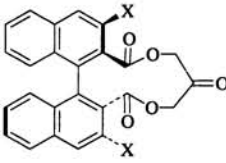
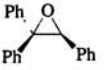
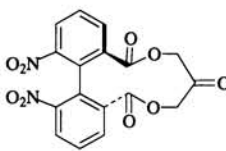
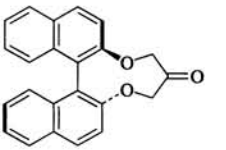
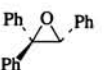
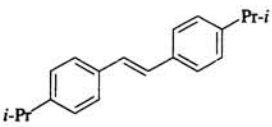
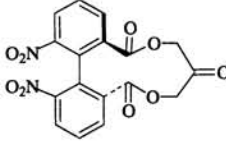
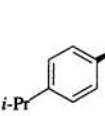
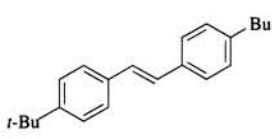
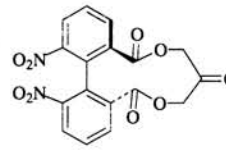
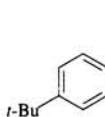
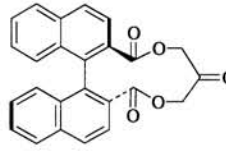
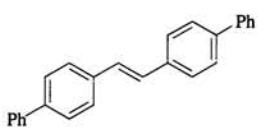
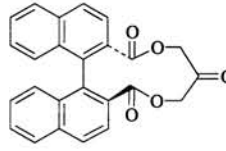
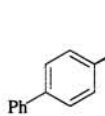
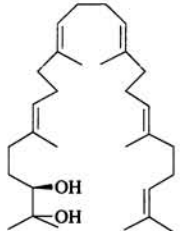
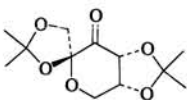
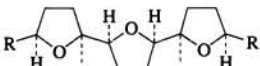
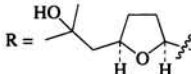
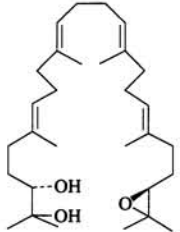
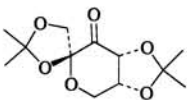
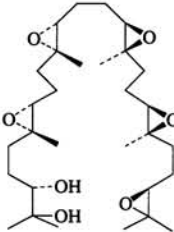
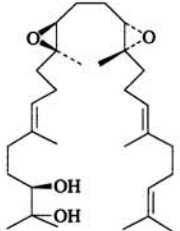
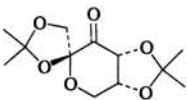
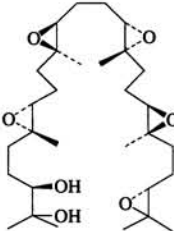
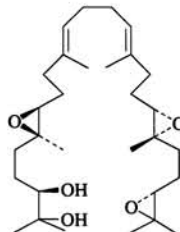
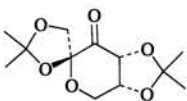
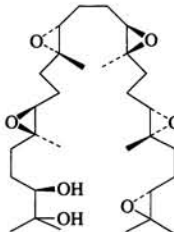
Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.																																			
C ₂₀ 		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt	 I 24, 110, 111																																			
			<table border="1"> <thead> <tr> <th>X</th> <th>Time</th> <th>Yield (%)</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>24 h</td> <td>(82)</td> <td>81</td> </tr> <tr> <td>Cl</td> <td>24 h</td> <td>(96)</td> <td>76</td> </tr> <tr> <td>H</td> <td>75 min</td> <td>(97)</td> <td>48</td> </tr> <tr> <td>CH₂OMe</td> <td>2.3 h</td> <td>(95)</td> <td>67</td> </tr> <tr> <td>1,3-dioxolan-2-yl</td> <td>3 h</td> <td>(90)</td> <td>73</td> </tr> </tbody> </table>	X	Time	Yield (%)	% ee	Br	24 h	(82)	81	Cl	24 h	(96)	76	H	75 min	(97)	48	CH ₂ OMe	2.3 h	(95)	67	1,3-dioxolan-2-yl	3 h	(90)	73											
			X	Time	Yield (%)	% ee																																
			Br	24 h	(82)	81																																
			Cl	24 h	(96)	76																																
H	75 min	(97)	48																																			
CH ₂ OMe	2.3 h	(95)	67																																			
1,3-dioxolan-2-yl	3 h	(90)	73																																			
	Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 60 min	I (82) 49% ee 24																																				
	Oxone [®] , K ₂ CO ₃ , CH ₃ CN, Na ₂ B ₄ O ₇ buffer, rt, 1.5 h	 (–) 24% ee 113																																				
		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 35 min	 (94) 66% ee 24																																			
C ₂₂ 		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 35 min	 I (91) 77% ee 24																																			
		Oxone [®] , NaHCO ₃ , solvent, EDTA	<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>Time</th> <th>Yield (%)</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>DME-H₂O</td> <td>rt</td> <td>0.5 h</td> <td>(92)</td> <td>77</td> </tr> <tr> <td>CH₃CN-H₂O</td> <td>rt</td> <td>0.7 h</td> <td>(95)</td> <td>76</td> </tr> <tr> <td>Dioxane-H₂O</td> <td>rt</td> <td>24 h</td> <td>(52)</td> <td>76</td> </tr> <tr> <td>THF-H₂O</td> <td>rt</td> <td>24 h</td> <td>(41)</td> <td>75</td> </tr> <tr> <td>DME-H₂O</td> <td>0°</td> <td>20 h</td> <td>(91)</td> <td>83</td> </tr> <tr> <td>DME-H₂O</td> <td>-20°</td> <td>20 h</td> <td>(2)</td> <td>84</td> </tr> </tbody> </table>	Solvent	Temp	Time	Yield (%)	% ee	DME-H ₂ O	rt	0.5 h	(92)	77	CH ₃ CN-H ₂ O	rt	0.7 h	(95)	76	Dioxane-H ₂ O	rt	24 h	(52)	76	THF-H ₂ O	rt	24 h	(41)	75	DME-H ₂ O	0°	20 h	(91)	83	DME-H ₂ O	-20°	20 h	(2)	84
	Solvent	Temp	Time	Yield (%)	% ee																																	
DME-H ₂ O	rt	0.5 h	(92)	77																																		
CH ₃ CN-H ₂ O	rt	0.7 h	(95)	76																																		
Dioxane-H ₂ O	rt	24 h	(52)	76																																		
THF-H ₂ O	rt	24 h	(41)	75																																		
DME-H ₂ O	0°	20 h	(91)	83																																		
DME-H ₂ O	-20°	20 h	(2)	84																																		
		Oxone [®] , NaHCO ₃ , CH ₃ CN/H ₂ O, EDTA, rt, 8 h	 (83) 18% ee 24																																			

TABLE 5. ENANTIOSELECTIVE EPOXIDATION OF OLEFINS BY ENANTIOMERICALLY ENRICHED DIOXIRANES (Continued)

Substrate	Ketone/Catalyst	Conditions	Product(s), Yield(s) (%) and Enantioselectivities (ee)Refs.
<p>C₃₀</p> 		<p>1. Oxone[®], MeCN, DMM, H₂O, (pH 10.5), 0°, 1.5 h 2. CSA, toluene, 0°, 1 h,</p>	 (31) 126 
		<p>Oxone[®], MeCN, DMM, H₂O, (pH 10.5), 0°, 1.5 h</p>	 (–) 126
		<p>Oxone[®], MeCN, DMM, H₂O, (pH 10.5), 0°, 1.5 h</p>	 (–) 126
		<p>Oxone[®], MeCN, DMM, H₂O, (pH 10.5), 0°, 1.5 h</p>	 (–) 126

8. Acknowledgments

Generous financial support of the *Deutsche Forschungsgemeinschaft* (*Schwerpunktprogramm: Peroxidchemie*) and the *Fonds der Chemischen Industrie* and a doctoral fellowship for C.-G. Z. from the *Deutscher Akademischer Austauschdienst (DAAD)* are gratefully appreciated. The authors also thank Mrs. Ana-Maria Krause for her help in preparing the tabular and graphical material.

References

1. Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* 1989, **22**, 205.
2. Murray, R. W. *Chem. Rev.* 1989, **89**, 1187.
3. Curci, R. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI: Greenwich CT, 1990, Vol. **2**, Chapter "I"; pp. 1–59.
4. Adam, W.; Hadjiarapoglou, L. P.; Curci, R.; Mello, R. In *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992, Chapter "4"; pp. 195–219.
5. Adam, W.; Hadjiarapoglou, L. *Top. Curr. Chem.* 1993, **164**, 45.
6. Curci, R.; Dinoi, A.; Rubino, M. F. *Pure Appl. Chem.* 1995, **67**, 811.
7. Lévai, A.; Adam, W.; Halász, J.; Nemes, C.; Patonay, T.; Tóth, G. *Khim. Geterotsikl. Soedin. (Engl. Trans.)* 1995, **10**, 1345; *Chem. Abstr.* 1991, **125**, 1049z.
8. Adam, W.; Smerz, A. K. *Bull. Soc. Chim. Belg.* 1996, **105**, 581.
9. Murray, R. W.; Singh, M. In *Comprehensive Heterocyclic Chemistry II*; Padwa, A., Ed.; Elsevier: Oxford, 1996, Vol. **1A**; pp. 429–456.
10. Adam, W.; Smerz, A. K.; Zhao, C.-G. *J. Prakt. Chem.* 1997, **339**, 298.
11. Denmark, S. E.; Wu, Z. *Synlett* 1999, 847.
12. Adam, W.; Degen, H.-G.; Pastor, A.; Saha-Möller, C. R.; Schambony, S. B.; Zhao, C.-G. In *Peroxide Chemistry: Mechanistic and Preparative Aspects of Oxygen Transfer*; Adam, W., Ed.; Wiley-VCH: Weinheim, 2000, pp. 78–112.
13. Adam, W.; Curci, R.; D'Accolti, L.; Dinoi, A.; Fusco, C.; Gasparrini, F.; Kluge, R.; Paredes, R.; Schulz, M.; Smerz, A. K.; Veloza, L. A.; Weinkötz, S.; Winde, R. *Chem. Eur. J.* 1997, **3**, 105.
14. Adam, W.; Fröhling, B.; Peters, K.; Weinkötz, S. *J. Am. Chem. Soc.* 1998, **120**, 8914.
15. Baumstark, A. L.; McCloskey, C. J. *Tetrahedron Lett.* 1987, **28**, 3311.
16. Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* 1988, **53**, 3437.
17. Houk, K. N.; Liu, J.; DeMello, N. C.; Condroski, K. R. *J. Am. Chem. Soc.* 1997, **119**, 10147.
18. Liu, J.; Houk, K. N.; Dinoi, A.; Fusco, C.; Curci, R. *J. Org. Chem.* 1998, **63**, 8565.
19. Jenson, C.; Liu, J.; Houk, K. N.; Jorgensen, W. L. *J. Am. Chem. Soc.* 1997, **119**, 12982.
20. Bach, R. D.; Canepa, C.; Winter, J. E.; Blanchette, P. E. *J. Org. Chem.* 1997, **62**, 5191.
21. Bach, R. D.; Glukhovtsev, M. N.; Gonzalez, C.; Marquez, M.; Estévez, C. M.; Baboul, A. G.; Schlegel, H. B. *J. Phys. Chem. A* 1997, **101**, 6092.

22. Miaskiewicz, K; Smith, D. A. J. Am. Chem. Soc. 1998, **120**, 1872.
23. Freccero, M.; Gandolfi, R.; Sarzi-Amadè, M.; Rastelli, A. Tetrahedron 1998, **54**, 12323.
24. Yang, D.; Wong, M.-K.; Yip, Y.-C.; Wang, X.-C.; Tang, M.-W.; Zheng, J.-H.; Cheung, K.-K. J. Am. Chem. Soc. 1998, **120**, 5943.
25. Wang, Z.-X.; Tu, Y.; Frohn, M.; Zhang, J.-R.; Shi, Y. J. Am. Chem. Soc. 1997, **119**, 11224.
26. Adam, W.; Fell, R. T.; Saha-Möller, C. R.; Zhao, C.-G. Tetrahedron: Asymmetry 1998, **9**, 397.
27. Adam, W.; Curci, R.; González Nuñez, M. E.; Mello, R. J. Am. Chem. Soc. 1991, **113**, 7654.
28. Shea, K. J.; Kim, J.-S. J. Am. Chem. Soc. 1992, **114**, 3044.
29. Bravo, A.; Fontana, F.; Fronza, G.; Minisci, F.; Serri, A. Tetrahedron Lett. 1995, **36**, 6945.
30. Bravo, A.; Fontana, F.; Fronza, G.; Minisci, F.; Zhao, L. J. Org. Chem. 1998, **63**, 254.
31. Edwards, J. O.; Pater, R. H.; Curci, R.; Di Furia, F. Photochem. Photobiol. 1979, **30**, 63.
32. Curci, R.; Fiorentino, M.; Troisi, L.; Edwards, J. O.; Pater, R. H. J. Org. Chem. 1980, **45**, 4758.
33. Jeyaraman, R.; Murray, R. W. J. Am. Chem. Soc. 1984, **106**, 2462.
34. Adam, W.; Hadjarapoglou, L.; Smerz, A. Chem. Ber. 1991, **124**, 227.
35. Yang, D.; Wong, M.-K.; Yip, Y.-C. J. Org. Chem. 1995, **60**, 3887.
36. Frohn, M.; Wang, Z.-X.; Shi, Y. J. Org. Chem. 1998, **63**, 6425.
37. Denmark, S. E.; Wu, Z. J. Org. Chem. 1998, **63**, 2810.
38. Yang, D.; Yip, Y.-C.; Jiao, G.-S.; Wong, M.-K. J. Org. Chem. 1998, **63**, 8952.
39. Yang, D.; Yip, Y.-C.; Tang, M.-W.; Wong, M.-K.; Cheung, K.-K. J. Org. Chem. 1998, **63**, 9888.
40. Carnell, A. J.; Johnstone, R. A. W.; Parsy, C. C.; Sanderson, W. R. Tetrahedron Lett. 1999, **40**, 8029.
41. Bentley, T. W.; Norman, S. J.; Gerstner, E.; Kemmer, R.; Christl, M. Chem. Ber. 1993, **126**, 1749.
42. Hofland, A.; Steinberg, H.; de Boer, T. J. Recl. Trav. Chim. Pays-Bas 1985, **104**, 350.
43. Trost, B. M.; Bogdanowicz, M. J. J. Am. Chem. Soc. 1973, **95**, 5321.
44. Adam, W.; Hadjarapoglou, L.; Jäger, V.; Klicic, J.; Seidel, B.; Wang, X. Chem. Ber. 1991, **124**, 2361.
45. Adam, W.; Hadjarapoglou, L.; Wang, X. Tetrahedron Lett. 1989, **30**, 6497.

46. Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tetrahedron Lett.* 1974, **15**, 4319.
47. Adam, W.; Hadjiarapoglou, L.; Mosandl, T.; Saha-Möller, C. R.; Wild, D. *Angew. Chem., Int. Ed. Engl.* 1991, **30**, 200.
48. Adam, W.; Bialas, J.; Hadjiarapoglou, L.; Sauter, M. *Chem. Ber.* 1992, **125**, 231.
49. Sauter, M.; Adam, W. *Acc. Chem. Res.* 1995, **28**, 289.
50. Adam, W.; Sauter, M. unpublished results.
51. Baertschi, S. W.; Raney, K. D.; Stone, M. P.; Harris, T. M. *J. Am. Chem. Soc.* 1988, **110**, 7929.
52. Patai, S.; Rappoport, Z. In *The Chemistry of Alkenes*; Patai, S., Ed.; Wiley: New York, 1964, Vol. **1**, pp. 512–517.
53. Adam, W.; Hadjiarapoglou, L.; Nestler, B. *Tetrahedron Lett.* 1990, **31**, 331.
54. Piers, E.; Boulet, S. L. *Tetrahedron Lett.* 1997, **38**, 8815.
55. Porter, M. J.; Skidmore, J. J. *Chem. Soc., Chem. Commun.* 2000, 1215.
56. Adam, W.; Hadjiarapoglou, L. *Chem. Ber.* 1990, **123**, 2077.
57. Adam, W.; Hadjiarapoglou, L.; Levai, A. *Synthesis* 1992, 436.

58. Adam, W.; Golsch, D.; Hadjiarapoglou, L.; Patonay, T. *Tetrahedron Lett.* 1991, **32**, 1041.
59. Adam, W.; Golsch, D.; Hadjiarapoglou, L.; Patonay, T. *J. Org. Chem.* 1991, **56**, 7292.
60. Lévai, A.; Adam, W.; Jekö, J.; Patonay, T.; Székely, A.; Vass, E. B. *J. Heterocycl. Chem.* 2000, **37**, 1065.
- 60a. Ferrer, M.; Sánchez-Baeza, F.; Messeguer, A.; Adam, W.; Golsch, D.; Görth, F.; Kiefer, W.; Nagel, V. *Eur. J. Org. Chem.* 1998, 2527.
61. Murray, R. W.; Jeyaraman, R.; Pillay, M. K. *J. Org. Chem.* 1987, **52**, 746.
- 61a. Scammells, P. J.; Baker, S. P.; Bellardinelli, L.; Olsson, R. A.; Russell, R. A.; Knevitt, S. A. *Bioorg. Med. Chem. Lett.* 1996, **6**, 811.
62. Ferrer, M.; Sánchez-Baeza, F.; Messeguer, A. *Tetrahedron* 1997, **53**, 15877.
63. Ferrer, M.; Sánchez-Baeza, F.; Messeguer, A.; Diez, A.; Rubiralta, M. J. *Chem. Soc., Chem. Commun.* 1995, 293.
64. Adam, W.; Ahrweiler, M.; Paulini, K.; Reißig, H.-U.; Voerckel, V. *Chem. Ber.* 1992, **125**, 2719.
65. Asensio, G.; Mello, R.; Boix-Bernardini, C.; González-Núñez, M. E.; Castellano, G. *J. Org. Chem.* 1995, **60**, 3692.
66. Adam, W.; Golsch, D.; Hadjiarapoglou, L.; Lévai, A.; Nemes, C.;

- Patonay, T. *Tetrahedron* 1994, **50**, 13113.
67. Murray, R. W.; Singh, M.; Williams, B. L.; Moncrieff, H. M. *J. Org. Chem.* 1996, **61**, 1830.
68. Armstrong, A.; Barsanti, P. A.; Clarke, P. A.; Wood, A. J. *Chem. Soc., Perkin Trans. 1* 1996, 1373.
69. Foglia, T. A.; Sonnet, P. E.; Nunez, A.; Dudley, R. L. *J. Am. Oil Chem. Soc.* 1998, **75**, 601.
70. Rodríguez, G.; Castedo, L.; Domínguez, D.; Saá, C.; Adam, W.; Saha-Möller, C. R. *J. Org. Chem.* 1999 **64**, 877.
71. Wang, X.; Ramos, B.; Rodriguez, A. *Tetrahedron Lett.* 1994, **35**, 6977.
72. Adam, W.; Smerz, A. K. *J. Org. Chem.* 1996, **61**, 3506.
73. Adam, W.; Prechtel, F.; Richter, M. J.; Smerz, A. K. *Tetrahedron Lett.* 1993, **34**, 8427.
74. Adam, W.; Prechtel, F.; Richter, M. J.; Smerz, A. K. *Tetrahedron Lett.* 1995, **36**, 4991.
75. Adam, W.; Paredes, R.; Smerz, A. K.; Veloza, L. A. *Liebigs Ann./Recl.* 1997, 547.
76. de Macedo Puyau, P.; Perie, J. J. *Synth. Commun.* 1998, **28**, 2679.
- 76a. Mello, R.; Fiorentino, M.; Fusco, C.; Curci, R. *J. Am. Chem. Soc.* 1989, **111**, 6749.
77. Bovicelli, P.; Lupattelli, P.; Mincione, E. *J. Org. Chem.* 1994, **59**, 4304.
78. Messeguer, A.; Fusco, C.; Curci, R. *Tetrahedron* 1993, **49**, 6299.
79. Adam, W.; Wirth, T. *Acc. Chem. Res.* 1999, **32**, 703.
80. Adam, W.; Paredes, R.; Smerz, A. K.; Veloza, L. A. *Eur. J. Org. Chem.* 1998, 349.
81. Yang, D.; Jiao, G.-S.; Yip, Y.-C.; Wong, M.-K. *J. Org. Chem.* 1999, **64**, 1635.
82. Vedejs, E.; Dent, W. H., III; Kendall, J. T.; Oliver, P. A. *J. Am. Chem. Soc.* 1996, **118**, 3556.
83. Adam, W.; Mitchell, C. M.; Saha-Möller, C. R. *Eur. J. Org. Chem.* 1999, 785.
84. Mello, R.; Ciminale, F.; Fiorentino, M.; Fusco, C.; Prencipe, T.; Curci, R. *Tetrahedron Lett.* 1990, **31**, 6097.
85. Bovicelli, P.; Lupattelli, P.; Mincione, E.; Prencipe, T.; Curci, R. *J. Org. Chem.* 1992, **57**, 5052.
86. Ebenezer, W.; Pattenden, G. *Tetrahedron Lett.* 1992, **33**, 4053.
87. Adam, W.; Smerz, A. K. *Tetrahedron* 1995, **51**, 13039.
88. Freccero, M.; Gandolfi, R.; Sarzi-Amede, M.; Rastelli, A. *J. Org. Chem.* 2000, **65**, 2030.

89. Adam, W.; Bach, R. D.; Dmitrenko, O.; Saha-Möller, C. R. *J. Org. Chem.* 2000, **65**, 6715.
90. Evans, D. A.; Trotter, B. W.; Coleman, P. J.; Côté, B.; Dias, L. C.; Rajapakse, H. A.; Tyler, A. N. *Tetrahedron* 1999, **55**, 8671.
91. Halcomb, R. L.; Danishefsky, S. J. *J. Am. Chem. Soc.* 1989, **111**, 6661.
92. Liu, K. K.-C.; Danishefsky, S. J. *J. Org. Chem.* 1994, **59**, 1892.
93. Randolph, J. T.; McClure, K. F.; Danishefsky, S. J. *J. Am. Chem. Soc.* 1995, **117**, 5712.
94. Roberge, J. Y.; Beebe, X.; Danishefsky, S. J. *J. Am. Chem. Soc.* 1998, **120**, 3915.
95. Deshpande, P. P.; Kim, H. M.; Zatorski, A.; Park, T.-K.; Ragupathi, G.; Livingston, P. O.; Live, D.; Danishefsky, S. J. *J. Am. Chem. Soc.* 1998, **120**, 1600.
96. Swindell, C. S.; Chander, M. C. *Tetrahedron Lett.* 1994, **35**, 6001.
97. Adam, W.; Müller, M.; Prechtel, F. *J. Org. Chem.* 1994, **59**, 2358.
98. Adam, W.; Prechtel, F. *Chem. Ber.* 1994, **127**, 667.
99. Adam, W.; Pastor, A.; Peters, K.; Peters, E.-M. *Org. Lett.* 2000, **2**, 1019.
100. Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993, pp. 159–202.
101. Katsuki, T. *Coord. Chem. Rev.* 1995, **140**, 189.
102. Adam, W.; Jekö, J.; Lévai, A.; Nemes, C.; Patonay, T.; Sebök, P. *Tetrahedron Lett.* 1995, **36**, 3669.
103. Lévai, A.; Adam, W.; Fell, R. T.; Gessner, R.; Patonay, T.; Simon, A.; Tóth, G. *Tetrahedron* 1998, **54**, 13105.
104. Adam, W.; Fell, R. T.; Lévai, A.; Patonay, T.; Peters, K.; Simon, A.; Tóth, G. *Tetrahedron: Asymmetry* 1998, **9**, 1121.
105. Curci, R.; Fiorentino, M.; Serio, M. *R. J. Chem. Soc., Chem. Commun.* 1984, 155.
106. Curci, R.; D'Accolti, L.; Fiorentino, M.; Rosa, A. *Tetrahedron Lett.* 1995, **36**, 5831.
107. Denmark, S. E.; Wu, Z.; Crudden, C. M.; Matsushashi, H. *J. Org. Chem.* 1997, **62**, 8288.
108. Armstrong, A.; Hayter, B. R. *J. Chem. Soc., Chem. Commun.* 1998, 621.
109. Yang, D.; Yip, Y.-C.; Chen, J.; Cheung, K.-K. *J. Am. Chem. Soc.* 1998, **120**, 7659.
110. Yang, D.; Yip, Y.-C.; Tang, M.-W.; Wong, M.-K.; Zheng, J.-H.; Cheung, K.-K. *J. Am. Chem. Soc.* 1996, **118**, 491.
111. Yang, D.; Wang, X.-C.; Wong, M.-K.; Yip, Y.-C.; Tang, M.-W. *J. Am. Chem. Soc.* 1996, **118**, 11311.
112. Song, C. E.; Kim, Y. H.; Lee, K. C.; Lee, S.-g.; Jin, B. W. *Tetrahedron*:

- Asymmetry 1997, **8**, 2921.
113. Adam, W.; Zhao, C.-G. *Tetrahedron: Asymmetry* 1997, **8**, 3995.
114. Wang, Z.-X.; Shi, Y. *J. Org. Chem.* 1997, **62**, 8622.
115. Wang, Z.-X.; Miller, S. M.; Anderson, O. P.; Shi, Y. *J. Org. Chem.* 1999, **64**, 6443.
116. Adam, W.; Saha-Möller, C. R.; Zhao, C.-G. *Tetrahedron: Asymmetry* 1999, **10**, 2749.
117. Tu, Y.; Wang, Z.-X.; Shi, Y. *J. Am. Chem. Soc.* 1996, **118**, 9806.
118. Wang, Z.-X.; Tu, Y.; Frohn, M.; Shi, Y. *J. Org. Chem.* 1997, **62**, 2328.
119. Tu, Y.; Wang, Z.-X.; Frohn, M.; He, M.; Yu, H.; Tang, Y.; Shi, Y. *J. Org. Chem.* 1998, **63**, 8475.
120. Adam, W.; Staab, E. Institut für Organische Chemie, Universität Würzburg, Würzburg, Germany, unpublished results.
121. Zhu, Y.; Tu, Y.; Yu, H.; Shi, Y. *Tetrahedron Lett.* 1998, **39**, 7819.
122. Frohn, M.; Dalkiewicz, M.; Tu, Y.; Wang, Z.-X.; Shi, Y. *J. Org. Chem.* 1998, **63**, 2948.
123. Cao, G.-A.; Wang, Z.-X.; Tu, Y.; Shi, Y. *Tetrahedron Lett.* 1998, **39**, 4425.
124. Wang, Z.-X.; Cao, G.-A.; Shi, Y. *J. Org. Chem.* 1999, **64**, 7646.
125. Frohn, M.; Zhou, X.; Zhang, J.-R.; Tang, Y.; Shi, Y. *J. Am. Chem. Soc.* 1999, **121**, 7718.
126. Xiong, Z.; Corey, E. J. *J. Am. Chem. Soc.* 2000, **122**, 4831.
127. Swern, D. *Org. React.* 1953, **7**, 378.
128. Dryuk, V. G. *Russ. Chem. Rev.* 1985, **54**, 986; *Chem. Abstr.* 1986, **104**, 109449.
129. Adam, W.; Saha-Möller, C. R.; Ganeshpure, P. *Chem. Rev.* 2001, **101**, 3499.
130. Ganeshpure, P. A.; Adam, W. *Synthesis* 1996, 179.
131. Plesniar, B. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: Chichester, 1983, pp. 567–584.
132. Davis, F. A.; Sheppard, A. C.; Chen, B.-C.; Haque, M. S. *J. Am. Chem. Soc.* 1990, **112**, 6679.
133. Lusinch, X.; Hanquet, G. *Tetrahedron* 1997, **53**, 13727.
134. Minakata, S.; Takemiya, A.; Nakamura, K.; Ryu, I.; Komatsu, M. *Synlett* 2000, 1810.
- 134a Adam, W.; Mitchell, C. M.; Paredes, R.; Smerz, A. K.; Veloza, L. A. *Liebigs Ann./Recl.* 1997, 1365.
135. Adam, W.; Degen, H.-G.; Saha-Möller, C. R. *J. Org. Chem.* 1999, **64**, 1274.

136. Adam, W.; Stegmann, V. R.; Saha-Möller, C. R. *J. Am. Chem. Soc.* 1999, **121**, 1879.
137. Jørgensen, K. A. *Chem. Rev.* 1989, **89**, 431.
138. Mimoun, H. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: Chichester, 1983, pp. 463–482.
139. Bortolini, O.; Di Furia, F.; Modena, G.; Seraglia R. *J. Org. Chem.* 1985, **50**, 2688.
140. Prat, D.; Lett, R. *Tetrahedron Lett.* 1986, **27**, 707.
141. Prandi, J.; Kagan, H. B.; Mimoun, H. *Tetrahedron Lett.* 1986, **27**, 2617.
142. Venturello, C.; D'Aloisio, R. *J. Org. Chem.* 1988, **53**, 1553.
143. Adam, W.; Mitchell, C. M. *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 533.
144. Adam, W.; Mitchell, C. M.; Saha-Möller, C. R.; Weichold, O. In *Structure and Bonding, Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations*; Meunier, B., Ed.; Springer Verlag: Berlin Heidelberg, 2000, Vol. **97**, pp. 237–285.
145. Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* 1991, **30**, 1638.
146. Rozen, S.; Kol, M. *J. Org. Chem.* 1990, **55**, 5155.
147. Adam, W.; Lazarus, M.; Saha-Möller, C. R.; Weichold, O.; Hoch, U.; Häring, D.; Schreier P. In *Advances in Biochemical Engineering/Biotechnology*; Faber, K., Ed.; Springer Verlag: Heidelberg, 1999, Vol. **63**, pp. 73–108.
148. Katsuki, T.; Martin, V. S. *Org. React.* 1996, **48**, 1.
149. Jacobsen, E. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G.; Hegedus, L. S., Eds.; Pergamon: New York, 1995, Vol. **12**, Chapter "11.1", pp. 1097–1135.
- 149a Wang, Z.-X.; Shi, Y. *J. Org. Chem.* 1998, **63**, 3099.
150. Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993, pp. 103–158.
151. Katsuki, T. *J. Mol. Cat. A* 1966, **113**, 87.
152. Davies, R. J. H.; Boyd, D. R.; Kumar, S.; Sharma, N. D.; Stevenson, C. *Biochem. Biophys. Res. Commun.* 1990, **169**, 87.
153. Adam, W.; Bialas, J.; Hadjiarapoglou, L. *Chem. Ber.* 1991, **124**, 2377.
154. Adam, W.; Golsch, D.; Zhao, C.-G. Institut für Organische Chemie, Universität Würzburg, Würzburg, Germany, unpublished result, which was adapted from refs. 76a and 155.
155. Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* 1988, **53**, 3890.
156. Murray, R. W.; Singh, M.; Jeyaraman, R. *J. Am. Chem. Soc.* 1992, **114**,

- 1346.
157. Smerz, A. K. Ph. D. Dissertation, University of Würzburg, 1996.
158. Adam, W.; Makosza, M.; Stalinski, K.; Zhao, C.-G. *J. Org. Chem.* 1998, **63**, 4390.
159. Adam, W.; Pastor, A.; Zhao, C.-G. Institut für Organische Chemie, Universität Würzburg, Würzburg, Germany, unpublished results.
160. Curci, R.; D'Accolti, L.; Fiorentino, M.; Fusco, C.; Adam, W.; González-Nuñez, M. E.; Mello, R. *Tetrahedron Lett.* 1992, **33**, 4225.
161. Hull, L. A.; Badai, L. *Tetrahedron Lett.* 1993, **34**, 5039.
162. Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* 1985, **50**, 2847.
163. Murray, R. W.; Singh, M. *Org. Synth. Coll. Vol.* 9 1998, 288.
164. Gibert, M.; Ferrer, M.; Sánchez-Baeza, F.; Messeguer, A. *Tetrahedron* 1997, **53**, 8643.
165. Ferrer, M.; Sánchez-Baeza, F.; Casas J.; Messeguer, A. *Tetrahedron Lett.* 1994, **35**, 2981.
166. Zhao, C.-G. Ph. D. Dissertation, University of Würzburg, 1999.
167. Adam, W.; Reinhardt, D.; Reißig, H.-U.; Paulini, K. *Tetrahedron* 1995, **51**, 12257.
168. Denmark, S. E.; Forbes, D. C.; Hays, D. S.; DePue, J. S.; Wilde, R. G. *J. Org. Chem.* 1995, **60**, 1391.
169. Rahman, M.; McKee, M. L.; Shevlin, P. B.; Szyrbicka, R. *J. Am. Chem. Soc.* 1988, **110**, 4002.
170. Abou-Elzahab, M.; Adam, W.; Saha-Möller, C. R. *Liebigs Ann. Chem.* 1991, 445.
171. Righi, G.; Bovicelli, P.; Sperandio, A. *Tetrahedron Lett.* 1999, **40**, 5889.
172. Sander, W.; Schroeder, K.; Muthusamy, S.; Kirschfeld, A.; Kappert, W.; Boese, R.; Kraka, E.; Sosa, C.; Cremer, D. *J. Am. Chem. Soc.* 1997, **119**, 7265.
173. Kirschfeld, A.; Muthusamy, S.; Sander, W. *Angew. Chem., Int. Ed. Engl.* 1994, **33**, 2212.
174. Murray, R. W.; Gu, D. J. *Chem. Soc., Perkin Trans. 2* 1993, 2203.
175. Murray, R. W.; Kong, W.; Rajadhyaksha, S. N. *J. Org. Chem.* 1993, **58**, 315.
176. Murray, R. W.; Gu, H. J. *Phys. Org. Chem.* 1996, **9**, 751.
177. Murray, R. W.; Pillay, M. K.; Jeyaraman, R. *J. Org. Chem.* 1988, **53**, 3007.
178. Murray, R. W.; Pillay, M. K. *Tetrahedron Lett.* 1988, **29**, 15.
179. Nojima, T.; Hirano, Y.; Ishiguro, K.; Sawaki, Y. *J. Org. Chem.* 1997, **62**, 2387

180. Adam, W.; Hadjiarapoglou, L. P.; Meffert, A. *Tetrahedron Lett.* 1991, **32**, 6697.
181. Murray, R. W.; Singh, M. *Org. Synth.* 1997, **74**, 91.
182. Adam, W.; Smerz, A. K. *Tetrahedron* 1996, **52**, 5799.
183. Mock-Knoblauch, C. Ph.D. Dissertation, University of Würzburg, 2000.
184. Bolli, M. H.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* 1998, 2243.
185. Lin, H.-C.; Wu, H.-J. *Tetrahedron* 2000, **56**, 341.
186. Bujons, J.; Camps, F.; Messeguer, A. *Tetrahedron Lett.* 1990, **31**, 5235.
187. Asouti, A.; Hadjiarapoglou, L. P. *Tetrahedron Lett.* 2000, **41**, 539.
188. von Zezschwitz, P.; Voigt, K.; Lansky, A.; Noltemeyer, M., de Meijere, A. *J. Org. Chem.* 1999, **64**, 3806.
189. Gibert, M.; Ferrer, M.; Sánchez-Baeza, F.; Messeguer, A. *Tetrahedron* 1997, **53**, 8643.
190. Abou-Elzahab, M. M.; Adam, W.; Saha-Möller, C. R. *Liebigs Ann. Chem.* 1992, 731.
191. Roush, W. R.; Grover, P. T. *Tetrahedron* 1992, **48**, 1981.
192. Piguel, S.; Ulibarri, G.; Grierson, D. S. *Tetrahedron Lett.* 1999, **40**, 295.
193. Rodríguez, G.; Castedo, L.; Domínguez, D.; Saá, C.; Adam, W. *J. Org. Chem.* 1999, **64**, 4830.
194. Bickers, P. T.; Halton, B.; Kay, A. J.; Northcote, P. T. *Aust. J. Chem.* 1999, **52**, 647.
195. Camps, P.; Font-Bardia, M.; Méndez, N.; Pérez, F.; Pujol, X.; Solans, X.; Vázquez, S.; Vilalta, M. *Tetrahedron* 1998, **54**, 4679.
196. Reisch, J.; Top, M. *Pharmazie* 1991, **46**, 745; *Chem. Abstr.* 1992, **116**, 128716u.
197. Sakanishi, K.; Kato, Y.; Mizukoshi, E.; Shimizu, K. *Tetrahedron Lett.* 1994, **35**, 4789.
198. Ikeno, T.; Harada, J.; Tomoda, S. *Chem. Lett.* 1999, 409.
199. Sano, H.; Kawata, K.; Kosugi, M. *Synlett* 1993, 831.
200. Roush, W. R.; Marron, T. G. *Tetrahedron Lett.* 1993, **34**, 5421.
201. Park, M.; Gu, F.; Loepky, R. N. *Tetrahedron Lett.* 1998, **39**, 1287.
202. Okazaki, O.; Persmark, M.; Guengerich, F. P. *Chem. Res. Toxicol.* 1993, **6**, 168; *Chem. Abstr.* 1993, **118**, 11872v.
203. Ndakala, A. J.; Howell, A. R. *J. Org. Chem.* 1998, **63**, 6098.
204. Adam, W.; Blancafort, L. *J. Org. Chem.* 1996, **61**, 8432.
205. Adam, W.; Hadjiarapoglou, L.; Klicic, J. *Tetrahedron Lett.* 1990, **31**, 6517.
206. Lavilla, R.; Gullón, F.; Barón, X.; Bosch, J. *J. Chem. Soc., Chem. Commun.* 1997, 213.

207. Lavilla, R.; Barón, X.; Coll, O.; Gullón, F.; Masdeu, C.; Bosch, J. J. *Org. Chem.* 1998, **63**, 10001.
208. Murray, R. W.; Shiang, D. L.; Singh, M. J. *Org. Chem.* 1991, **56**, 3677.
209. Guertin, K. R.; Chan, T.-H. *Tetrahedron Lett.* 1991, **32**, 715.
210. Adam, W.; Prechtel, F. *Chem. Ber.* 1991, **124**, 2369.
211. Adam, W.; Peters, E.-M.; Peters, K.; von Schnering, H. G.; Voerckel, V. *Chem. Ber.* 1992, **125**, 1263.
212. Adam, W.; Hadjirapoglou, L.; Jäger, V.; Seidel, B. *Tetrahedron Lett.* 1989, **30**, 4223.
213. Adam, W.; Hadjirapoglou, L.; Wang, X. *Tetrahedron Lett.* 1991, **32**, 1295.
214. Baylon, C.; Hanna, I. *Tetrahedron Lett.* 1995, **36**, 6475.
215. Adam, W.; Hadjirapoglou, L.; Seebach, D. unpublished results.
216. Chenault, H. K.; Danishefsky, S. J. *J. Org. Chem.* 1989, **54**, 4249.
217. Fujiwara, K.; Tsunashima, M.; Awakura, D.; Murai, A. *Chem. Lett.* 1997, 665.
218. Maynard, G. D.; Paquette, L. A. *J. Org. Chem.* 1991, **56**, 5480.
219. Sayer, J. M.; Servé, P. M.; Jerina, D. M. *J. Org. Chem.* 1994, **59**, 977.
220. Meyer, C.; Spiteller, G. *Liebigs Ann. Chem.* 1993, 17.
221. Silverman, S. K.; Foote, C. S. *J. Am. Chem. Soc.* 1991, **113**, 7672.
222. Troisi, L.; Cassidei, L.; Lopez, L.; Mello, R.; Curci, R. *Tetrahedron Lett.* 1989, **30**, 257.
223. Kopecky, K. R.; Xie, Y.; Molina, J. *Can. J. Chem.* 1993, **71**, 272.
224. Adam, W.; Ahrweiler, M.; Balci, M.; Çakmak, O.; Saha-Möller, C. R. *Tetrahedron Lett.* 1995, **36**, 1429.
225. Gopalakrishnan, S.; Stone, M. P.; Harris, T. M. *J. Am. Chem. Soc.* 1989, **111**, 7232.
226. Saladino, R.; Mezzetti, M.; Mincione, E.; Torrini, I.; Paradisi, M. P.; Mastropietro, G. *J. Org. Chem.* 1999, **64**, 8468.
227. Altamura, A.; Fusco, C.; D'Accolti, L.; Mello, R.; Prencipe, T.; Curci, R. *Tetrahedron Lett.* 1991, **32**, 5445.
228. Lluch, A.-M.; Gibert, M.; Sánchez-Baeza, F.; Messeguer, A. *Tetrahedron* 1996, **52**, 3973.
229. Evans, D. A.; Trotter, B. W.; Côté, B. *Tetrahedron Lett.* 1998, **39**, 1709.
230. Meng, D.; Sorensen, E. J.; Bertinato, P.; Danishefsky, S. J. *J. Org. Chem.* 1996, **61**, 7998.
231. Savin, K. A.; Woo, J. C. G.; Danishefsky, S. J. *J. Org. Chem.* 1999, **64**, 4183.
232. Russo, A.; DesMarteau, D. D. *Angew. Chem., Int. Ed. Engl.* 1993, **32**,

905.

233. Saladino, R.; Bernini, R.; Mincione, E.; Tagliatesta, P.; Boschi, T. *Tetrahedron Lett.* 1996, **37**, 2647.
234. Saladino, R.; Bernini, R.; Crestini, C.; Mincione, E.; Bergamini, A.; Marini, S.; Palamara, A. T. *Tetrahedron* 1995, **51**, 7561.
235. Lupattelli, P.; Saladino, R.; Mincione, E. *Tetrahedron Lett.* 1993, **34**, 6313.
236. Baumstark, A. L.; Harden, D. B., Jr. *J. Org. Chem.* 1993, **58**, 7615.
237. Prechtel, F. Diplomarbeit, University of Würzburg, 1990.
238. Baldwin, J. E.; O'Neil, I. A. *Tetrahedron Lett.* 1990, **31**, 2047.
239. Burgess, L. E.; Gross, E. K. M.; Jurka, J. *Tetrahedron Lett.* 1996, **37**, 3255.
240. Coats, S. J.; Wasserman, H. H. *Tetrahedron Lett.* 1995, **36**, 7735.
241. Patonay, T.; Lévai, A.; Nemes, C.; Timár, T.; Tóth, G.; Adam, W. *J. Org. Chem.* 1996, **61**, 5375.
242. Patonay, T.; Tóth, G.; Adam, W. *Tetrahedron Lett.* 1993, **34**, 5055.
243. Zander, N.; Langschwager, W.; Hoffmann, H. M. R. *Synth. Commun.* 1996, **26**, 4577.
244. Adam, W.; Schönberger, A. *Tetrahedron Lett.* 1992, **33**, 53.
245. Murray, R. W.; Singh, M.; Rath, N. *J. Org. Chem.* 1997, **62**, 8794.
246. Crandall, J. K.; Zucco, M.; Kirsch, R. S.; Coppert, D. M. *Tetrahedron Lett.* 1991, **32**, 5441.
247. Adam, W.; Bialas, J.; Hadjiarapoglou, L.; Patonay, T. *Synthesis* 1992, 49.
248. Burke, A. J.; O'Sullivan, W. I. *Tetrahedron* 1997, **53**, 8491.
249. Halász, J.; Tóth, G.; Lévai, A.; Nemes, C.; Jámbor, Z. *J. Chem. Res. (S)* 1994, 326.
250. Adam, W.; Halász, J.; Lévai, A.; Nemes, C.; Patonay, T.; Tóth, G. *Liebigs Ann. Chem.* 1994, 795.
251. Adam, W.; Halász, J.; Jámbor, Z.; Lévai, A.; Nemes, C.; Patonay, T.; Tóth, G. *Monatsh. Chem.* 1996, **127**, 683.
252. Adam, W.; Lévai, A.; Mérour, J.-Y.; Nemes, C.; Patonay, T. *Synthesis* 1997, 268.
253. Adam, W.; Halász, J.; Jámbor, Z.; Lévai, A.; Nemes, C.; Patonay, T.; Tóth, G. *J. Chem. Soc., Perkin Trans. 1* 1996, 395.
254. Fang, F. G.; Danishefsky, S. J. *Tetrahedron Lett.* 1989, **30**, 2747.
255. Adam, W.; Ahrweiler, M.; Vlček, P. *J. Am. Chem. Soc.* 1995, **117**, 9690.
256. Griesbeck, A. G.; Deufel, T.; Hohlneicher, G.; Rebentisch, R.; Steinwascher, J. *Eur. J. Org. Chem.* 1998, 1759.

257. Sieburth, S. M.; McGee, K. F., Jr.; Al-Tel, T. H. *Tetrahedron Lett.* 1999, **40**, 4007.
258. Bovicelli, P.; Lupattelli, P.; Mincione, E.; Prencipe, T.; Curci, R. *J. Org. Chem.* 1992, **57**, 2182.
259. Adam, W.; Jekő, J.; Lévai, A.; Nemes, C.; Patonay, T. *Liebigs Ann. Chem.* 1995, 1547.
260. Lacroix, I.; Biton, J.; Azerad, R. *Bioorg. Med. Chem.* 1997, **5**, 1369.
261. Horie, T.; Shibata, K.; Yamashita, K.; Kawamura, Y.; Tsukayama, M. *Chem. Pharm. Bull.* 1997, **45**, 446.
262. Liu, J.; Mander, L. N.; Willis, A. C. *Tetrahedron* 1998, **54**, 11637.
263. Ireland, R. E.; Liu, L.; Roper, T. D.; Gleason, J. L. *Tetrahedron* 1997, **53**, 13257.
264. Corey, P. F.; Ward, F. E. *J. Org. Chem.* 1986, **51**, 1925.
265. Jones, C. W.; Sankey, J. P.; Sanderson, W. R.; Rocca, M. C.; Wilson, S. L. *J. Chem. Res. (S)* 1994, 114.
266. Boehlow, T. R.; Buxton, P. C.; Grocock, E. L.; Marples, B. A.; Waddington, V. L. *Tetrahedron Lett.* 1998, **39**, 1839.
267. Traylor, T. G.; Kim, C.; Richards, J. L.; Xu, F.; Perrin, C. L. *J. Am. Chem. Soc.* 1995, **117**, 3468.
268. Camporeale, M.; Fiorani, T.; Troisi, L.; Adam, W.; Curci, R.; Edwards, J. O. *J. Org. Chem.* 1990, **55**, 93.
269. Gallopo, A. R.; Edwards, J. O. *J. Org. Chem.* 1981, **46**, 1684.
270. Nakamura, N.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* 1987, **109**, 4969.
271. Schulz, M.; Liebsch, S.; Kluge, R.; Adam, W. *J. Org. Chem.* 1997, **62**, 188.
272. Cristau, H.-J.; Mbianda, X. Y.; Geze, A.; Beziat, Y.; Gasc, M.-B. *J. Organomet. Chem.* 1998, **571**, 189.
273. Denmark, S. E.; Wu, Z. *J. Org. Chem.* 1997, **62**, 8964.
274. Suprun, W. Y.; Schulze, D. *J. Prakt. Chem.* 1997, **339**, 71; *Chem. Abstr.* 1997, **126**, 143946u.
275. Schultz, A. G.; Harrington, R. E.; Tham, F. S. *Tetrahedron Lett.* 1992, **33**, 6097.
276. Suh, Y.-G.; Min, K.-H.; Baek, S.-Y.; Chai, J.-H. *Heterocycles* 1998, **48**, 1527.
277. Tsui, H.-C.; Paquette, L. A. *J. Org. Chem.* 1998, **63**, 9968.
- 278a Liang, X.; Kingston, D. G. I.; Lin, C. M.; Hamel, E. *Tetrahedron Lett.* 1995, **36**, 2901.
278. Altstadt, T. J.; Gao, Q.; Wittman, M. D.; Kadow, J. F.; Vyas, D. M. *Tetrahedron Lett.* 1998, **39**, 4965.

279. Dyker, G.; Hölzer, B. *Tetrahedron* 1999, **55**, 12557.
280. Ballistreri, F. P.; Tomaselli, G. A.; Toscano, R. M.; Bonchio, M.; Conte, V.; Di Furia, F. *Tetrahedron Lett.* 1994, **35**, 8041.
281. Ballini, R.; Papa, F.; Bovicelli, P. *Tetrahedron Lett.* 1996, **37**, 3507.
282. Adam, W.; Saha-Möller, C. R.; Schmid, K. S. *J. Org. Chem.* 2001, **66**, 7365.
283. van Heerden, F. R.; Dixon, J. T.; Holzapfel, C. W. *Tetrahedron Lett.* 1992, **33**, 7399.
284. Branam, B. M.; Wang, X.; Jankowski, P.; Wicha, J.; Paquette, L. A. *J. Org. Chem.* 1994, **59**, 6874.
285. Wasserman, H. H.; Baldino, C. M.; Coats, S. J. *J. Org. Chem.* 1995, **60**, 8231.
286. Ley, S. V.; Meek, G.; Metten, K.-H.; Pique, C. *J. Chem. Soc., Chem. Commun.* 1994, 1931.
- 287a Link, J. T.; Danishefsky, S. J.; Schulte, G. *Tetrahedron Lett.* 1994, **35**, 9131.
287. Link, J. T.; Danishefsky, S. J.; Schulte, G. *Tetrahedron Lett.* 1995, **36**, 3584.
288. Messeguer, A.; Sánchez-Baeza, F.; Casas, J.; Hammock, B. D. *Tetrahedron* 1991, **47**, 1291.
289. Simbi, L.; van Heerden, F. R. *J. Chem. Soc., Perkin Trans. 1* 1997, 269.
290. Abad, J.-L.; Casas, J.; Sánchez-Baeza, F.; Messeguer, A. *J. Org. Chem.* 1993, **58**, 3991.
291. Abad, J.-L.; Casas, J.; Sánchez-Baeza, F.; Messeguer, A. *Bioorg. Med. Chem. Lett.* 1992, **2**, 1239.
292. Adam, W.; Corma, A.; Martínez, A.; Mitchell, C. M.; Reddy, T. I.; Renz, M.; Smerz, A. K. *J. Mol. Catal. A.* 1997, **117**, 357.
293. Adam, W.; Mitchell, C. M.; Saha-Möller, C. R. *J. Org. Chem.* 1999, **64**, 3699.
294. D'Accolti, L.; Fiorentino, M.; Fusco, C.; Rosa, A. M.; Curci, R. *Tetrahedron Lett.* 1999, **40**, 8023.
295. Freccero, M.; Gandolfi, R.; Sarzi-Amadè, M. *Tetrahedron* 1999, **55**, 11309.
296. Murray, R. W.; Singh, M.; Williams, B. L.; Moncrieff, H. M. *Tetrahedron Lett.* 1995, **36**, 2437.
297. Kurihara, M.; Ito, S.; Tsutsumi, N.; Miyata, N. *Tetrahedron Lett.* 1994, **35**, 1577.
298. Adam, W.; Brünker, H.-G.; Kumar, A. S.; Peters, E.-M.; Peters, K.; Schneider, U.; von Schnering, H. G. *J. Am. Chem. Soc.* 1996, **118**, 1899.

299. Murray, R. W.; Singh, M.; Rath, N. P. *Tetrahedron* 1999, **55**, 4539.
300. Adam, W.; Jekö, J.; Lévai, A.; Majer, Z.; Nemes, C.; Patonay, T.; Párkányi, L.; Sebök, P. *Tetrahedron: Asymmetry* 1996, **7**, 2437.
301. Yang, D.; Tang, Y.-C.; Chen, J.; Wang, X.-C.; Bartberger, M. D.; Houk, K. N.; Olson, L. J. *Am. Chem. Soc.* 1999, **121**, 11976.
302. Cicala, G.; Curci, R.; Fiorentino, M.; Laricchiuta, O. J. *Org. Chem.* 1982, **47**, 2670.
303. de Sousa, S. E.; O'Brien, P.; Pilgram, C. D.; Roder, D.; Towers, T. D. *Tetrahedron Lett.* 1999, **40**, 391.
304. Yang, D.; Wong, M.-K.; Cheung, K.-K.; Chan, E. W. C.; Xie, Y. *Tetrahedron Lett.* 1997, **38**, 6865.
305. Brimble, M. A.; Johnston, A. D.; Furneaux, R. H. *J. Org. Chem.* 1998, **63**, 471.
306. Marzabadi, C. H.; Spilling, C. D. *J. Org. Chem.* 1993, **58**, 3761.
307. Benbow, J. W.; Katoch, R.; Martinez, B. L.; Shetzline, S. B. *Tetrahedron Lett.* 1997, **38**, 4017.
308. King, S. B.; Ganem, B. J. *Am. Chem. Soc.* 1994, **116**, 562.
309. Haag, R.; Zuber, R.; Donon, S.; Lee, C.-H.; Noltemeyer, M.; Johnsen, K.; de Meijere, A. *J. Org. Chem.* 1998, **63**, 2544.
310. Adam, W.; Roschmann, K. unpublished results.
311. Linker, T.; Fröhlich, L. *J. Am. Chem. Soc.* 1995, **117**, 2694.
312. Adam, W.; Korb, M. N. *Tetrahedron* 1996, **52**, 5487.
313. Zimmermann, P. J.; Blanarikova, I.; Jäger, V. *Angew. Chem., Int. Ed. Engl.* 2000, **39**, 910.
314. Kurihara, M.; Ishii, K.; Kasahara, Y.; Kameda, M.; Pathak, A. K.; Miyata, N. *Chem. Lett.* 1997, 1015.
315. Tagliatesta, P.; Bernini, R.; Crestini, C.; Monti, D.; Boschi, T.; Mincione, E.; Saladino, R. *J. Org. Chem.* 1999, **64**, 5361.
316. Hambalek, R.; Just, G. *Tetrahedron Lett.* 1990, **31**, 4693.
317. Bols, M.; Hazell, R. G.; Thomsen, I. B. *Chem. Eur. J.* 1997, **3**, 940.
318. Adam, W.; Schuhmann, R. M. *J. Org. Chem.* 1996, **61**, 874.
319. Bartels, A.; Jones, P. G.; Liebscher, J. *Tetrahedron Lett.* 1995, **36**, 3673.
320. Griesbeck, A. G.; Mauder, H.; Müller, I. *Chem. Ber.* 1992, **125**, 2467.
321. Crimmins, M. T.; Jung, D. K.; Gray, J. L. *J. Am. Chem. Soc.* 1993, **115**, 3146.
322. Luker, T.; Hiemstra, H.; Speckamp, W. N. *Tetrahedron Lett.* 1996, **37**, 8257.
323. Thompson, S. K.; Heathcock, C. H. *J. Org. Chem.* 1992, **57**, 5979.
324. Asensio, G.; Biox-Bernardini, C.; Andreu, C.; González-Núñez, M. E.;

- Mello, R.; Edwards, J. O.; Carpenter, G. B. *J. Org. Chem.* 1999, **64**, 4705.
325. Nicolaou, K. C.; Prasad, C. V. C.; Ogilvie, W. W. *J. Am. Chem. Soc.* 1990, **112**, 4988.
326. Nan, F.; Chen, X.; Xiong, Z.; Li, T.; Li, Y. *Synth. Commun.* 1994, **24**, 2319.
327. Gerlach, K.; Hoffmann, H. M. R.; Wartchow, R. *J. Chem. Soc., Perkin Trans. 1* 1998, 3867.
328. Randolph, J. T.; Danishefsky, S. J. *J. Am. Chem. Soc.* 1993, **115**, 8473.
329. Linker, T.; Peters, K.; Peters, E.-M.; Rebien, F. *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 2487.
330. Anklam, S.; Liebscher, J. *Tetrahedron* 1998, **54**, 6369.
331. Bhatia, G. S.; Lowe, R. F.; Pritchard, R. G.; Stoodley, R. J. *J. Chem. Soc., Chem. Commun.* 1997, 1981.
332. Cambie, R. C.; Grimsdale, A. C.; Rutledge, P. S.; Walker, M. F.; Woodgate, P. D. *Aust. J. Chem.* 1991, **44**, 1553.
333. He, F.; Foxman, B. M.; Snider, B. B. *J. Am. Chem. Soc.* 1998, **120**, 6417.
334. Yang, D.; Ye, X.-Y.; Xu, M. *J. Org. Chem.* 2000, **65**, 2208.
335. Gallant, M.; Link, J. T.; Danishefsky, S. J. *J. Org. Chem.* 1993, **58**, 343.
336. Chow, K.; Danishefsky, S. J. *J. Org. Chem.* 1990, **55**, 4211.
337. Nemes, C.; Lévai, A.; Patonay, T.; Tóth, G.; Boros, S.; Halász, J.; Adam, W.; Golsch, D. *J. Org. Chem.* 1994, **59**, 900.
338. Link, J. T.; Gallant, M.; Danishefsky, S. J.; Huber, S. *J. Am. Chem. Soc.* 1993, **115**, 3782.
339. Gervay, J.; Peterson, J. M.; Oriyama, T.; Danishefsky, S. J. *J. Org. Chem.* 1993, **58**, 5465.
340. Smith, S. C.; Heathcock, C. H. *J. Org. Chem.* 1992, **57**, 6379.
341. Berkowitz, D. B.; Danishefsky, S. J.; Schulte, G. K. *J. Am. Chem. Soc.* 1992, **114**, 4518.
342. Grieco, P. A.; Henry, K. J.; Nunes, J. J.; Matt, J. E., Jr. *J. Chem. Soc., Chem. Commun.* 1992, 368.
343. Hosoyama, H.; Shigemori, H.; In, Y.; Ishida, T.; Kobayashi, J. *Tetrahedron* 1998, **54**, 2521.
344. Nicolaou, K. C.; He, Y.; Vourloumis, D.; Vallberg, H.; Roschangar, F.; Sarabia, F.; Ninkovic, S.; Yang, Z.; Trujillo, J. I. *J. Am. Chem. Soc.* 1997, **119**, 7960.
345. Krohn, K.; Micheel, J. *Tetrahedron* 1998, **54**, 4827.
346. Nicotra, F.; Panza, L.; Russo, G. *Tetrahedron Lett.* 1991, **32**, 4035.
347. Timmers, C. M.; van der Marel, G. A.; van Boom, J. H. *Recl. Trav. Chim.*

- Pays-Bas 1993, **112**, 609.
348. Dushin, R. G.; Danishefsky, S. J. *J. Am. Chem. Soc.* 1992, **114**, 3471.
349. Gervay, J.; Danishefsky, S. J. *J. Org. Chem.* 1991, **56**, 5448.
350. Nicolaou, K. C.; Ninkovic, S.; Sarabia, F.; Vourloumis, D.; He, Y.; Vallberg, H.; Finlay, M. R. V.; Yang, Z. *J. Am. Chem. Soc.* 1997, **119**, 7974.
351. Curci, R.; Detomaso, A.; Prencipe, T.; Carpenter, G. B. *J. Am. Chem. Soc.* 1994, **116**, 8112.
352. Marples, B. A.; Muxworthy, J. P.; Baggaley, K. H. *Tetrahedron Lett.* 1991, **32**, 533.
353. Park, T. K.; Peterson, J. M.; Danishefsky, S. J. *Tetrahedron Lett.* 1994, **35**, 2671.
354. Paquette, L. A.; Zhao, M. *J. Am. Chem. Soc.* 1998, **120**, 5203.
355. Paquette, L. A.; Zhao, M. *J. Am. Chem. Soc.* 1993, **115**, 354.
356. Charette, A. B.; Côté, B. *Tetrahedron: Asymmetry* 1993, **4**, 2283.
357. Park, T. K.; Danishefsky, S. J. *Tetrahedron Lett.* 1994, **35**, 2667.
358. Gordon, D. M.; Danishefsky, S. J. *J. Am. Chem. Soc.* 1992, **114**, 659.
359. Ireland, R. E.; Armstrong, J. D.; Lebreton, J.; Meissner, R. S.; Rizzacasa, M. A. *J. Am. Chem. Soc.* 1993, **115**, 7152.
360. White, J. D.; Hong, J.; Robarge, L. A. *J. Org. Chem.* 1999, **64**, 6206.
361. Veras, A. T.; Gundersen, L.-L.; Rise, F. *Tetrahedron* 1997, **53**, 1777.
362. Lay, L.; Nicotra, F.; Panza, L.; Russo, G. *Synlett* 1995, 167.
363. Takikawa, H.; Muto, S.-e.; Mori, K. *Tetrahedron* 1998, **54**, 3141.
364. Friesen, R. W.; Sturino, C. F. *J. Org. Chem.* 1990, **55**, 5808.
365. Liu, K. K.-C.; Danishefsky, S. J. *J. Am. Chem. Soc.* 1993, 4933.
366. Liu, K. K.-C.; Danishefsky, S. J. *J. Org. Chem.* 1994, **59**, 1895.
367. Izzo, I.; De Riccardis, F.; Sodano, G. *J. Org. Chem.* 1998, **63**, 4438.
368. Shu, L.; Shi, Y. *Tetrahedron Lett.* 1999, **40**, 8721.
369. Brown, D. S.; Marples, B. A.; Smith, P.; Walton, L. *Tetrahedron* 1995, **51**, 3587.
370. Warren, J. D.; Shi, Y. *J. Org. Chem.* 1999, **64**, 7675.

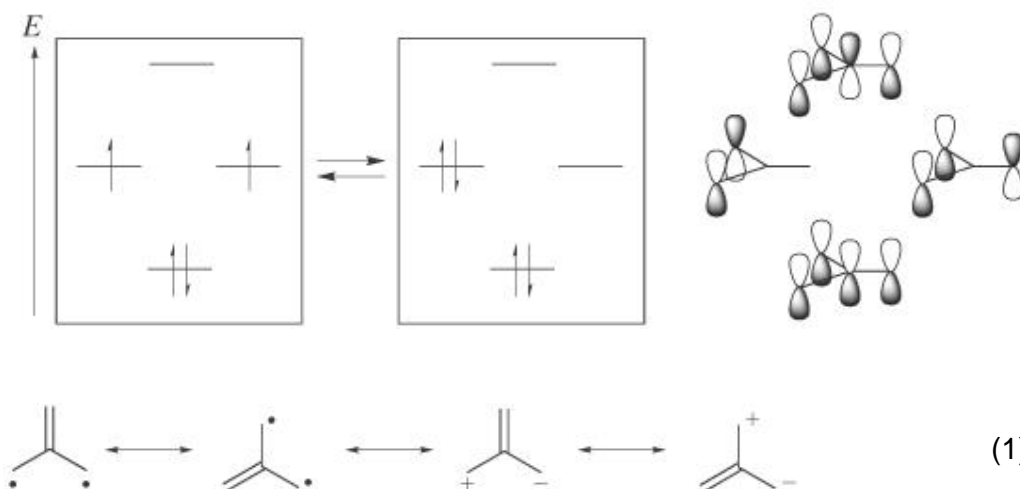
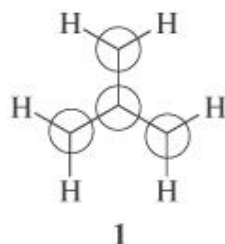
[3+2] Cycloaddition of Trimethylenemethane and its Synthetic Equivalents

Shigeru Yamago, Kyoto University, Kyoto, Sakyo-ku, Japan

Eiichi Nakamura, The University of Tokyo, Tokyo, Bunkyo-ku, Japan

1. Introduction

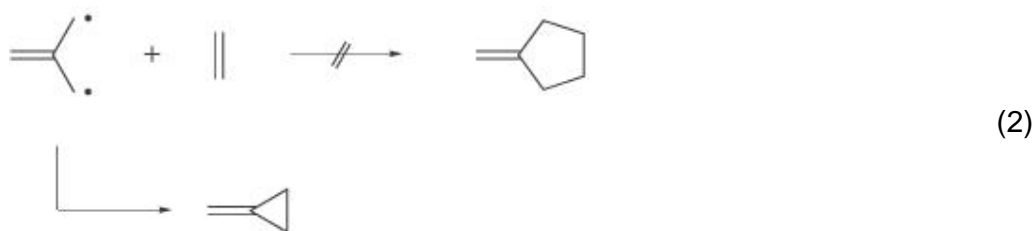
Trimethylenemethane (TMM, **1**) is a non-Kekulé molecule composed of four carbons, six hydrogens, and four π -orbitals. Therefore, TMM can only be expressed as resonance structures involving 1,3-diyls and zwitterions (Eq. 1). The two degenerate nonbonding molecular orbitals in the Hückel molecular orbital of **1** as shown below indicate the existence of singlet and triplet electronic configurations which play significant roles in the TMM chemistry.



TMMs were imaginary molecules until the late 1960's, and parent TMM (**1**) was first isolated in a low-temperature matrix. (1-3) It is stable for several weeks at

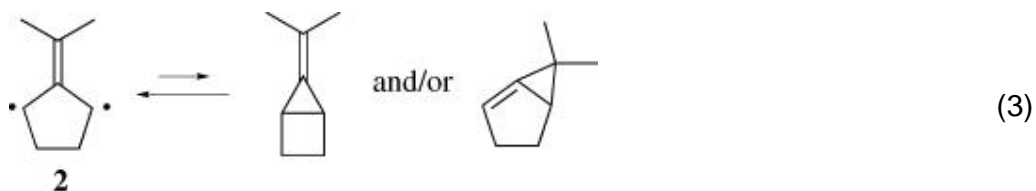
77 K, and is a ground-state triplet with a D_{3h} -planar structure as assigned by ESR spectroscopy. (4, 5) The unique structures coupled with the complex electronic states of TMM derivatives have been topics of theoretical, mechanistic, and synthetic studies.

By analogy with the Diels-Alder reaction for the synthesis of six-membered rings through [4 + 2] cycloadditions, the use of TMM as a three-carbon unit for [3 + 2] cycloadditions appears to represent a viable synthetic possibility (Eq. 2), because the



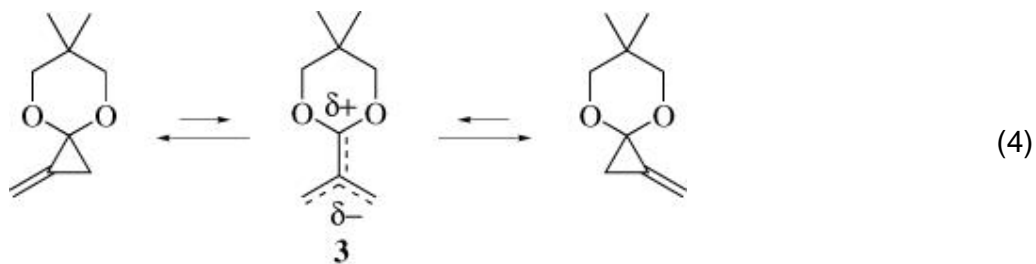
four π -electron orbital system of TMM is theoretically suitable for the $[4\pi_s + 2\pi_s]$ cycloaddition. As expected, however, rapid ring closure to methylenecyclopropane (MCP) is preferred to cycloaddition with a 2π acceptor as shown in Eq. 2. (6, 7) Therefore, for synthetic use, tailor-made derivatives of TMM and its equivalents need to be designed to achieve [3 + 2] cycloaddition reactions.

The first breakthrough in the use of TMMs for [3 + 2] cycloaddition reactions was reported in the reaction of isopropylidenecyclopentane-1,3-diyI (**2**, Eq. 3), which has a considerable lifetime and reacts with electron-deficient alkenes. (8, 9) Structural constraints in intermediate **2** retard cyclization to the corresponding MCPs and increase the efficiency of the intermolecular reaction with a 2π acceptor. Whereas stereochemical control of the reaction is difficult, intramolecular versions attain high levels of stereoselectivity and are used for various cyclopentanoid syntheses. (10-13)



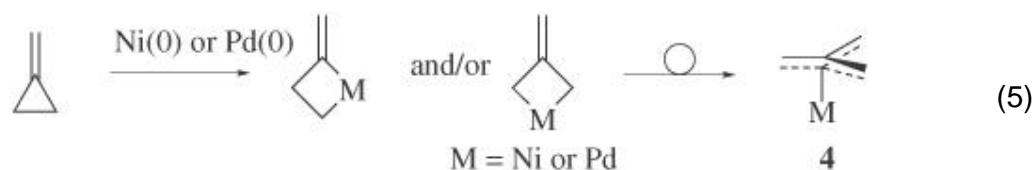
Because the parent TMM **1** gives methylenecyclopropane and many MCP derivatives undergo thermal isomerization, MCPs have been considered to

serve as precursors for TMMs. (14, 15) However, direct evidence for the formation of TMMs from MCPs and their synthetic use as TMM precursors was rather scant until recently. Alkoxy substitution on the cyclopropane ring of MCPs dramatically alters their reactivity as well as the nature of the generated TMM species. A gem-dialkoxy TMM, **3** (Eq. 4), generated thermally from a dialkoxy MCP, is a short-lived intermediate that has a polar and singlet nature and reacts with high stereoselectivity with 2π acceptors. (16, 17)



Since TMM species are generally too short-lived and too reactive to be used for organic synthesis, various attempts have been made to stabilize them with transition metal templates. A variety of metal-TMM complexes have been synthesized after the first isolation of $\text{Fe}(\eta^4\text{-TMM})(\text{CO})_3$, (18-20) but these complexes are often too stable to react with 2π acceptors.

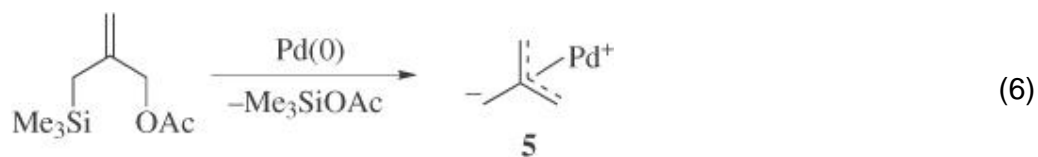
Efficient transition metal catalyzed TMM cycloaddition is achieved using MCPs and Ni(0) or Pd(0) catalysts. (21-24) The reaction proceeds via ring opening of the MCP to form (methylene)metallacyclobutane-type intermediates (Eq. 5). This reaction is more complex than it appears, as substrate, catalyst, and acceptor can influence



the regiochemistry of the cyclopropane ring cleavage. Although the detailed mechanism of the reaction is still unclear, the involvement of a TMM-metal complex **4** has been proposed in some reactions.

More recently, Pd(0)-catalyzed reactions of [2-(acetoxymethyl)allyl]trimethylsilane with 2π acceptors have emerged as a powerful method for cyclopentane synthesis. (25-28) This reaction is

considered to involve the zwitterionic TMM-Pd intermediate, **5** (Eq. 6). The reaction serves well for the [3 + 2] cycloaddition to electron-deficient acceptors, and it has been applied to the synthesis of several cyclopentanoid natural products.



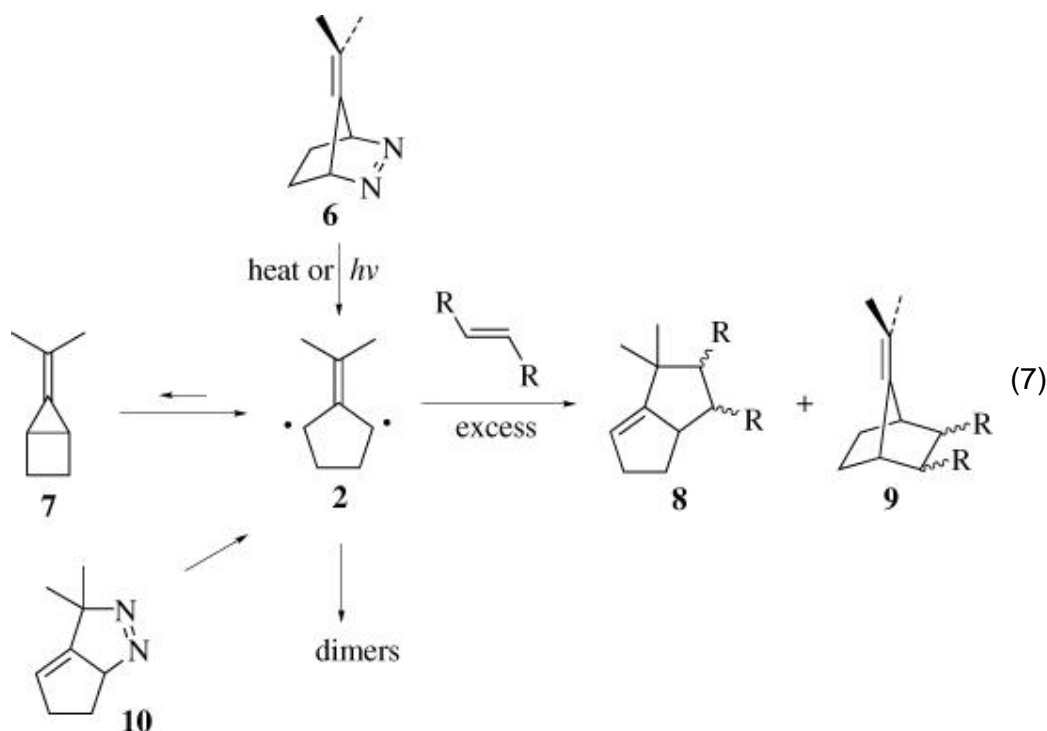
This review surveys the [3 + 2] cycloaddition reactions of TMMs and their metal complexes to 2π acceptors. The reactions are divided into five categories, defined by reaction types and precursors: (1) cycloadditions of free TMMs generated from diazenes, (2) cycloadditions of free TMMs generated from MCPs, (3) transition metal catalyzed reactions of MCPs, (4) transition metal catalyzed reactions of silylated allylic acetates, and (5) cycloaddition of stable TMM-metal complexes. Transformations that accomplish a net cycloaddition but require several steps using TMM equivalents are not covered. Various aspects of TMMs, including physical and synthetic chemistry, have already been reviewed. (2, 3, 9-13, 22-34)

2. Mechanism and Selectivities

2.1. Free Trimethylenemethanes from Diazenes

2.1.1. Generation

Free TMMs can often be made from diazenes. For example, bicyclic diazene **6** is the most commonly used precursor of the TMM **2** (Eq. 7). (8, 9)



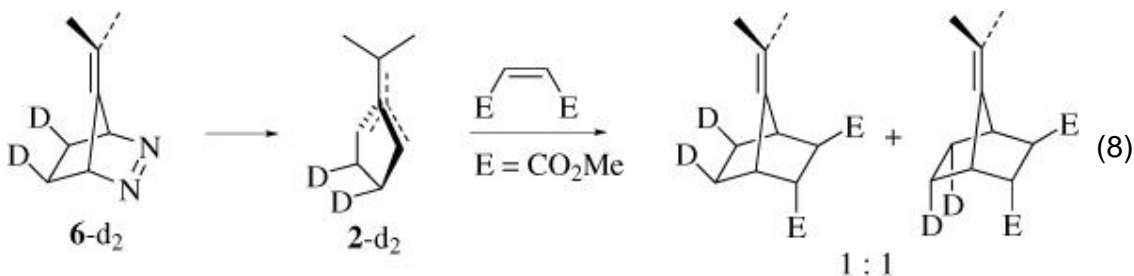
Thermolysis above 40° or photolysis of diazene **6** smoothly generates TMM **2** with loss of nitrogen. The latter has a considerable lifetime because of the structural restrictions that prevent ring closure to the corresponding MCP **7**. TMM **2** undergoes cycloaddition to an electron-deficient alkene to afford a mixture of a fused adduct **8** and a bridged adduct **9** (Eq. 7). (35, 36) In the absence of an alkenic acceptor (or with an unreactive acceptor) dimerization of TMM **2** occurs. MCP **7** and diazene **10** also serve as precursors of TMM **2**, but they are of limited synthetic utility owing to the difficulty of their preparation and/or their instability.

The chemical reactivities of biradical species depend critically on their electronic configuration, which, in turn, is related to the conformation of the biradicals. TMM **2** is stable at 77 K and is a ground-state triplet. The singlet state is estimated to lie less than 1.4–3.5 kcal/mol above the triplet. Because the energy gap between the singlet and the triplet is small, spin equilibrium between these two states occurs readily. (37-39) Therefore, under thermal

conditions, the initially formed singlet state of TMM **2** undergoes intersystem crossing to the triplet, and the dimerization of TMM **2** takes place even in the presence of a diyl acceptor. Singlet TMM can be selectively channeled to undergo a [3 + 2] cycloaddition by conducting the reaction under a high concentration of an alkene acceptor or in the presence of a triplet scavenger, such as oxygen. On the other hand, the triplet state can be selectively generated under photosensitization. (40) Although TMM **2** and its derivatives are short lived (for example, in the case of TMM **2**, 0.28 ns lifetime for the singlet and 916 ns for the triplet), they participate in a wide range of reactions. (13)

2.1.2. Structure of the TMM

Although diazene **6** possesses chemically nonequivalent exo and endo hydrogens, the corresponding geminal hydrogens are chemically equivalent in TMM **2**. Deuterium labeling experiments in the cycloaddition of exo deuterated **6-d₂** with dimethyl maleate indeed gives a 1:1 mixture of bridged products (Eq. 8). (41) This experiment shows that any asymmetric species formed in the decomposition of **6-d₂** become effectively symmetric before trapping by the alkenic diophile.



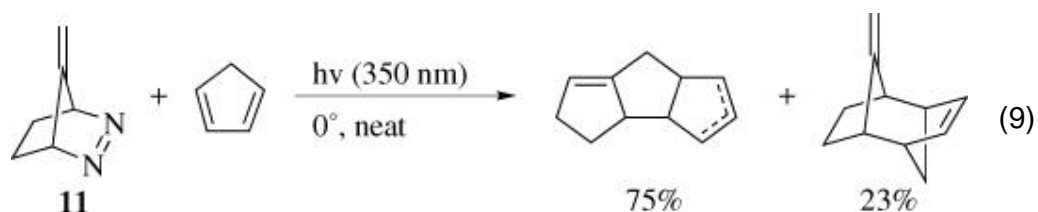
2.1.3. Regioselectivity

Singlet TMM **2** adds to an alkene with high regioselectivity, giving the fused cycloadduct **8** in preference to the bridged adduct **9** in a ratio of 31–75:1 under thermal conditions (Eq. 7). On the other hand, the cycloaddition of triplet **2** with an alkene shows very low regioselectivity, the **8:9** ratio ranging from 0.8 to 2.7:1. (36) In good agreement with the radical nature of the TMM species, the effect of solvent polarity on the product composition is small.

2.1.4. Periselectivity

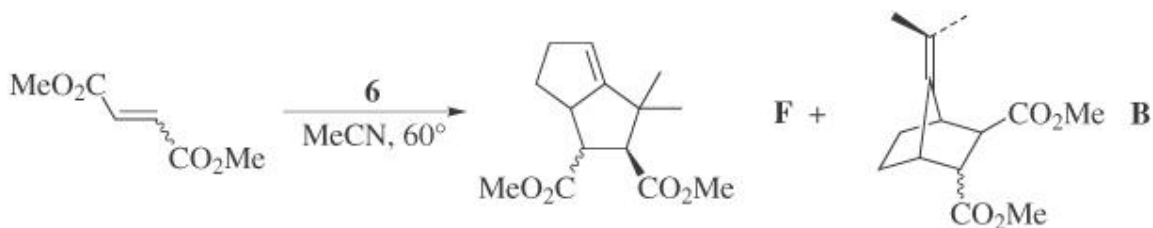
The reaction of TMMs with dienes potentially gives a mixture of [3 + 2] cycloadduct and [3 + 4] cycloadduct, which gives rise to an issue of periselectivity. Acyclic dienes preferentially give fused [3 + 2] cycloadducts, whereas cyclic dienes give a mixture of [3 + 2] and [3 + 4] cycloadducts. For example, the photolysis of diazene **11** in the presence of cyclopentadiene

gives a 3:1 mixture of the fused [3 + 2] cycloadduct and the bridged [3 + 4] cycloadduct, which are derived from the singlet TMM generated from **11** (Eq. 9). (42) This result most likely arises from the frontier orbital control in the reaction as discussed below.



2.1.5. Stereospecificity

As in reactions of carbenes, the configuration of the alkene is maintained in the cycloaddition of a singlet TMM, but is not retained in the reaction of a triplet TMM (Eq. 10). (39) Cycloaddition of the singlet TMM **2** generated from diazene **6** with dimethyl fumarate or dimethyl maleate in the presence of molecular oxygen (triplet trap) exclusively gives the fused product (**F**) with high regioselectivity. The high stereospecificity for the singlet cycloaddition suggests that the reaction proceeds via a highly ordered transition-state structure wherein the two new C — C bonds are formed almost simultaneously. On the other hand, loss of stereochemical integrity is observed in the absence of molecular oxygen for both the fused product (**F**) and the bridged product (**B**), indicating that cycloaddition of the triplet takes place in a stepwise manner.



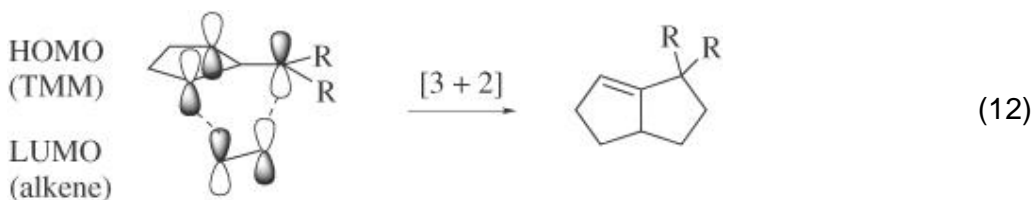
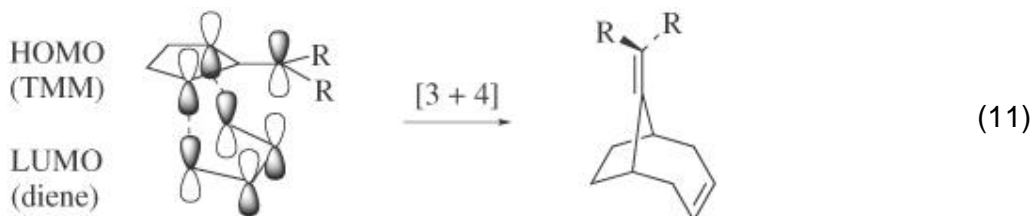
olefin conc. ([M])	O ₂	F (<i>trans:cis</i>) : B (<i>trans:cis</i>)
<i>E</i> (0.224)	+	99 (>99/0) : 1 (>99/0)
<i>E</i> (0.075)	+	99 (>99/0) : 1 (>99/0)
<i>E</i> (0.515)	-	89 (>99/1) : 11 (10/1)
<i>E</i> (0.007)	-	48 (>99/1) : 52 (6.7/1)
<i>Z</i> (6.6)	+	98 (1/49) : 2 (1/1)
<i>Z</i> (1.3)	+	93 (1/24) : 7 (2.4/1)
<i>Z</i> (6.6)	-	74 (1/4.6) : 27 (13/1)

(10)

The regioselectivity as well as the stereospecificity in the singlet cycloaddition is believed to operate under frontier orbital control. In TMM **2**, the two degenerate nonbonding molecular orbitals (NBMO) are symmetric (**S**) and antisymmetric (**A**) with respect to a symmetry plane. The periselectivity in the cycloaddition of TMM

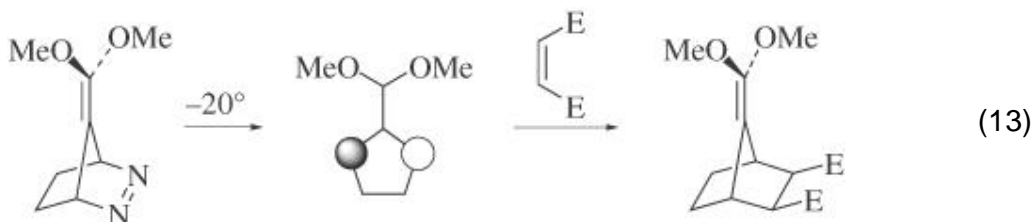


2 (R = Me) with a diene suggests that the S orbital is the HOMO of the TMM, and that the HOMO of the TMM and the LUMO of the diene interact in a symmetry-allowed fashion to promote the [3 + 4] addition, thus leading to a bridged structure (Eq. 11). (42) In the cycloaddition with simple alkenes, a symmetry-allowed interaction between the HOMO of the TMM and the LUMO of the double bond gives the fused [3 + 2] cycloadduct (Eq. 12).



2.1.6. Substituent Effects

Polar R substituents will lift the degeneracy of the NBMOs of the TMM and alter its reactivity and selectivity. (43) An electron-withdrawing R group stabilizes the S-NBMO, and an electron-donating group stabilizes the A-NBMO. Therefore, the HOMO of the alkoxy-substituted TMM (R = OMe) is an A-NBMO, thus allowing the reaction with alkenes to give the bridged adduct with high stereospecificity, as would be expected for a concerted singlet reaction (Eq. 13). (44) Although electron-withdrawing groups are also expected to lift the degeneracy, no such examples have been reported so far.

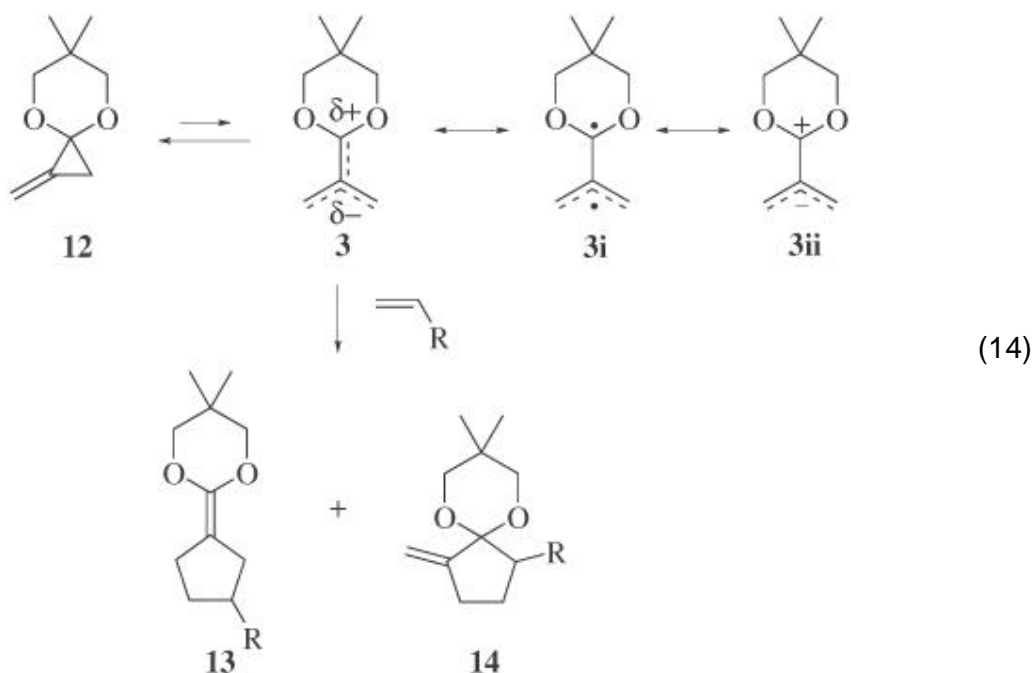


2.2. Dipolar Trimethylenemethanes from methylenecyclopropanes

2.2.1. Generation

The reaction of TMMs generated from a monocyclic MCP is strongly affected by the substituents on the MCP ring. Several examples of intramolecular rearrangement of MCPs are known, which may involve TMM intermediates. (14, 15, 45-47) However, these putative TMM species are usually unreactive in [3 + 2] cycloadditions and instead give [2 + 2] or [2 + 4] cycloadducts in which the cyclopropyl group remains intact.

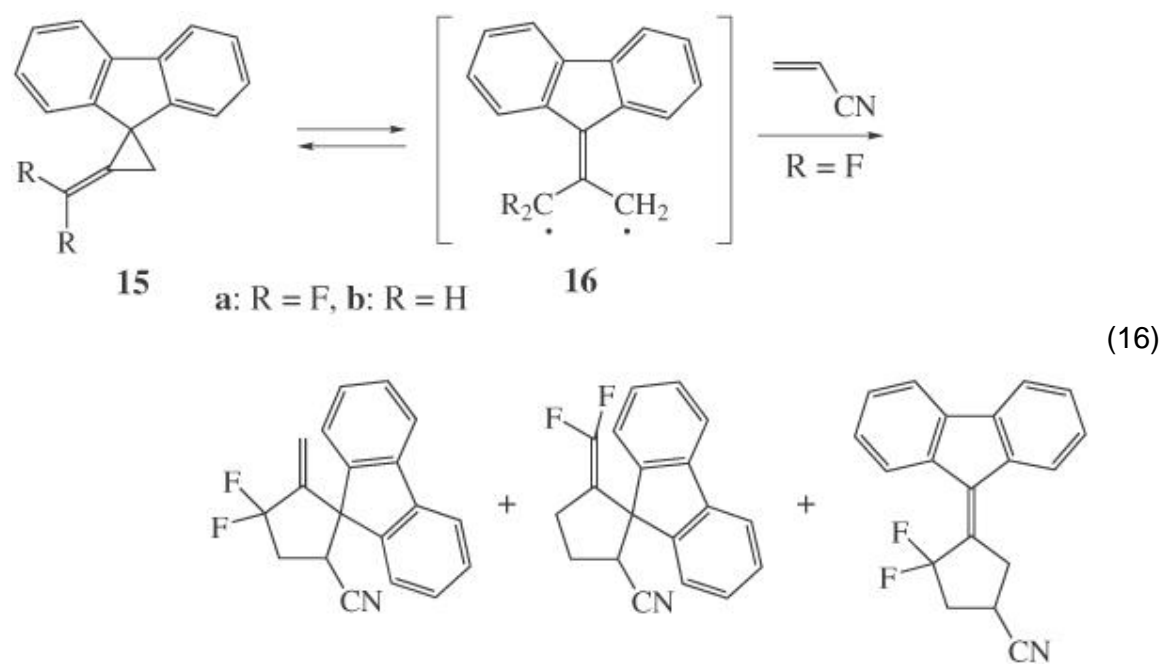
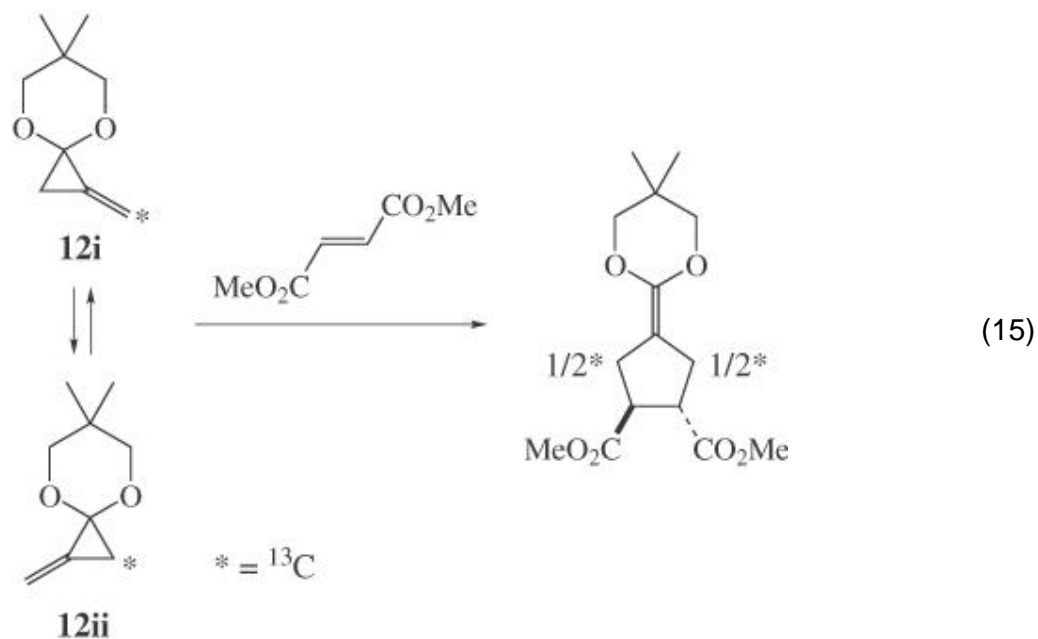
Heteroatom substitution on the cyclopropyl ring exerts pronounced effects on the properties of MCPs and TMMs. (34) 1,1-Dialkoxy-2-MCP **12** generates the dialkoxy TMM **3** upon mild thermolysis above 40° (Eq. 14). (48) One of the typical features of



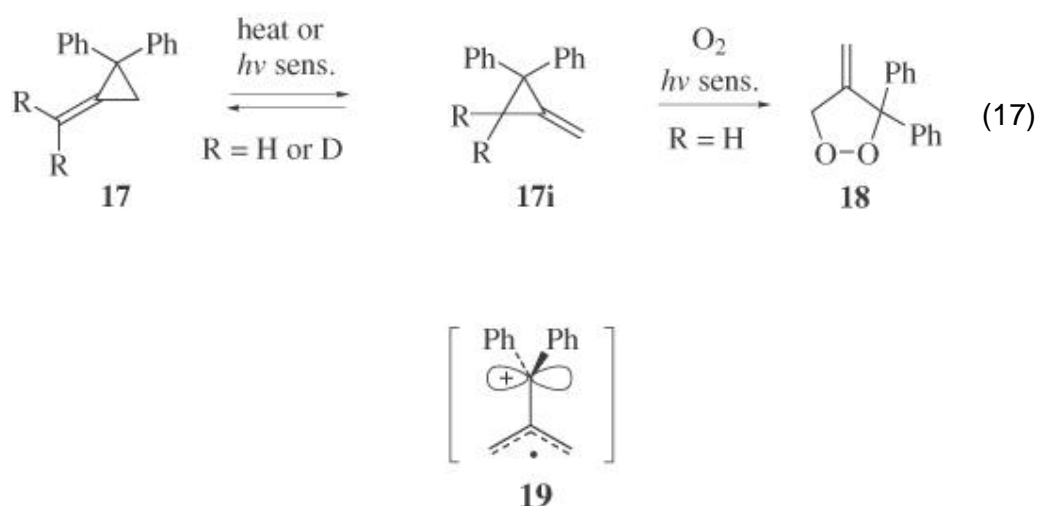
this process is its reversibility, and degenerate rearrangement takes place in the absence of an alkenic acceptor. The dialkoxy groups dramatically facilitate the MCP rearrangement. The activation energy of the degenerate isomerization of MCP **12** is 22–25 kcal/mol, which is much lower than the value determined for the parent MCP (41.2 kcal/mol) (Eq. 14). (49) Heteroatom substitution also alters the electronic state of the TMM, and TMM **3** behaves as the zwitterion **3ii** rather than the diradical **3i**. The dialkoxy TMM **3** has nucleophilic character and undergoes cycloaddition with electron-deficient alkenes rather than with electron-rich alkenes. Isomer **13** is obtained exclusively when the R group on the alkene is a moderately electron-withdrawing group, whereas a mixture of products **13** and **14** is obtained when R is a powerful electron-withdrawing group such as a nitro group.

Degenerate isomerization of MCP **12** by way of TMM **3** is usually faster than cycloaddition to an external unsaturated linkage. In ¹³C labeling experiments, the methylene-labeled methylenecyclopropane **12i** isomerized to its cyclopropanelabeled isomer **12ii** prior to the cycloaddition, even when a reactive dienophile such as dimethyl fumarate was used (Eq. 15). (50)

TMM **16** is thermally generated from fluorene-substituted MCP **15**, and it reacts with electron-deficient alkenes (for **15a**) to give isomeric [3 + 2] cycloadducts (Eq. **16**). (51) Both TMMs **16a** and **16b** possess triplet character and react readily with molecular oxygen.

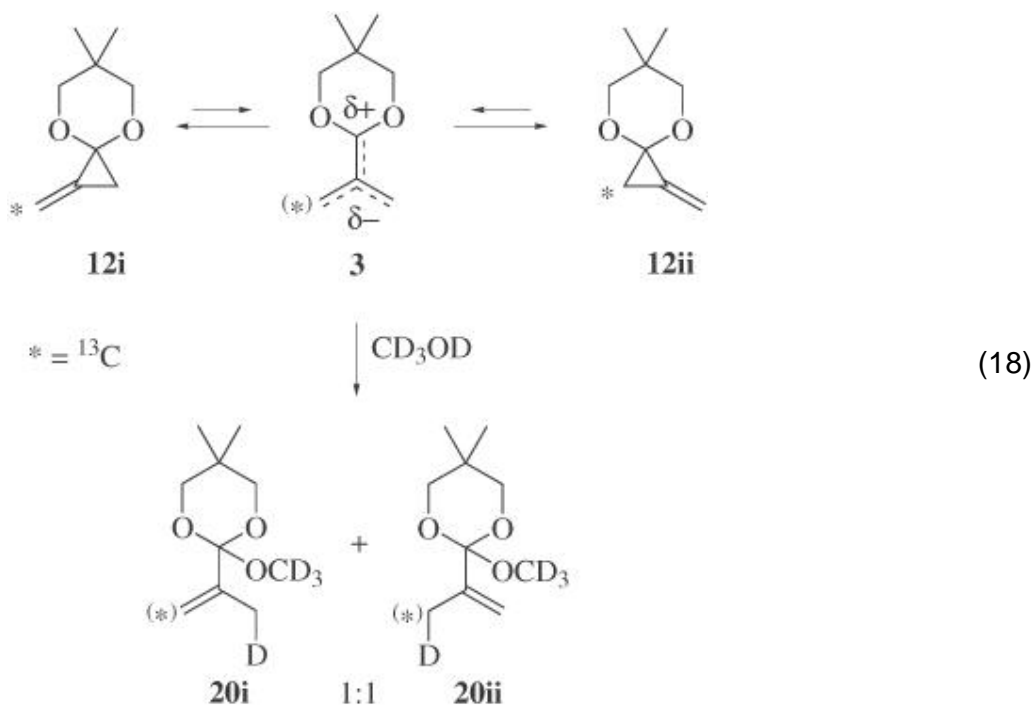


It is rather surprising that the structurally related diphenyl-substituted MCP **17** does not react with alkenes or molecular oxygen through a TMM intermediate under thermal conditions (Eq. 17). (51-53) Degenerate isomerization of MCP **17** takes place with an activation energy of 22.7 kcal/mol. (54) This value is almost identical to that of the dialkoxy MCP **12**. These results may be attributed to insufficient equilibrium concentration of the TMM species. Under photosensitization, MCP **17** reacts with molecular oxygen to give the corresponding peroxy compound **18** (Eq. 17). (51) The reaction is believed to proceed through a bisected radical cation TMM **19**.

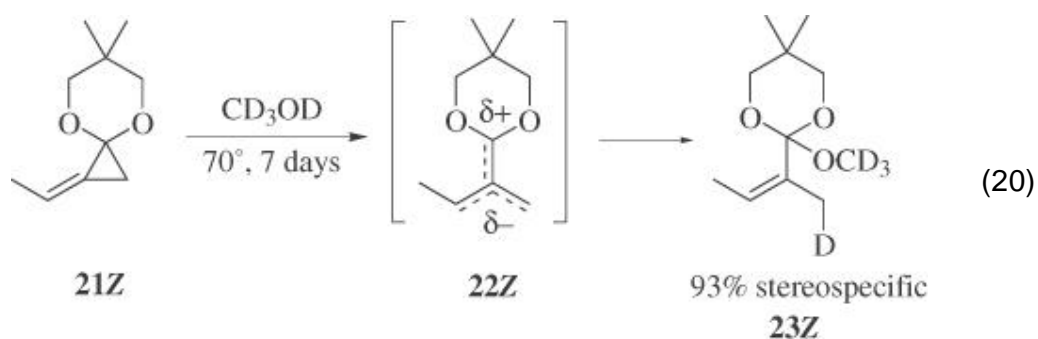
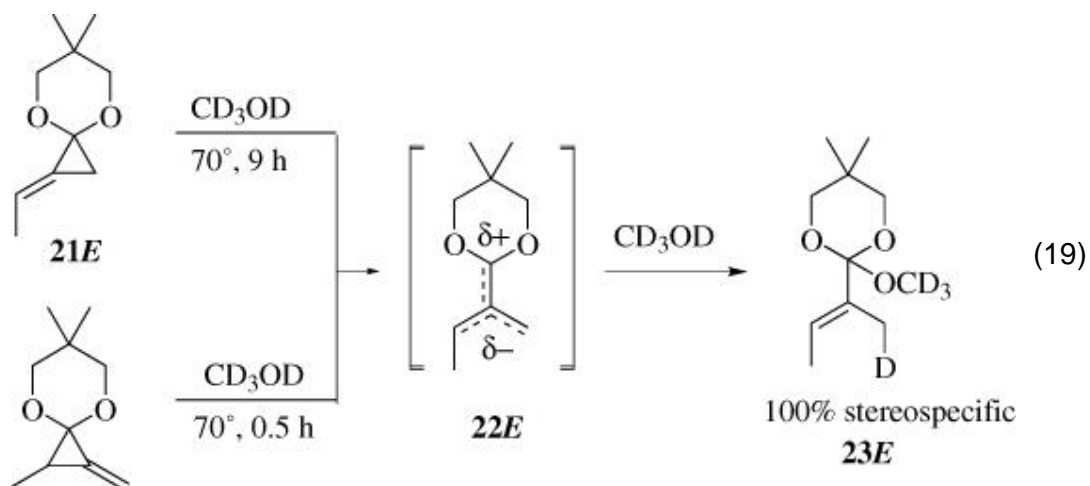


2.2.2. Structure of TMMs

In contrast to dialkoxy MCP **12**, the two terminal methylene groups in dialkoxy TMM **3** are chemically equivalent. Thermolysis of ^{13}C -labeled MCP **12i** in CD_3OD gives orthoesters of methyl acrylate **20i** and **20ii**, wherein complete scrambling of the ^{13}C label occurs with specific placement of a deuterium on the allylic methyl group (Eq. 18). (48) This experiment clearly indicates the formation of a symmetrical zwitterionic TMM species **3**, in which the two methylene groups are nucleophilic and chemically equivalent (as seen by CD_3OD). Theoretical calculations also support the dipolar character of **3**. (48)



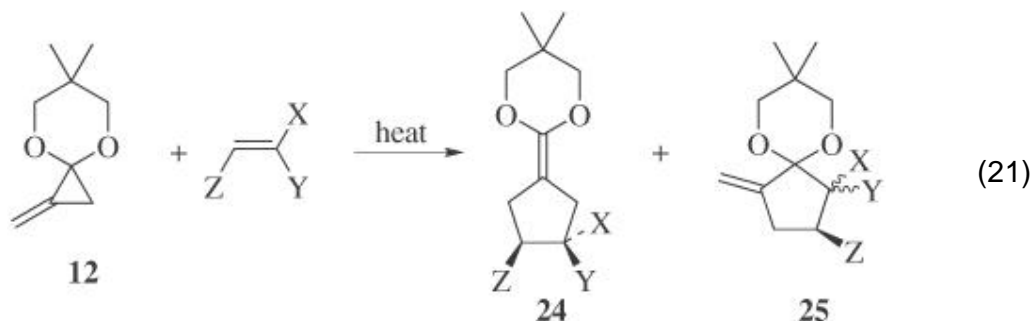
Substituted dialkoxy TMM species can be formed stereospecifically from the corresponding dialkoxy MCPs. In situ methanolysis of *E* and *Z* isomers of methyl-substituted MCPs **21E** and **21Z** gives *E*- and *Z*-tiglate orthoesters **23E** and **23Z** with 100% and 93% retention of the configuration of the starting alkenes, respectively (Eqs. 19 and 20). (48) This stereospecificity reveals that isomeric TMMs **22E** and **22Z** are generated from the corresponding *E* and *Z* MCPs, and that they exist as discrete intermediates. The methanolysis of the isomeric methyl-substituted dialkoxy MCP also gives *E*-tiglate orthoester **23E** with 100% specificity. Some loss of the stereospecificity from MCP **21Z** to product **23Z** indicates that orthoester **22Z** is less thermodynamically



stable than its isomer **22E**, and that intermediate **22Z** to some extent undergoes bond rotation to form intermediate **22E**. In addition, since the generation of *Z*-TMM **22Z** from MCP **21Z** is much slower than that of *E*-TMM **22E** from MCP **21E**, only the *E*-TMM participates in the cycloaddition reaction.

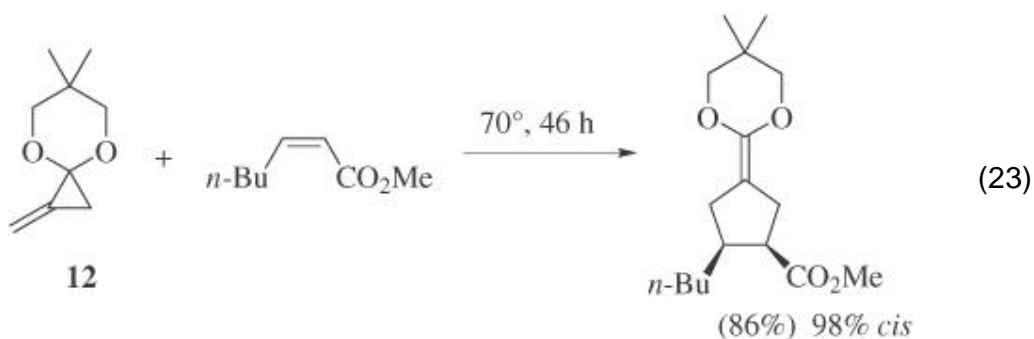
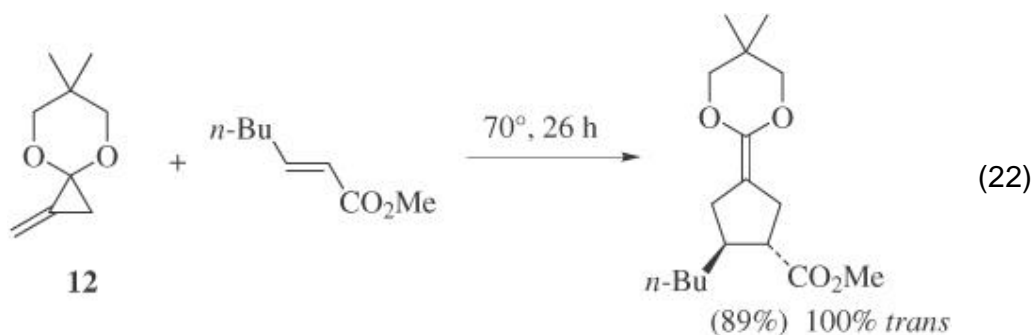
2.2.3. Regioselectivity

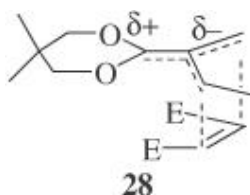
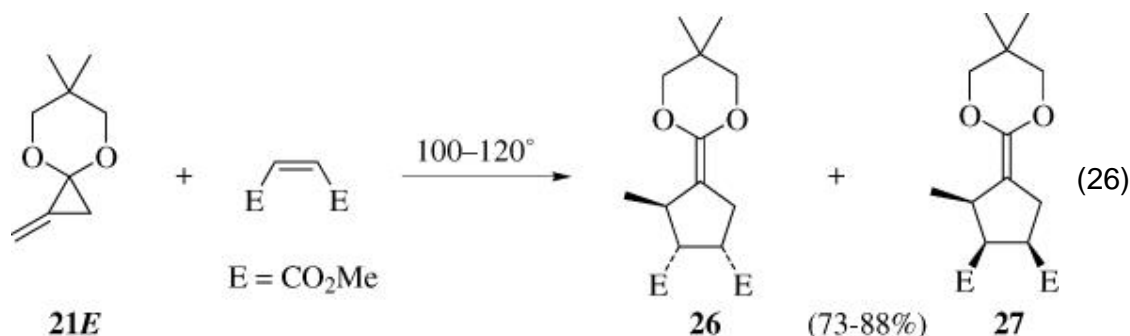
Whereas the cycloaddition of MCP **12** with an electron-deficient alkene usually gives a ketene acetal cycloadduct **24**, cycloaddition with a more highly electron-deficient alkene gives a mixture of **24** and a regioisomeric exomethylene isomer **25** (Eq. 21). (55) Formation of isomer **24** is predominant with moderately electron-deficient alkenes, such as X = ester, ketone; Y = H, alkyl; Z = H, alkyl. Formation of product **25** is general for an alkene whose reduction potential is larger than -1.8 V (vs. SCE) such as X = Y = CO₂Me, Z = alkyl. The isomer ratio of products **24** to **25** is highly dependent on the nature of the electron-withdrawing group and the substitution patterns.



2.2.4. Stereospecificity

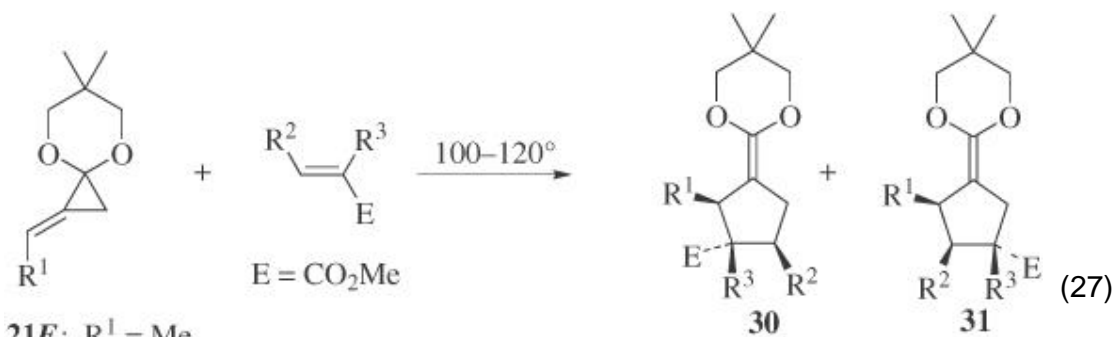
The cycloaddition of MCP **12** with moderately electron-deficient alkenes is highly stereospecific. The reactions with the *E* and *Z* isomers of methyl 2-heptenoate give ketene acetal products with 100% and 98% retention of configuration, respectively (Eqs. **22** and **23**).⁽¹⁶⁾ The high stereospecificity and the negligible solvent effect suggest that the cycloaddition proceeds through a highly ordered transition state in which the allylic carbon of **3** serves as a 4 π electron system in a concerted cycloaddition with a 2 π acceptor.





increased from octane ($\epsilon = 1.9$) to DMSO ($\epsilon = 46.7$). The observed polar effect is consistent with the endo transition state **28**, wherein polar interactions between the directing groups control the stereoselectivity.

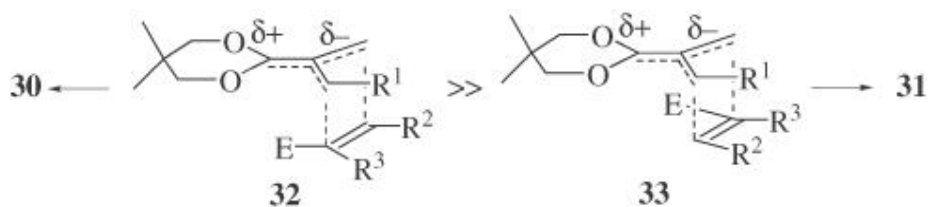
Complete endo selectivity is observed in the cycloaddition of MCP **21E** with methyl *trans*-crotonate and methyl methacrylate, but equal amounts of the regioisomers **30** and **31** are formed (Eq. **27**).⁽⁵⁶⁾ However, when R^1 and R^2 are bulky in endo transition state **33**, a high level of regiocontrol is achieved because of the severe steric interaction between the two substituents. This unfavorable interaction does not occur in transition state **32**. Therefore, isopropyl-substituted MCP **29** reacts with methyl *trans*-crotonate to give a single endo adduct, with other isomers accounting for only 4% of the cycloadducts. Similarly, methyl (*E*)-4,4-dimethyl-2-pentenoate, bearing a bulky substituent (R^2) on the alkene, reacts with MCP **21E** to give a single cycloadduct in more than 97% isomeric purity.



21E: R¹ = Me

29: R¹ = *i*-Pr

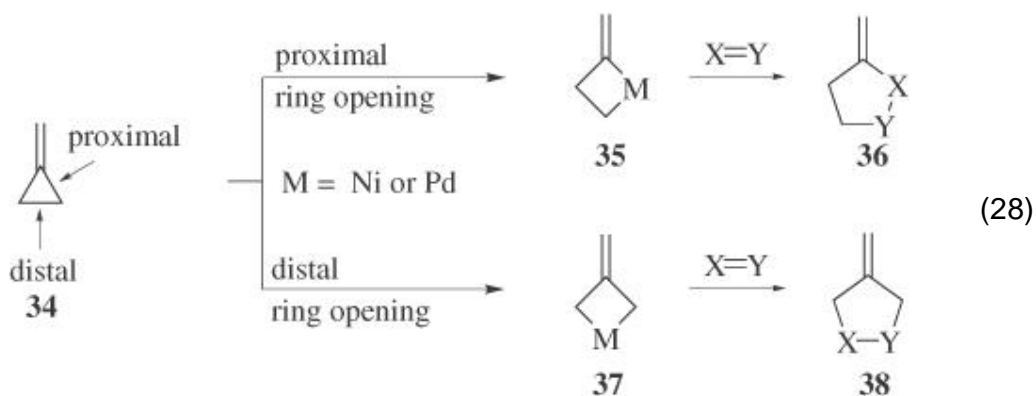
R ¹	R ²	R ³	30:31	
Me	Me	H	1:1	(81%)
Me	H	Me	1:1	(72%)
<i>i</i> -Pr	Me	H	25:1	(71%)
Me	<i>t</i> -Bu	H	>32:1	(89%)



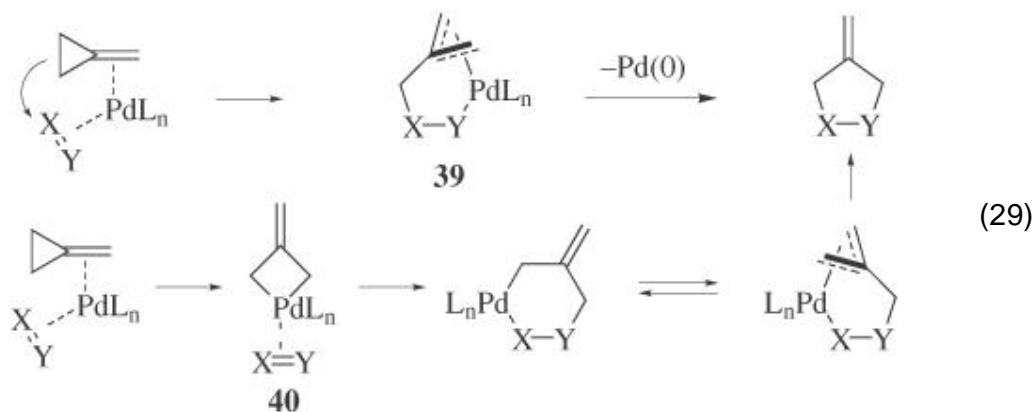
2.3. Transition Metal Catalyzed Reactions of methylenecyclopropanes

2.3.1. Generation

Methylenecyclopropanes undergo [3 + 2] cycloaddition reactions with alkenes in the presence of Ni(0) or Pd(0) catalysts. (23, 24) The transformations can be formally regarded as reactions of metallacyclobutane intermediates **35** and **37**, generated by oxidative addition into the proximal or distal bond of methylenecyclopropane (**34**), respectively. Subsequent alkene insertion followed by reductive elimination leads to the formation of cyclopentane derivatives **36** and **38** (Eq. 28).



Mechanistic studies and theoretical calculations suggest that the Pd(0)-catalyzed reaction proceeds by direct attack of the distal bond of MCP on the double bond of the alkene-metal complex to generate π -allyl palladium complex **39**, although a mechanism that involves a palladacyclobutane intermediate **40** cannot be completely ruled out (Eq. 29). (33, 57-59) Mechanistic details of the Ni(0)-catalyzed reaction are unknown.

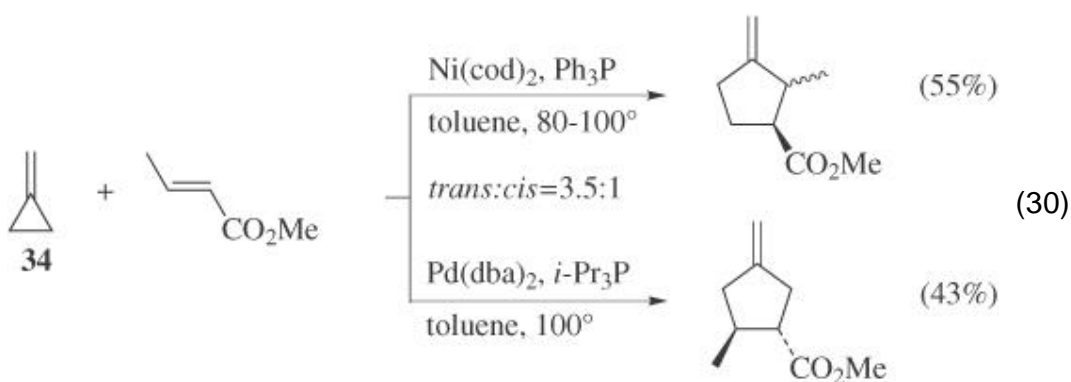


The most commonly used Ni(0) catalysts are Ni(acrylonitrile)₂ [Ni(an)₂], Ni(1,5-cyclooctadiene)₂ [Ni(cod)₂], and triarylphosphine modified Ni(cod)₂. Addition of a phosphine ligand usually retards the cycloaddition and also alters the regioselectivity of the ring opening. Pd(0) catalysts usually require a phosphine ligand, and *i*-Pr₃P is most commonly used. Although the reactivities of Pd catalysts are lower than Ni catalysts, the reaction is more predictable, making Pd catalysts synthetically more valuable.

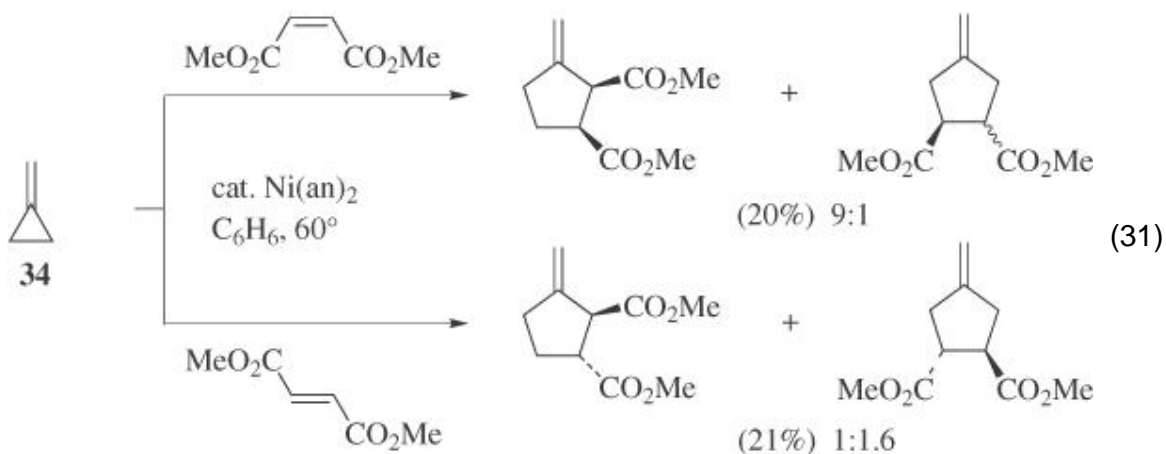
2.3.2. Regioselectivity

The regiochemical course of the ring opening is highly dependent on the substitution pattern of the substrate and the nature of the catalyst. Ni(0) catalysts preferentially give the cycloadduct by proximal ring opening, whereas Pd(0) catalysts promote distal ring opening (Eq. 30). (60, 61)

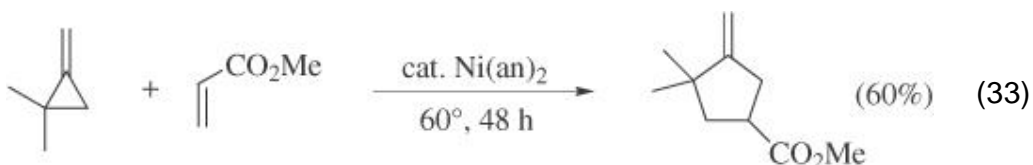
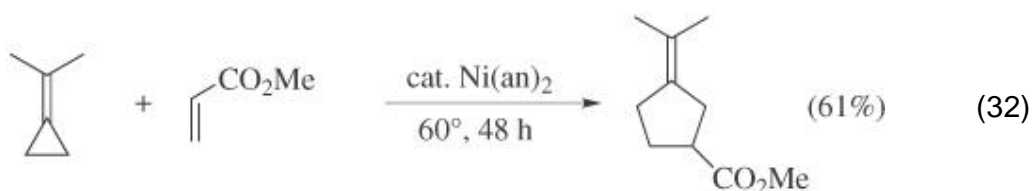
With Ni(0) catalysts, the selectivity of cyclopropane ring opening is also highly dependent on the olefinic substrate and the MCP substituent. For example, although cycloaddition of the parent MCP (34) with dimethyl maleate gives products predominantly derived from proximal ring opening, that with dimethyl fumarate gives a mixture in which the product of proximal ring opening slightly predominates



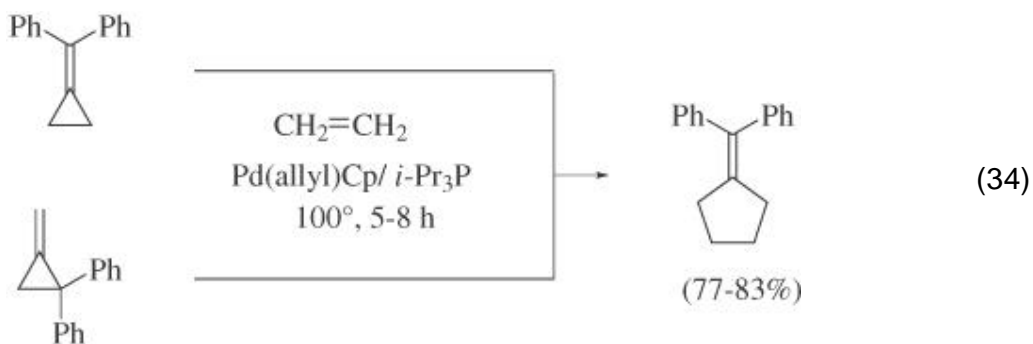
(Eq. 31). (62) Ligands also affect the selectivity, and phosphine- or phosphite-modified Ni catalysts favor distal bond cleavage. However, there is no clear rationale for this trend.



The reaction of monosubstituted MCPs leads to distal and proximal ring opening. MCPs that are disubstituted at the cyclopropyl or vinylic carbon mainly undergo distal ring opening. Therefore, isomeric MCPs with substitution at the cyclopropyl carbon and at the olefinic carbon give isomeric cycloadducts (Eqs. 32 and 33). (63) When the substitution is on the cyclopropane ring, the ring opening takes place selectively at the less substituted side.



In the presence of a Pd(0) catalyst, all types of MCPs undergo distal ring opening regardless of the substitution pattern. Aryl-substituted MCPs give exclusively alkylidene-type adducts regardless of the starting MCP (Eq. 34). (64)



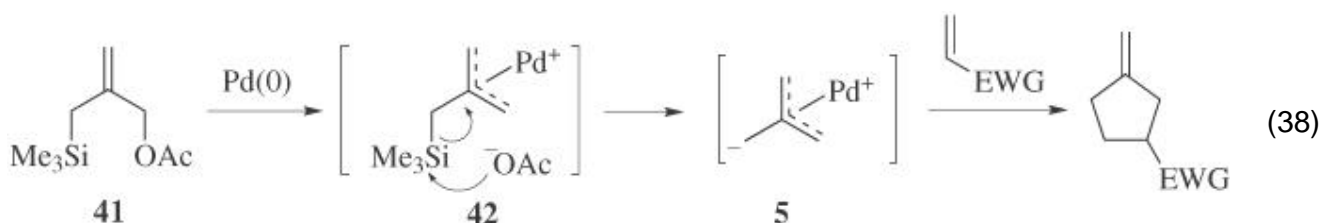
2.3.3. Stereospecificity

Although the geometry of the alkene is maintained in the nickel-catalyzed reaction of trans alkenes (Eq. 35), partial to complete scrambling of

2.4. Transition Metal Catalyzed Reactions of Silylated Allylic Acetates

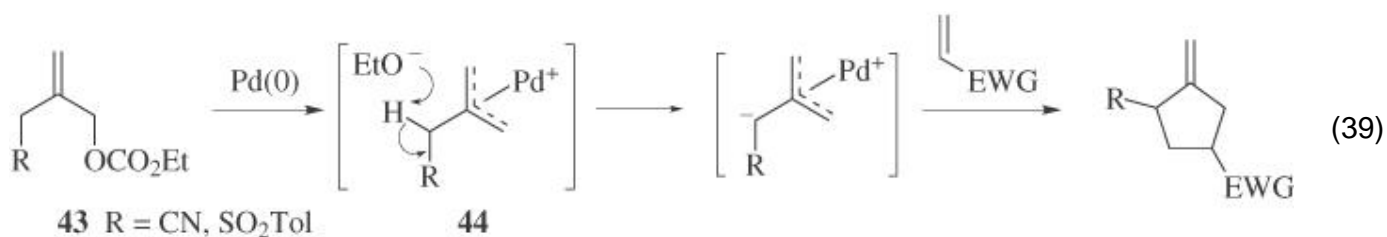
2.4.1. Generation

A zwitterionic TMM–Pd complex **5** is typically generated in situ via a Pd-catalyzed reaction of 1-(acetoxymethyl)allyltrimethylsilane (**41**) (Eq. 38). (26)



Ionization of **41** by Pd(0) generates the π -allylpalladium species **42**, which undergoes acetate anion promoted desilylation to form the zwitterionic TMM–Pd complex **5**, the formation of which is supported by labeling experiments and theoretical calculations. (66–68) Complex **5** is nucleophilic in nature, and undergoes cycloaddition with electron-deficient alkenes to form methylenecyclopentane derivatives. (69)

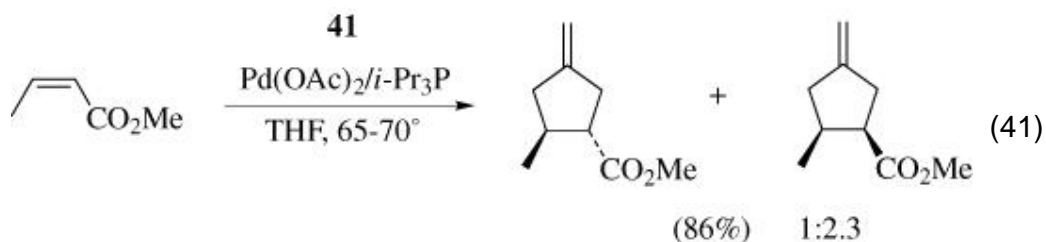
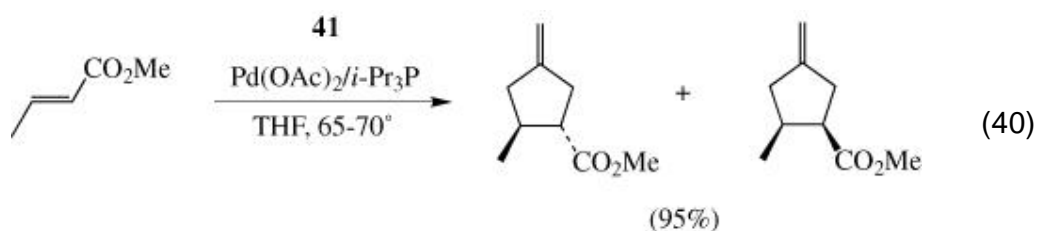
Allylic carbonate **43** bearing an anion-stabilizing functional group, for example R = CN and SO₂Tol, also undergoes [3 + 2] cycloaddition in the presence of Pd(0) catalysts (Eq. 39). (70) In this reaction, the ionization of substrate **43** with Pd(0) generates



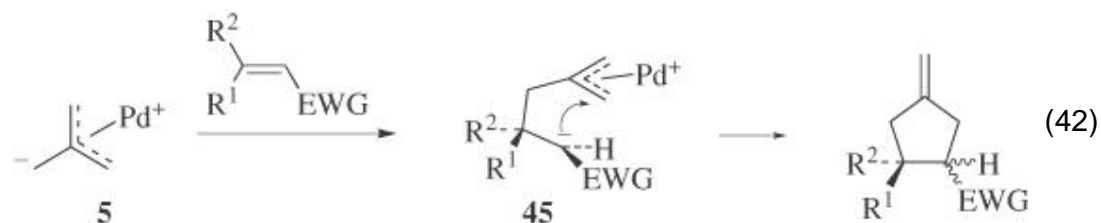
an alkoxide which serves as a base to deprotonate the π -allyl intermediate **44**. The resulting zwitterionic TMM–Pd intermediate undergoes cycloaddition to electron-deficient alkenes.

2.4.2. Stereospecificity

The reaction of **5** with alkenes exhibits moderate to high stereospecificity. In the reaction of methyl crotonate with **5**, the *E* isomer reacts stereospecifically, whereas the *Z* isomer reacts with significant loss of geometric integrity (Eqs. 40 and 41). (71)

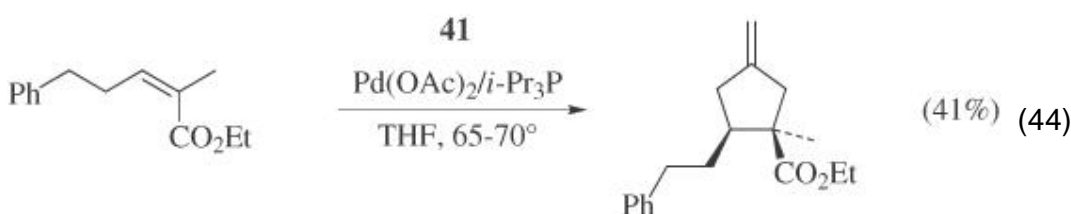
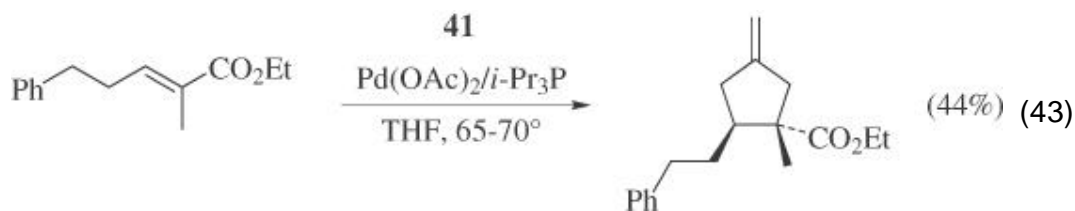


Since no detectable geometric isomerization of the starting alkenes is observed, the loss of stereospecificity must occur during ring closure. These results show that [3 + 2] cycloaddition takes place in a stepwise manner. Thus, Michael addition of the zwitterionic TMM–Pd complex **5** to an electron-deficient alkene generates stabilized zwitterion **45** that has a sufficient lifetime to undergo bond rotation before collapse to form the cycloadduct (Eq. 42). (67, 69) Despite the loss of stereochemical information of the alkenes to the products, a concerted mechanism has been proposed recently based on carbon kinetic isotope effects. (72)



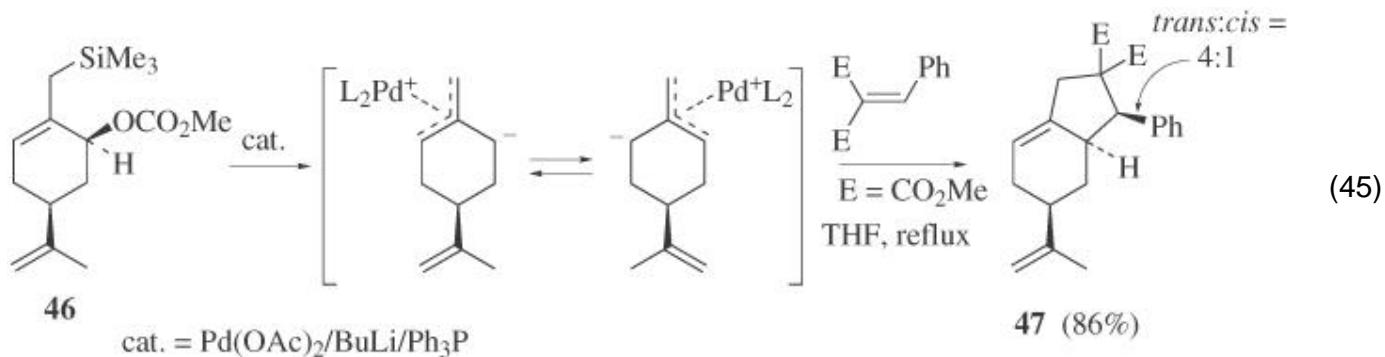
The reaction of trisubstituted alkenes is virtually completely stereospecific (Eqs. 43 and 44). (71) The observed high stereospecificity suggests that the zwitterionic intermediate, such as **44**, has a rather short lifetime and compact structure, because bond rotation is completely blocked by the α -methyl group. These observations indicate that the cycloaddition takes place in a stepwise

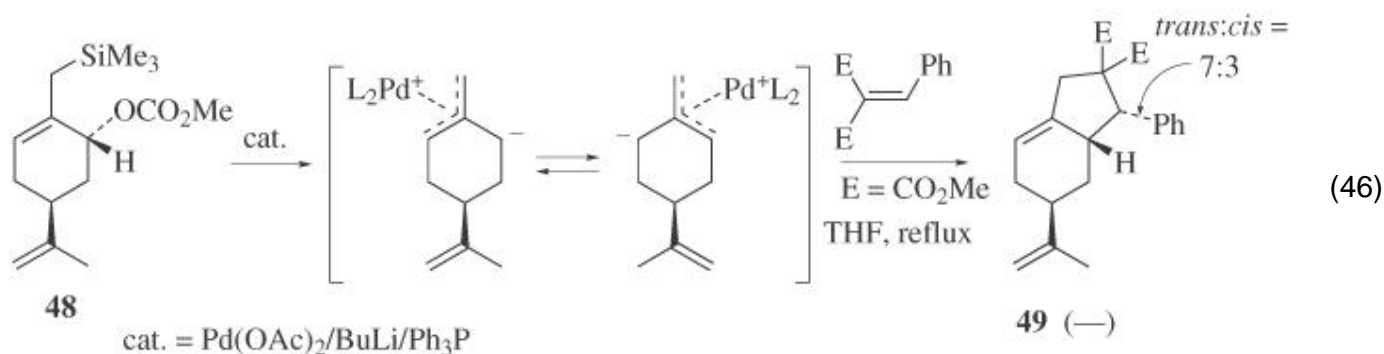
manner, in which the transition state geometries resemble what may be expected for a concerted cycloaddition.



2.4.3. Stereoselectivity

In the reactions of the TMM intermediate **5** (generated in situ from acetate **41**) the new C — C bond is formed with net retention of configuration with respect to the face of the allyl unit. The cycloaddition of the allylic carbonate derived from carveol shows a unique donor-dependent stereoselectivity. Reaction of the *trans* and *cis* derivatives **46** and **48** with dimethyl benzylidenemalonate gives exclusively 1,3-*trans*-**47** and 1,3-*cis*-**49**, respectively (Eqs. **45** and **46**). (73) The initial Pd-assisted ionization occurs with inversion of configuration, and the new C — C bond

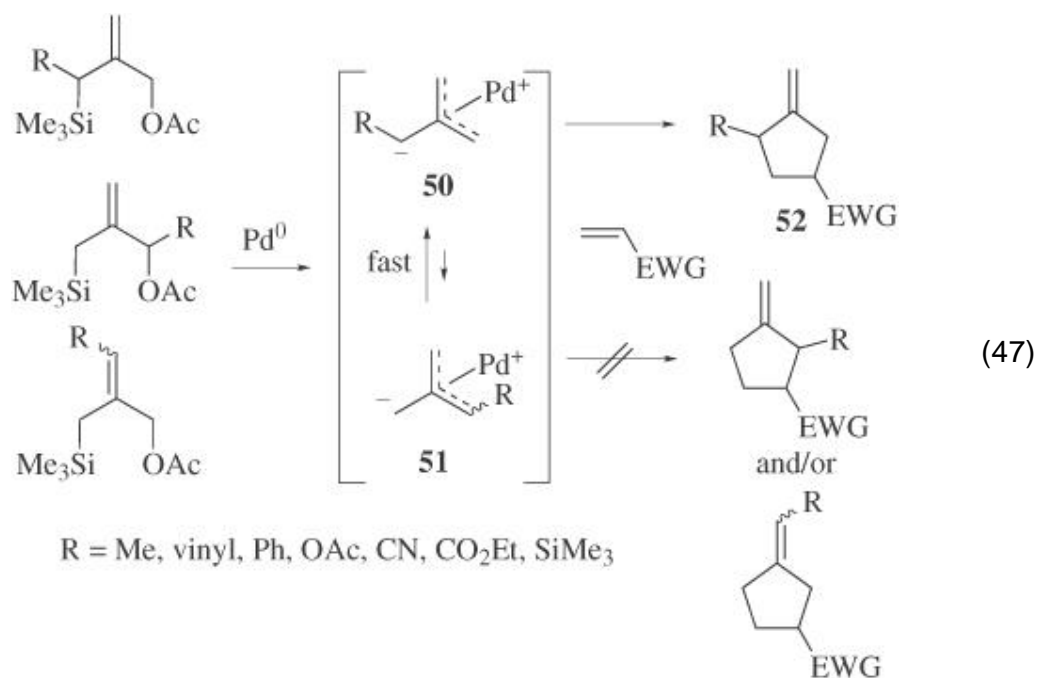




also forms with inversion. The results indicate that the approach of the alkene takes place from the side anti to the TMM-Pd species rather than from the inside after coordination of the alkene to the metal TMM species. Even though the starting materials are enantiomerically enriched, the products are racemic because of the rapid isomerization of the enantiomeric TMM-Pd complexes.

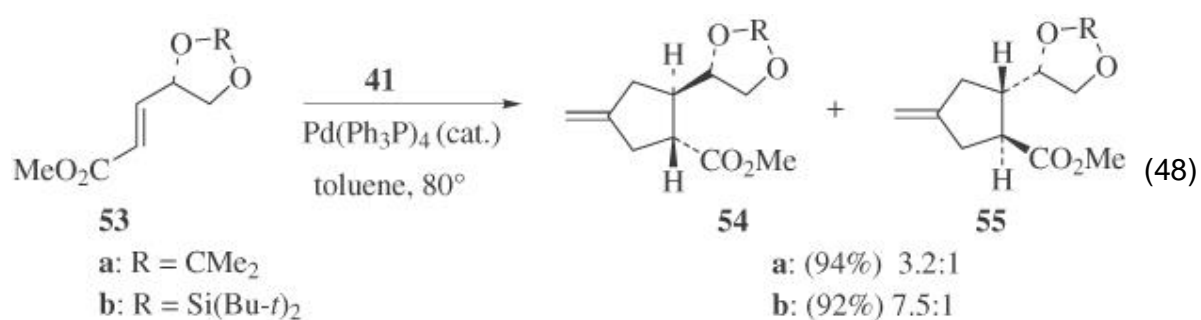
2.4.4. Regioselectivity

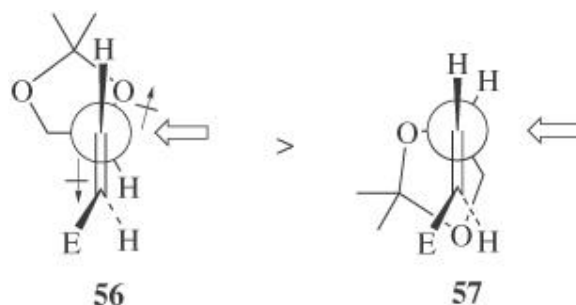
The cycloaddition of a substituted TMM-Pd complex with an alkene shows remarkable regioselectivity. Although the cycloaddition of substituted TMM species potentially can give two regioisomeric cycloadducts, in fact **52** is formed selectively regardless of both the structure of the starting acetoxymethylallyltrimethylsilanes, or of the electron-donating and electron-withdrawing nature of the R group (Eq. 47). (74, 75) This result may be rationalized by considering the rapid equilibrium of the TMM-Pd complexes and their relative stabilities and reactivities. One possible rationale is that the substituted TMM-Pd complex **51** (kinetically generated from the corresponding TMM precursors) rapidly isomerizes to the thermodynamically more stable isomer **50**, which then gives rise to product **52**. An alternative possibility is that the most negatively charged carbon on TMM-Pd complex **50** preferentially attacks the electron-deficient alkene regardless of the stabilities of the intermediates; theoretical calculations support this view. (68)



2.4.5. Diastereoselectivity

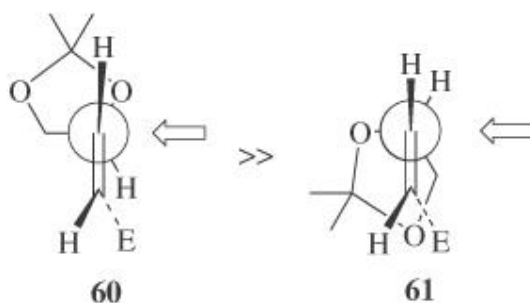
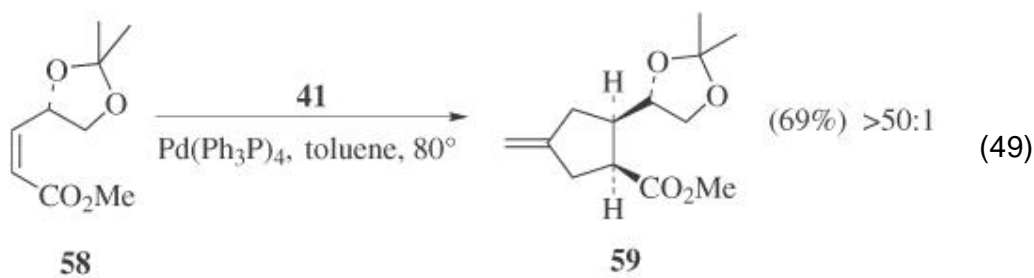
The 1,2-asymmetric induction in the cycloaddition of **5** shows moderate to high diastereoselectivity depending on the alkene acceptors. The cycloaddition of TMM–Pd complex **5** (generated from acetate **41**, Eq. 38) with *E*-enoate **53a** (R = CMe₂) in toluene at 80° gives the two cycloadducts **54a** and **55a** in a 3.2:1 ratio (Eq. 48). (76) The major isomer arises from reactive conformation **56**





on the basis of dipole-dipole and nonbonded steric interactions. Although the same isomer can arise from conformer **57** (which is predicted by the Felkin-Anh analysis), loss of selectivity in polar solvents may agree with the dominance of dipole-dipole effects. Reaction of complex **5** with the di-*tert*-butylsilylene derivative **53b** [R = Si(Bu-*t*)₂], wherein the silyl ether increases the dipole effect, increases the product ratio to 7.5:1.

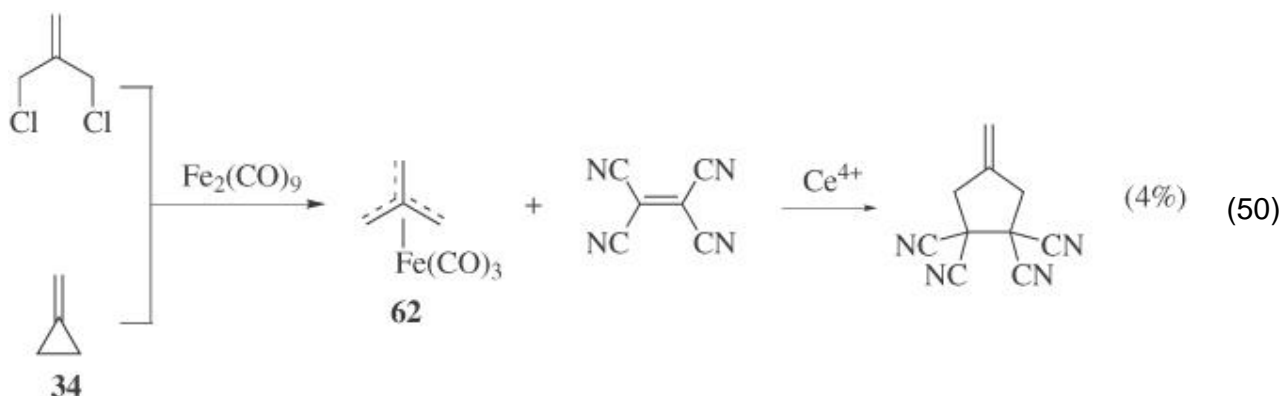
Cycloaddition of *Z*-enoate **58** with TMM-Pd complex **5** under identical conditions gives a single cycloadduct **59** (>50:1) in 69% yield (Eq. 49). (77) Since the conformer **61** from the Felkin-Anh analysis is disfavored because of A (1, 2) strain, this extremely high facial selectivity is in best accord with conformer **60** as the reactive species.



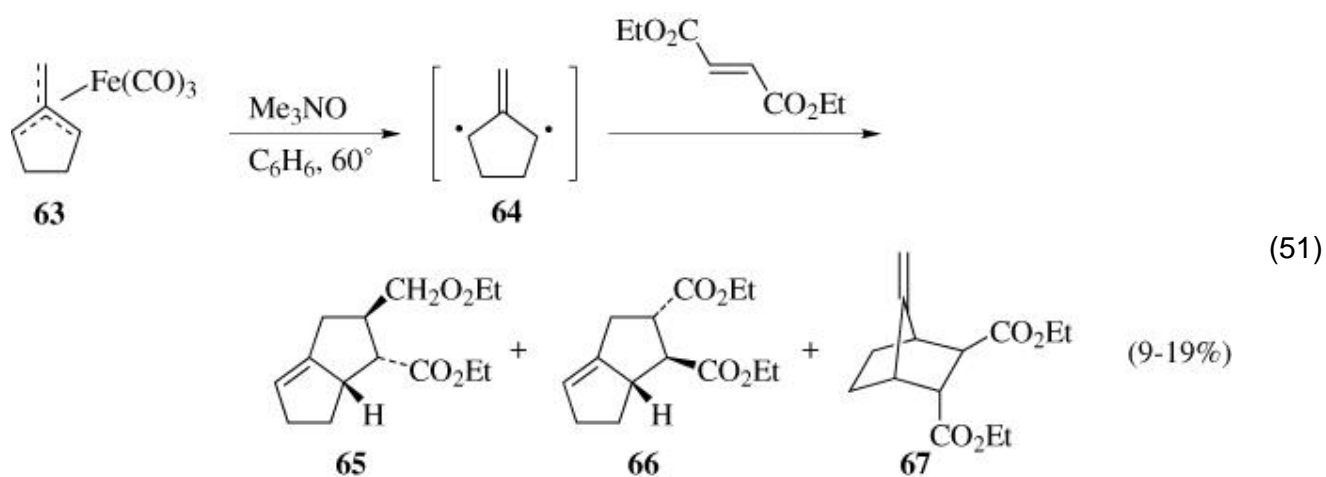
2.5. Cycloadditions of Stable TMM-Metal Complexes

Although various η (4)-TMM-metal complexes have been synthesized, they are usually too stable to react with external 2π acceptors. (20) The TMM

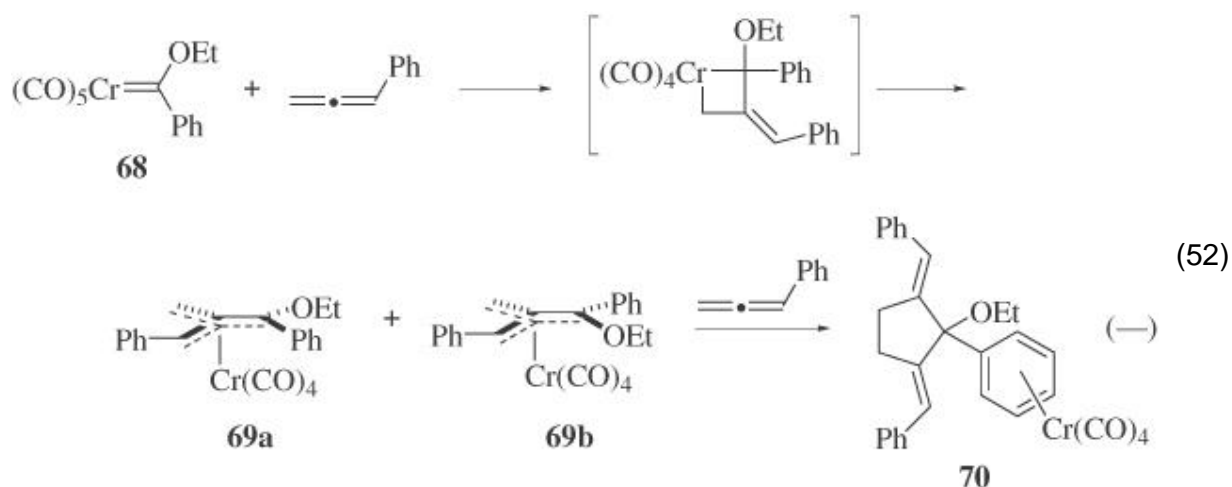
complex $\text{Fe}[\eta^4\text{-(TMM)(CO)}_3]$ (**62**), which is prepared by the reaction of $\text{Fe}_2(\text{CO})_9$ with 3-chloro-2-chloromethyl-1-butene or the parent MCP **34**, is stable and does not react with alkenes by itself. However, oxidation of complex **62** in the presence of tetracyanoethylene gives the [3 + 2] cycloadduct, albeit in very low yield (Eq. 50). (78)



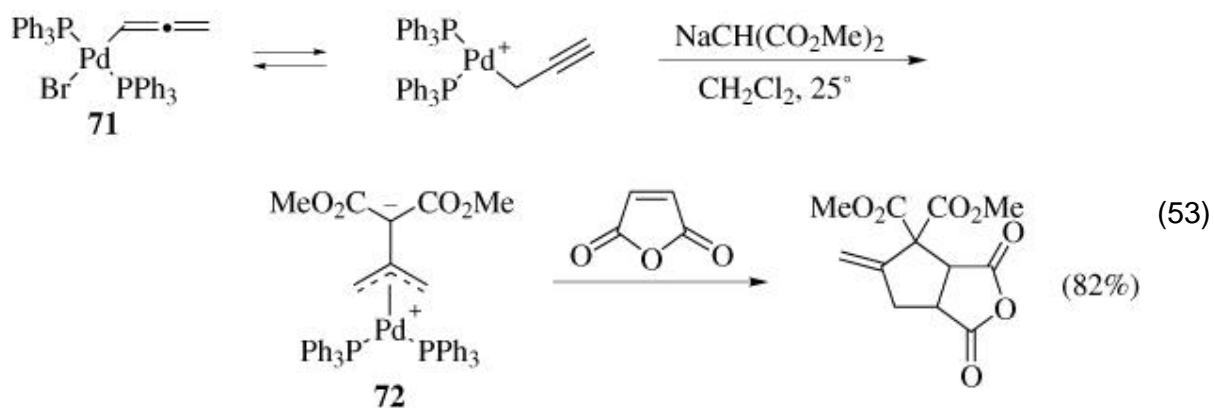
The cycloaddition of TMM–Fe complex **63** in the presence of a large excess of diethyl fumarate affords two fused cycloadducts **65** and **66** and a bridged adduct **67** (Eq. 51). (79) The similarity of the product distribution with that of the thermal cycloaddition of the diazene **11** suggests that the iron complex liberates free 1,3-diy type TMM **64**, which undergoes cycloaddition to electron-deficient alkenes.



Fischer chromium carbene complex **68** reacts with phenylallene with loss of carbon monoxide to form a mixture of diastereomeric η^4 -TMM–Cr complexes **69a** and **69b**, which react with a second molecule of phenylallene to give the five-membered ring product **70** (Eq. 52). (80)



Although zwitterionic η^3 -TMM complexes are believed to be generated in metal-catalyzed reactions, only a single example is known for the reaction of an isolable η^3 -TMM-metal complex. Stable zwitterionic η^3 -TMM–Pd complex **72** is synthesized by the nucleophilic addition of stable carbanions, such as the sodium salt of dimethyl malonate, to the metal allenyl complex **71** (Eq. 53). (81) Complex **72** is readily coupled with an electron-deficient acceptor such as tetracyanoethylene or



maleic anhydride to form cyclopentane cycloadducts. These particular reactions are not catalytic processes because these alkenes are good π

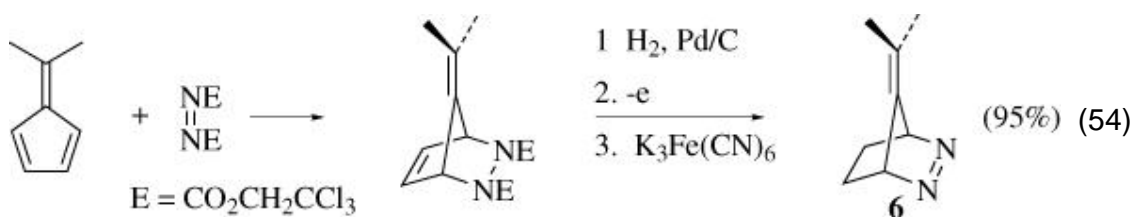
acceptors and react with the generated Pd(0) species upon cycloaddition before forming the TMM intermediate.

3. Scope and Limitations

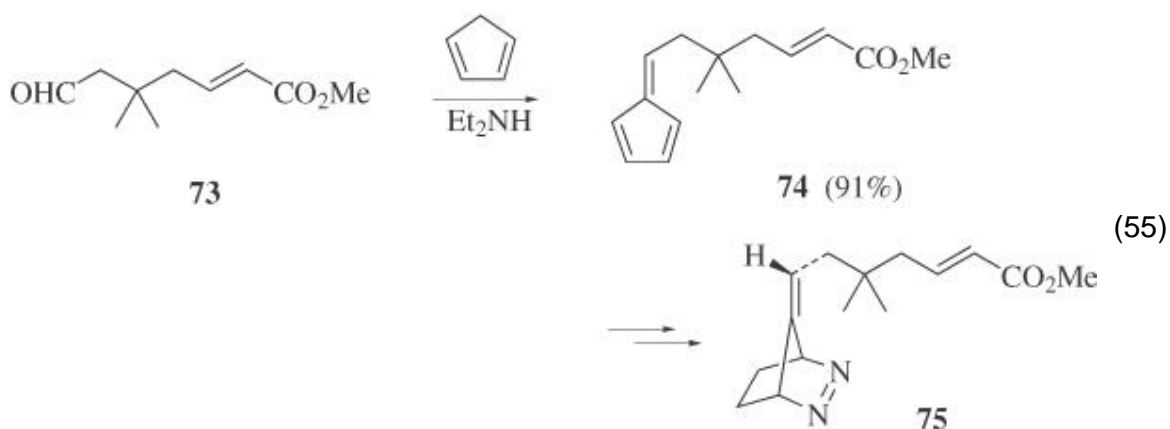
3.1. Free Trimethylenemethanes from Diazenes

3.1.1. Availability of TMM Precursors

The availability of TMM precursors is the key requirement for synthetic applications. Diazenes are usually synthesized in four steps from fulvenes and diazo compounds. For example, diazene **6** is prepared by the Diels-Alder reaction of 6,6-dimethylfulvene and bis(2,2,2-trichloroethyl) azodicarboxylate followed by selective alkene hydrogenation, reductive decarboxylation, and oxidation as shown in Eq. 54. (82)



Since fulvenes are easily prepared from cyclopentadiene and carbonyl compounds, diazenes for intramolecular reactions are easily synthesized in the same manner. For example, base-promoted condensation of cyclopentadiene with aldehyde **73** gives fulvene **74** which is transformed to diazene **75** (Eq. 55). (83)

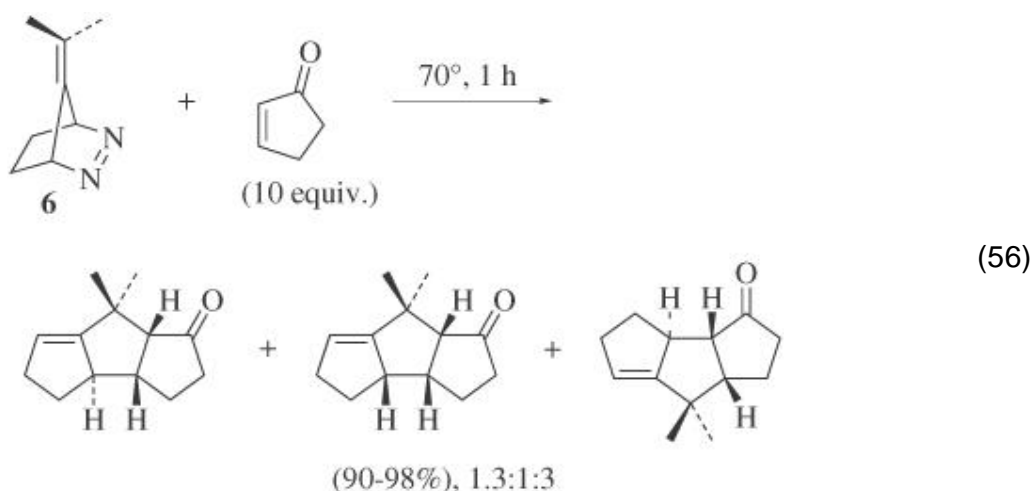


3.1.2. Intermolecular Applications

3.1.2.1. Cycloaddition to Alkenes

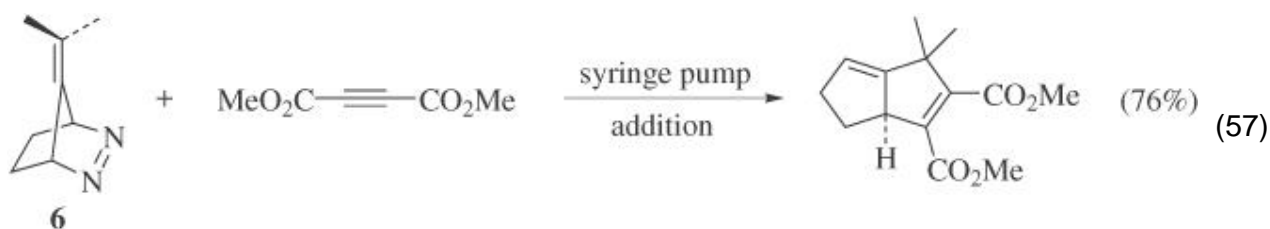
A high concentration of alkene acceptor is necessary to favor cycloaddition over dimerization of the TMM **2**. High yields of adducts with the fused and bridged structures **8** and **9** respectively, are formed with 1,3-dienes, aryl-substituted alkenes (styrene, stilbene), and α , β -unsaturated esters, nitriles, or anhydrides (Eq. 7), whereas unactivated alkenes do not form adducts. Singlet TMM **2** is nucleophilic in nature, and its reactivity toward alkenes roughly parallels the Diels-Alder dienophilic reactivity. (35, 36)

Although the intermolecular cycloaddition with alkenes provides a direct and simple route to linearly fused cyclopentanoid products, the major drawback of the reaction is low stereoselectivity and regioselectivity. For example, cycloaddition of diazene **6** with 2-cyclopentenone provides tricyclopentanoid products in a single step, but the reaction results in the formation of three regioisomers with low selectivity (Eq. 56). (84) As discussed later, intramolecular reactions solve many of the problems inherent in the intermolecular reactions,.

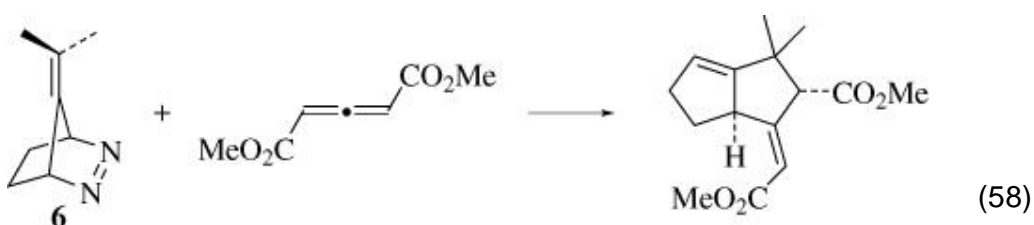


3.1.2.2. Cycloaddition to Alkynes and Allenes

Alkynes are poor acceptors for the parent TMM, and only highly activated alkynes are reactive acceptors. Polymeric products are usually obtained, and it is suggested that this side reaction might be caused by the reaction of the alkyne with the diazene prior to nitrogen extrusion. Useful yields (76%) of fused cycloadducts can be achieved only when the concentrations of the diazene and TMM are maintained at a very low level through the use of syringe pump techniques with a large excess of dimethyl acetylenedicarboxylate (Eq. 57). (85)



Electron-deficient allenes are good acceptors, and the reaction of the diazene with an allene diester takes place in a highly stereo- and regioselective manner to give the linearly fused cycloadduct as the sole product (Eq. 58). (86) The concentration of the

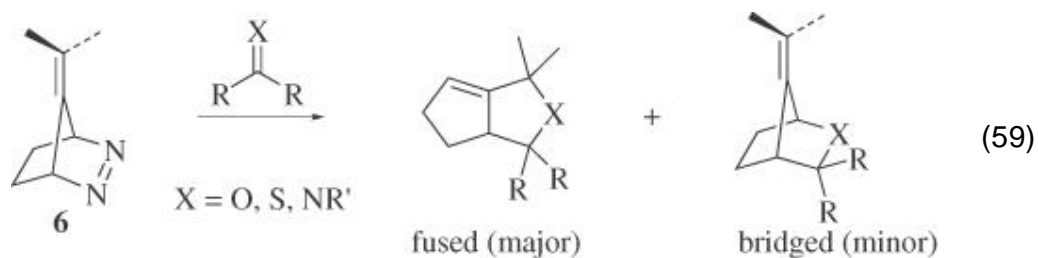


[diazene] M	[allene] M	yield
1.2	0.40	(15%)
0.051	$<2.6 \times 10^{-3}$	(70%)

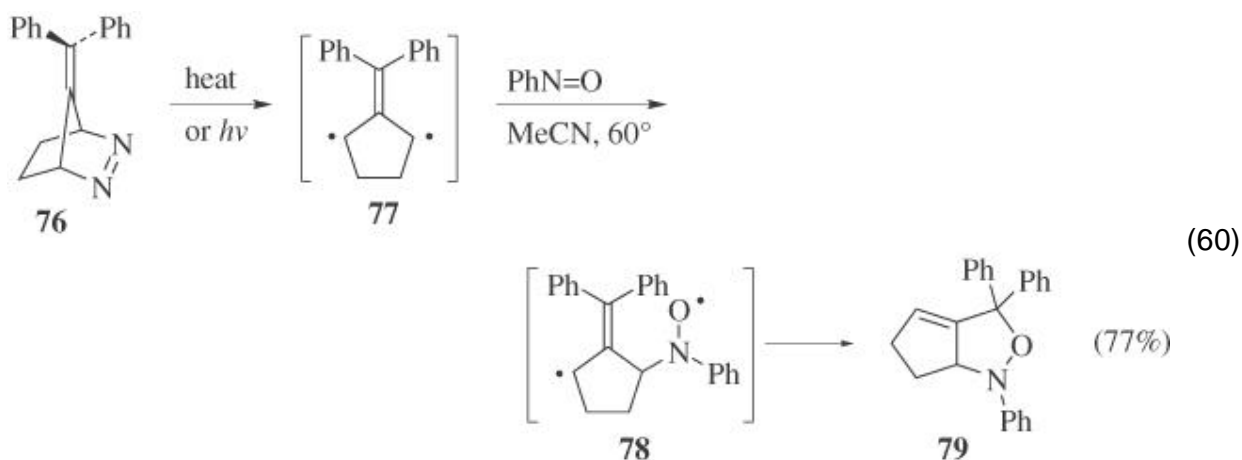
reactants markedly affects the results. Decreases in the concentrations of both allene and diazene cause a dramatic increase in the yield of the desired cycloadduct as well as a substantial decrease in oligomer formation. The best result is obtained when a ca. 2.5 mM solution of the diazene is added slowly over 4.5 hours to a 51 mM solution of the allene in refluxing hexanes.

3.1.2.3. Cycloaddition to Carbon-Heteroatom Double Bonds

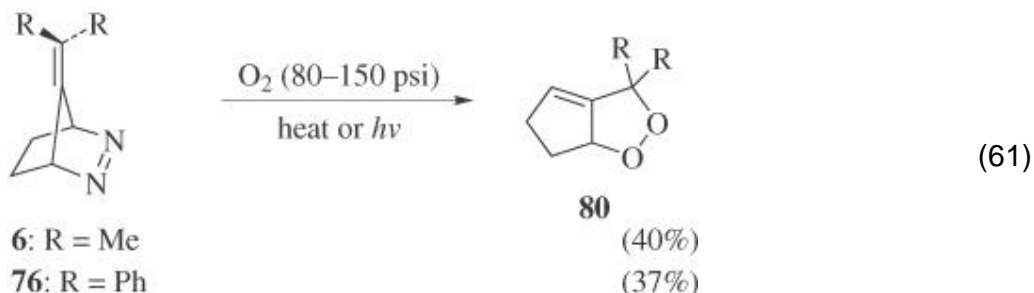
Various C = X hetero double bonds (X = O, N, and S) serve as TMM acceptors. Several points are worth noting. First, fused cycloadducts are formed to a larger extent than bridged adducts in all known cases. Second, in many instances, dimerization of the TMM occurs despite the use of syringe pump techniques and the use of a large excess of acceptor. Third, among acceptors tested, thiobenzophenone (X = S, R = Ph) proves to be the most reactive (Eq. 59). (85)



Although nitroso compounds are routinely used as spin-trapping reagents to scavenge transient radicals by forming more persistent radical species, they do undergo cycloaddition with TMM diradicals. Thus, thermolysis or photolysis of the diphenyl-substituted diazene **76** with nitrosobenzene gives the fused adduct **79** as the sole product (Eq. 60). (87) The reaction is believed to proceed in a stepwise manner through initial addition of the diphenyl TMM **77** to nitrosobenzene followed by intramolecular radical coupling of the intermediate diradical **78**. In thermal reactions, the formation of dimeric products derived from the triplet diradical is completely suppressed.



Molecular oxygen is an excellent triplet radical scavenger, and is also used as a chemical quencher of the triplet state of TMMs such as **2**. Thermolysis and photolysis of diazene **6** or **76** under medium pressure of molecular oxygen (80–150 psi;) completely suppresses the formation of the dimers of TMMs, and gives, instead, fused peroxide **80** in moderate yield (Eq. 61). (88)

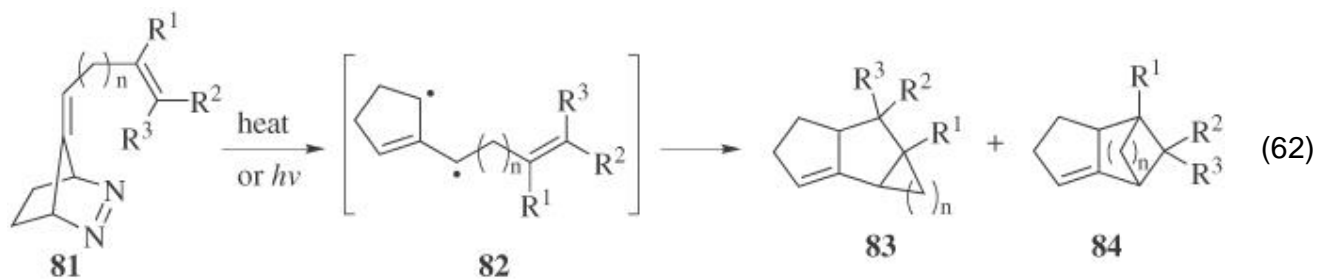


3.1.3. Intramolecular Applications

Intramolecular processes are superior to intermolecular ones for the following reasons: (1) Excess diophile is not required and fewer side products are formed, (2) intramolecular trapping is much more regioselective, (3) intermolecular trapping leads to a mixture of stereoisomers whereas intramolecular trapping is highly stereoselective, and (4) the configuration of the acceptor double bond is preserved in the product of intramolecular trapping, which is often not the case in intermolecular processes because of triplet participation.

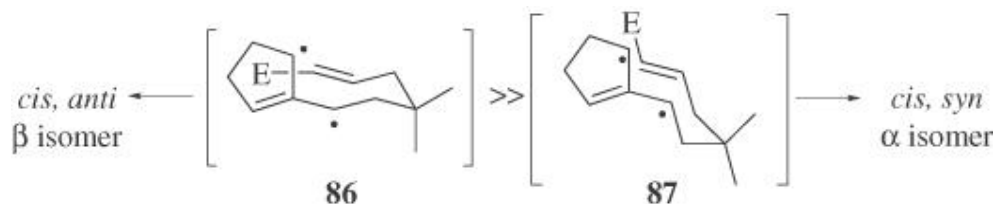
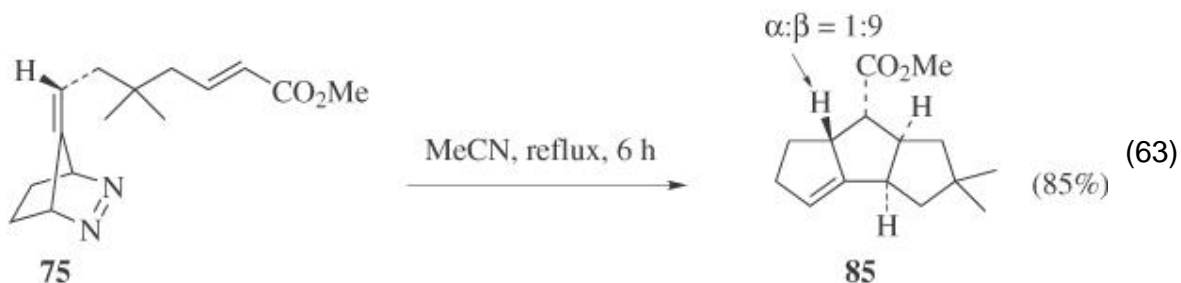
3.1.3.1. Regiochemistry

The regiochemical course of the intramolecular reaction is influenced by the location and electronic properties of the substituents appended to the double bond, as in diazene **81** (Eq. 62). (10-13) This influence can be explained by the facts that cycloaddition must compete with intersystem crossing from the singlet TMM to the more stable triplet, and that reactivity depends on the spin state of the TMM. When the tether length between the TMM and alkene is three in intermediate **82** ($n = 3$), the presence of an electron-withdrawing group at either the internal or terminal carbon leads to linearly fused cycloadducts **83** through the initial singlet TMM. On the other hand, the presence of an alkyl group on the internal carbon ($R^1 = \text{alkyl}$) shifts the pathway from singlet to triplet state, the latter leading predominantly to the formation of bridged cycloadducts **84**. As the alkyl group increases in size, the triplet contribution becomes more substantial, and a greater proportion of bridged products is observed.



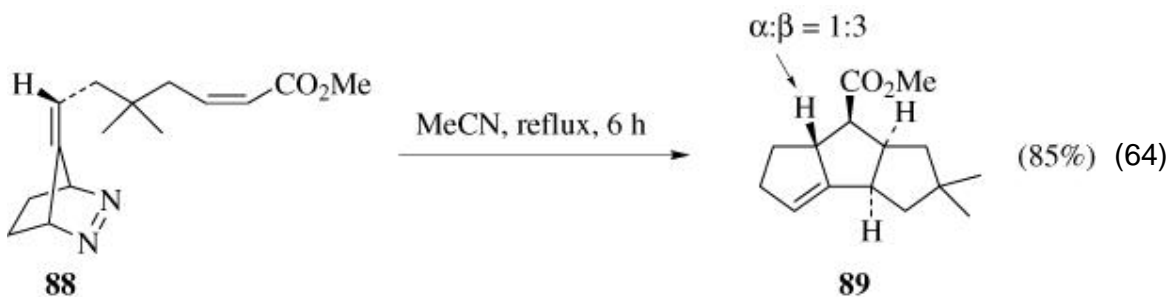
3.1.3.2. Effects of Double Bond Substituents

Thermolysis of diazene **75**, with a three-carbon tether, in refluxing MeCN results in the formation of a 9:1 mixture of linearly fused tricyclopentanooids **85** (Eq. 63). (**89, 90**), The relative configurations of the ring fusions in the major isomer are *cis, anti*, and those of the minor isomer are *cis, syn*. The *trans* configuration of the diazene **75** is completely translated into the *trans* configuration of the product. The ring-fusion stereoselectivity is attributed to the lower energy of the extended pseudochair transition structure **86** leading to the *cis, anti* product in comparison with that of the folded pseudochair **87** leading to *cis, syn* product.

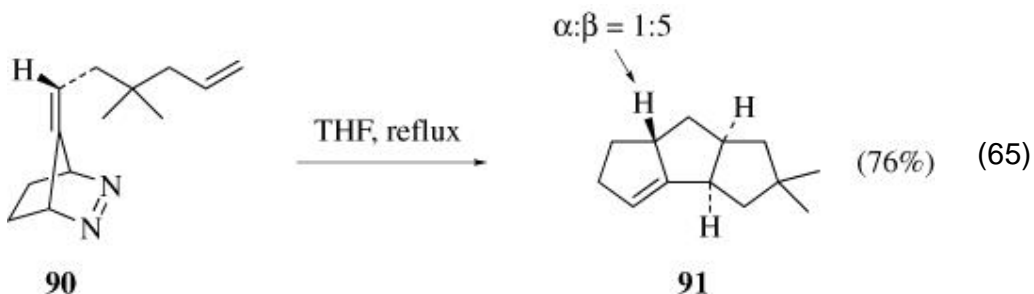


It is notable that the reaction of diazene **88** containing a *Z*-substituted double bond proceeds in a highly stereoselective manner, and the configuration is preserved in the product **89** (Eq. 64). (**91**) Since molecular oxygen (a triplet

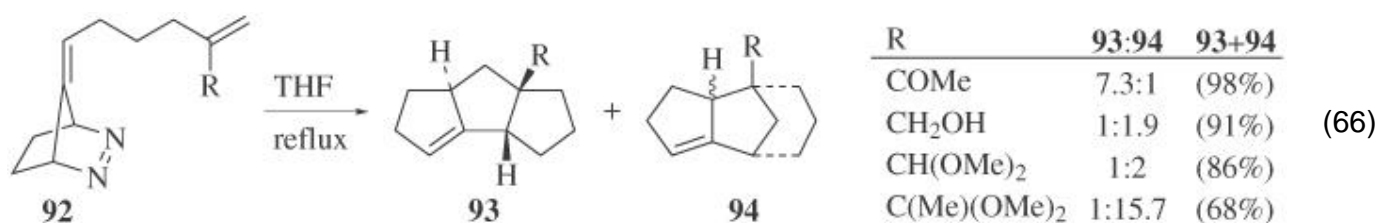
scavenger) has no effect on the product distribution, the main pathway of the cycloaddition must be a concerted process involving the singlet TMM.



Although unactivated alkenes do not participate in intermolecular cycloadditions because of the preferential dimerization of the TMMs, intramolecular cycloadditions can occur. Thus, the thermolysis of diazene **90** in THF gives the tricyclopentane **91** in 76% yield (Eq. 65). (92) The products consist of a 1:5 mixture of α and β products. ESR experiments suggest that both the singlet and triplet TMMs give the same adduct.

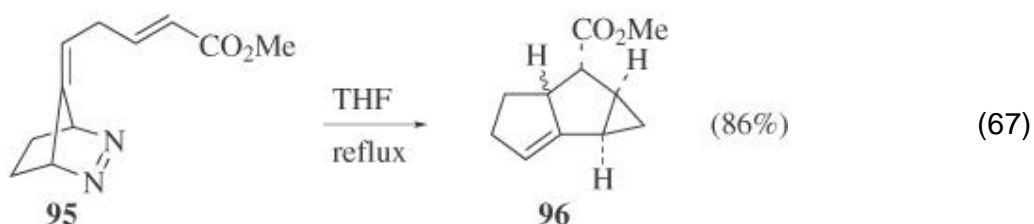


When a substituent R is attached to the internal carbon of the alkene **92**, synthetically useful quantities of either linearly fused or bridged cycloadducts **93** and **94**, respectively, can be obtained by proper choice of the R group (Eq. 66)). (93) When an electron-withdrawing group is attached to the alkene (R = COMe), the singlet TMM leads selectively to the linear cycloadduct **93**. On the other hand, the presence of a large alkyl group attached to the alkene [R = CMe(OMe)₂] affords the bridged cycloadduct **94** selectively via the triplet state.

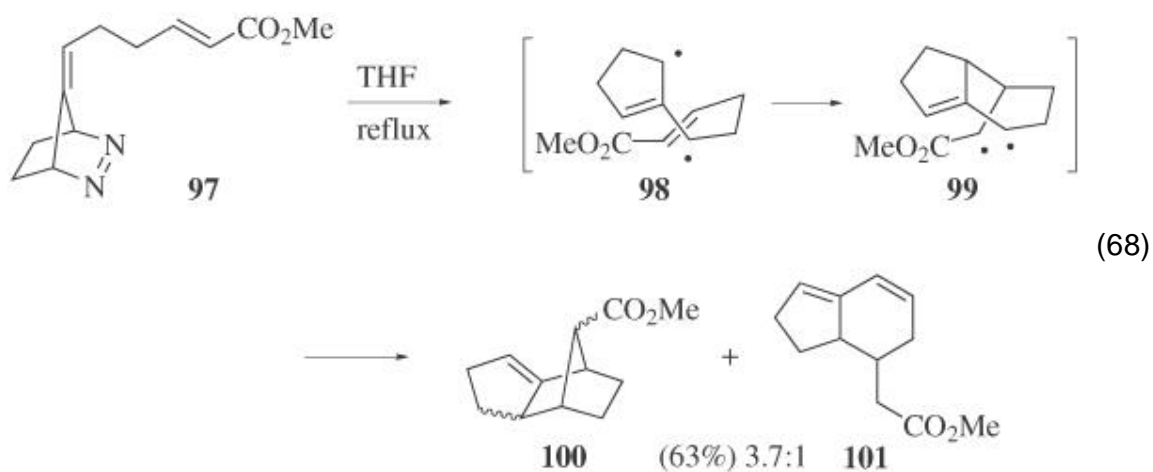


3.1.3.3. Effects of Tether Length

When a methylene tether ($n = 1$) separates the TMM and the alkene as in diazene **95**, linearly fused adduct **96** is selectively formed (Eq. 67)). (12)



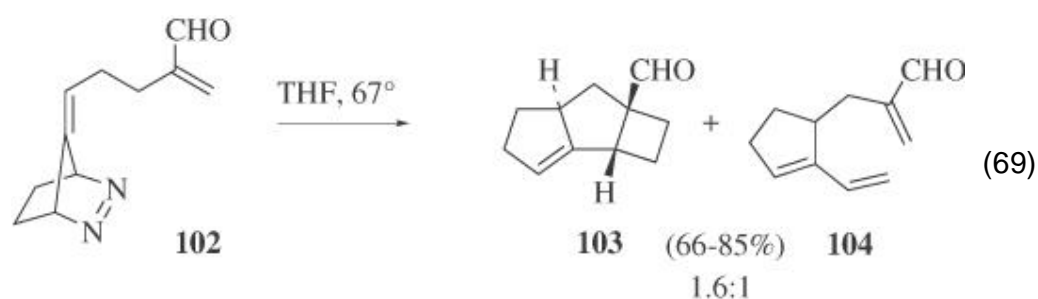
When $n = 2$, the chemistry of the triplet state dominates even when the terminal carbon bears an electron-withdrawing group (Eq. 68). (94) When substrate **97** is used,



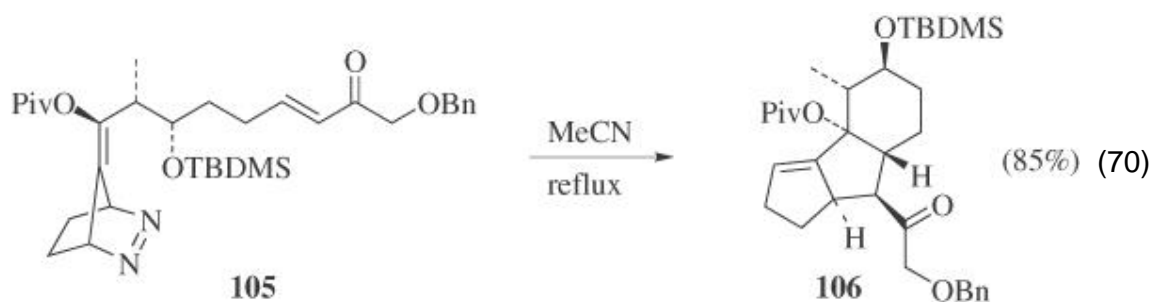
tricyclic adduct **100** and bicyclic adduct **101** are mainly formed; the linearly fused tricyclic product is not obtained at all. It is also noteworthy that the configuration of the alkene is lost in product **100**. These results suggest that the formation of product **100** is a stepwise reaction initiated by the kinetically

favored formation of a six-membered ring to give diradical **99** (via **98**), rather than that of a four-membered ring, followed by diradical coupling with concomitant bond rotation. Bicyclic adduct **101** is formed through hydrogen atom abstraction of the common intermediate.

When an electron-withdrawing group is attached to the internal carbon, such as in diazene **102**, 7-endo-trig cyclization is observed to form the linearly fused product **103** together with the uncyclized triene **104** (Eq. 69). (95) Quenching studies with dioxygen reveal that product **104** is derived exclusively from the triplet TMM and product **103** is derived from both the triplet and the singlet states.



When the tether contains four atoms, a fused cycloadduct is obtained selectively when an electron-withdrawing group is attached to the alkene. The highly functionalized and enantiomerically pure substrate **105** takes part in the intramolecular reaction to afford the fused tricyclic adduct **106** with high stereoselectivity (Eq. 70). (96)

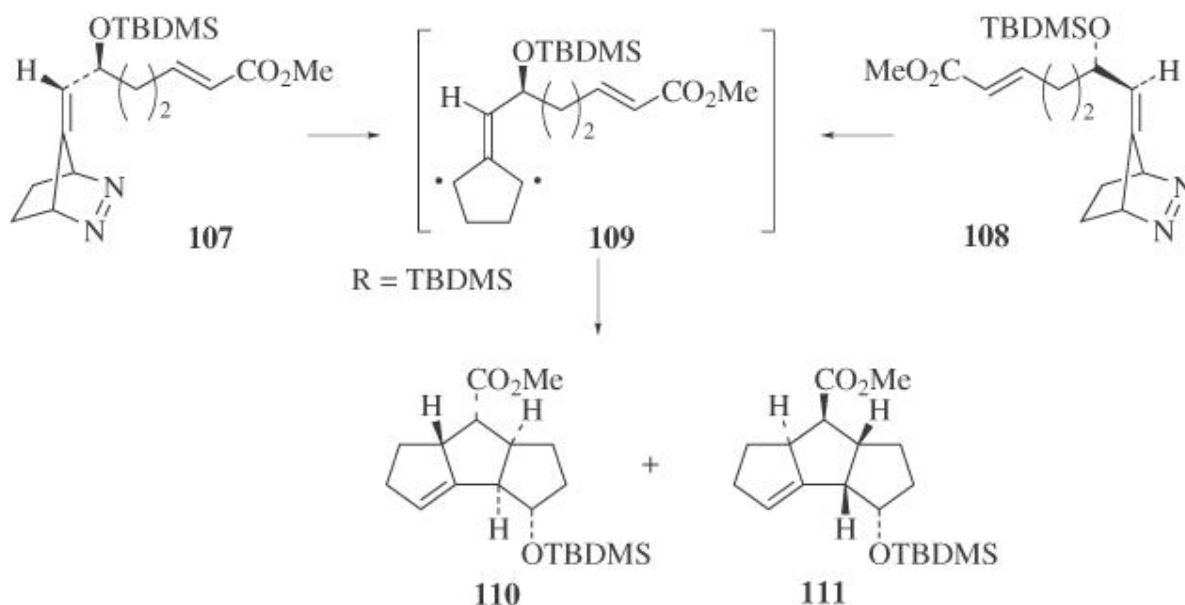


3.1.3.4. Asymmetric Induction

High levels of asymmetric induction have been observed through placement of a stereogenic center on the carbon chain that links the alkene to the TMM. Thermolysis of diastereomeric diazenes **107** and **108** in refluxing MeCN mainly provides the cis, anti products **110** and **111** in 80–91% yield as a 12:1 mixture (Eq. 71). (97) The complete lack of stereospecificity with respect to the diazene configuration supports the notion that the reaction proceeds through a common TMM intermediate **109**.

The reaction can be initiated by photochemical generation of the TMM at low temperature and this can lead to enhanced selectivity. Since the thermal and the photochemical processes give identical results at the same temperature, the same intermediate must be formed regardless of its mode of generation. Photolysis of substrate **107** at 7° in MeCN increases the diastereomeric ratio to 26:1, and the ratio increases to 49:1 in the reaction conducted at –30°.

As a result of the radical nature of this TMM species, the reactions tolerate free hydroxyl groups. When diazene **112** is heated in refluxing MeCN, five products, one major and four minor isomers, are produced with the ratio of the major isomer **113**

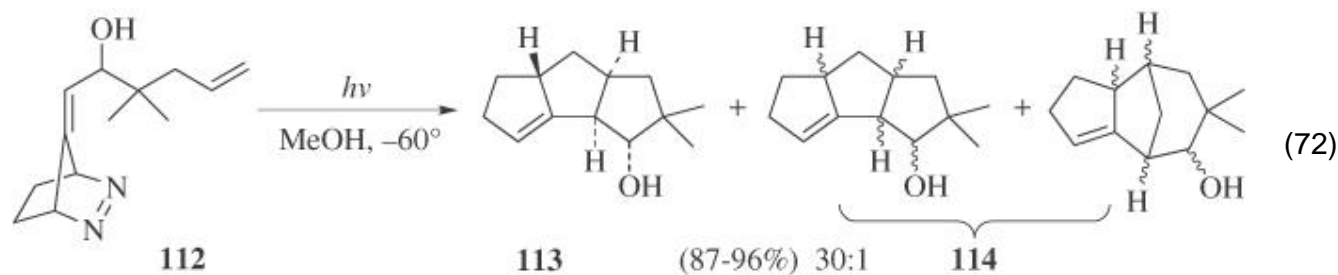


(71)

diazene	conditions	temp	110:111	yield
107	heat	81°	12:1	(91%)
	<i>hν</i>	7°	26:1	(85%)
	<i>hν</i>	–30°	49:1	(—)
108	heat	81°	12:1	(80-91%)

to the sum of the minor isomers **114** being 4:1 (Eq. 72). (98, 99) The ratio of **113** to **114** is insensitive to the solvent used (THF, MeOH, MeCN) at any

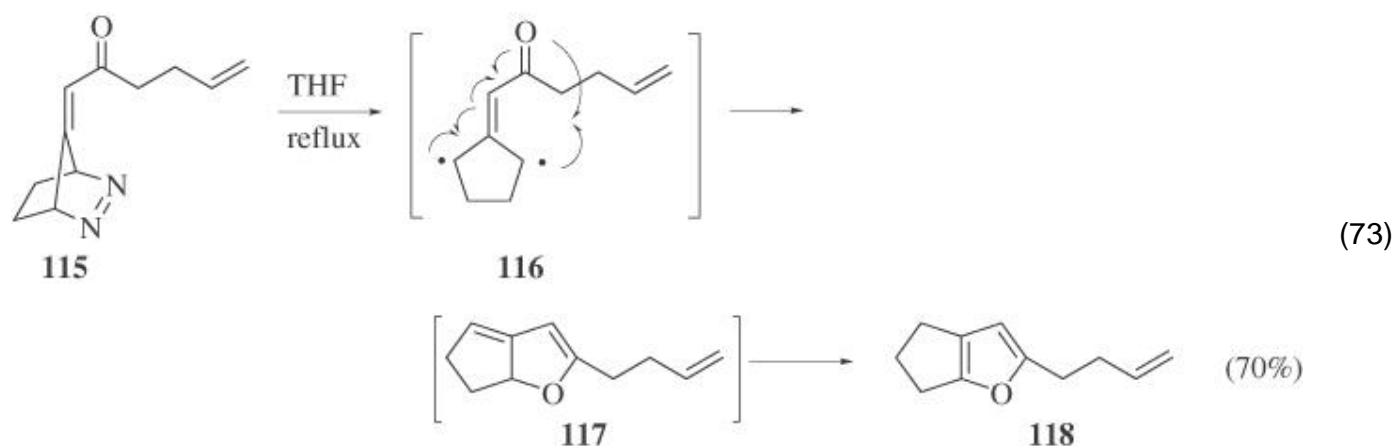
temperature. However, MeOH is very useful for low-temperature reactions, and photoinduced nitrogen extrusion in MeOH at -60° leads to an increase in stereoselectivity such that the ratio of **113** to **114** reaches 30:1.



No examples of useful asymmetric induction with chiral auxiliaries have been reported. When the diazenes bearing menthyl or 8-phenylmenthyl esters are used, only low levels of diastereoselectivity are observed. (100)

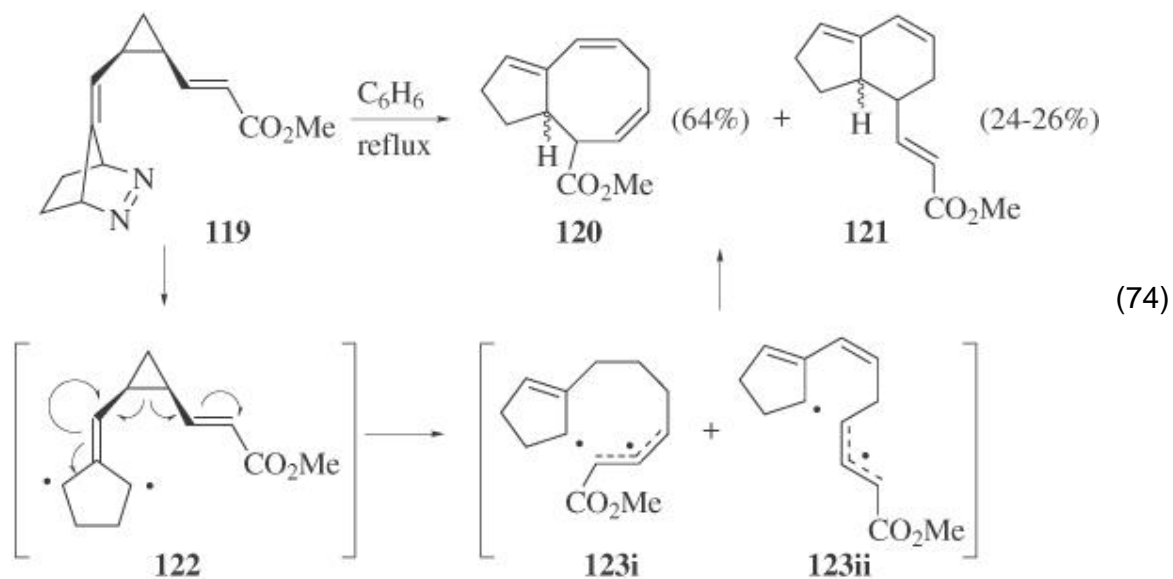
3.1.3.5. Effects of Substituents Adjacent to the TMM

When TMMs are conjugated to an alkene or a carbonyl group, intramolecular rearrangement predominates with the formation of a cyclopentene or a dihydrofuran. For example, diazene **115** is converted to the corresponding furan **118** even in the presence of an internal double bond (Eq. 73). (101) The initially formed dihydrofuran **117** (from intramolecular rearrangement of TMM **116**) is converted into furan **118** during chromatography on silica gel.



Cyclopropylcarbonyl radicals undergo rapid ring opening to the corresponding

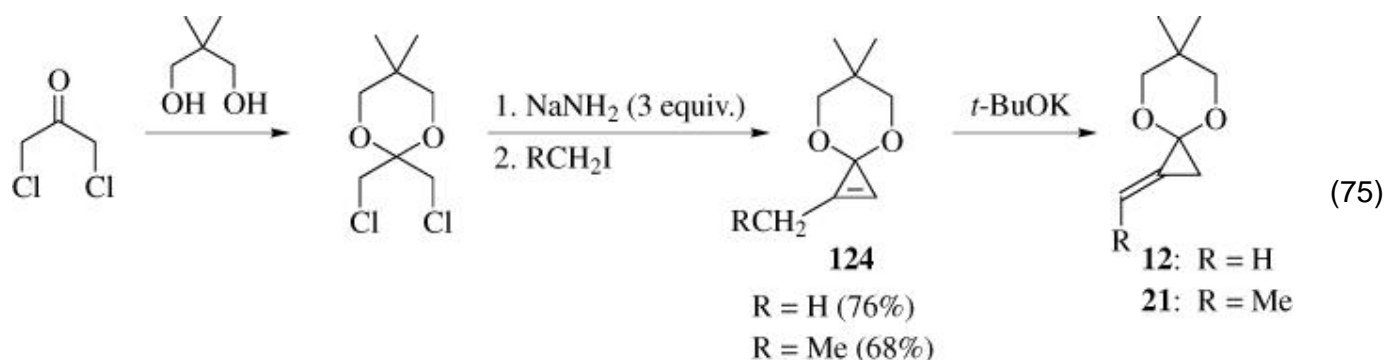
homoallylic radicals. (102-104) Ring-opening reactions also occur in diyl-type TMMs. Thus, diazene **119**, possessing an α -cyclopropyl group, does not give [3 + 2] cycloadducts but rather eight- and six-membered ring products **120** and **121**, respectively (Eq. 74). These compounds are formed from TMM **122**, which suffers subsequent cyclopropyl ring opening to form **123i** and **123ii**. Radical coupling forms either eight- or six-membered rings from **123i** and **123ii**, respectively. (105)



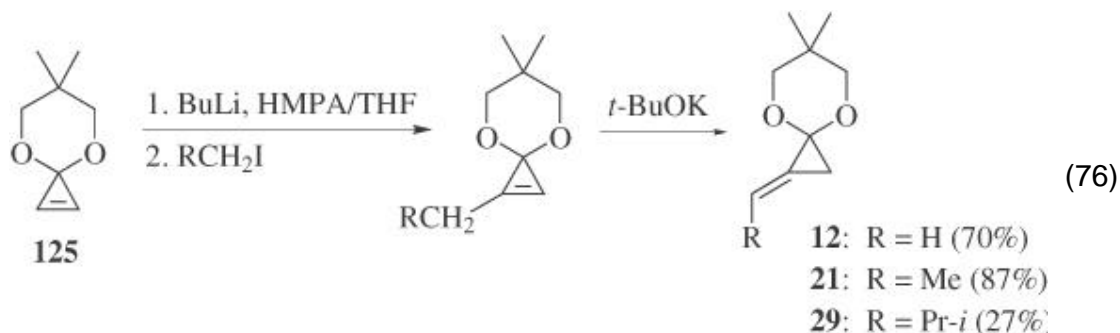
4. Dipolar Trimethylenemethane **5** from Methylene cyclopropanes

4.1.1. Availability of TMM Precursors

Dialkoxy MCP **12** and its derivatives are readily available on a large scale in two or three steps from 1,3-dichloroacetone. In one approach (Eq. 75), (16, 50) 1,3-dichloroacetone is first converted to the corresponding neopentyl glycol acetal. The acetal is treated with 3 equivalents of sodium amide, which effects cyclization and in situ deprotonation of the resulting cyclopropenone acetal to generate a 2-sodiocyclopropenone acetal. Treatment of the latter with an alkyl iodide gives methyl and ethyl cyclopropenone acetals **124** in about 80% overall yield. Base-catalyzed isomerization of the alkylated cyclopropene to the less strained alkylidenecyclopropane completes the synthesis of the target molecule **12** and its derivatives.



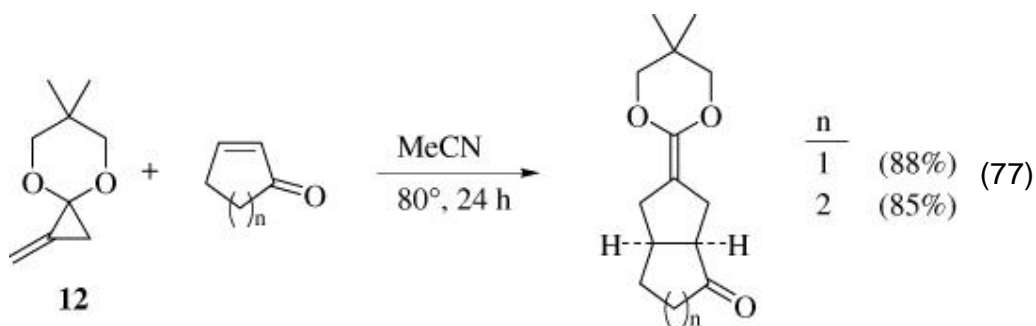
In another approach (Eq. 76), a purified unsubstituted cyclopropenone acetal **125** (106) is deprotonated with BuLi in the presence of HMPA, and the lithio derivative is alkylated with an alkyl halide. The sterically demanding MCPs such as **29** can be prepared only by this method. The merits of neopentyl glycol include its simple NMR signal pattern, the low cost of the diol, and the moderate temperature required for TMM formation. The acetals of 1,3-propanediol and 2,4-pentanediol can also be utilized as the TMM precursors, which are more rapidly converted into the TMMs than the neopentyl glycol analogs.



4.1.2. Intermolecular Applications

4.1.2.1. Cycloaddition to Alkenes

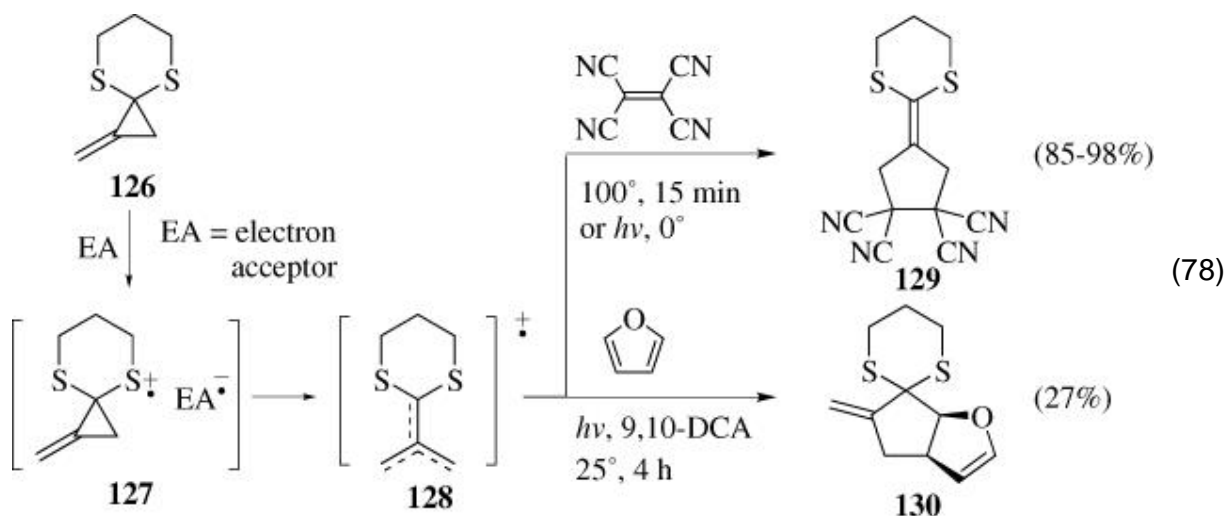
Since the dipolar TMM **3** derived from precursor **12** is nucleophilic, a wide variety of electron-deficient alkenes bearing ketone, ester, nitrile, and nitro functionalities take part in the cycloaddition, whereas unactivated olefins, such as norbornene, and electron-rich olefins, such as enol silyl ethers, are totally inert. The reaction proceeds cleanly not only with acyclic olefins but also with cyclic ones, and provides an efficient strategy for the construction of cis-fused bicyclo[3.n.0] systems (Eq. 77). (16) Such high nucleophilicity distinguishes the dipolar TMMs from the parent TMMs, which are usually generated by the diazene route.



The cycloaddition is only marginally subject to solvent effects. This reaction does not necessarily require the use of solvent and tolerates various aprotic solvents (hydrocarbon, haloalkane, nitrile, DMSO). The solvent polarity does not affect the regioselectivity for the formation of the ketene acetal **13** and the exomethylene product **14** (Eq. 14). An alkyl nitrile solvent is used routinely since TMM generation takes place faster in a polar solvent. The reaction does not necessarily require rigorous exclusion of moisture or air because the

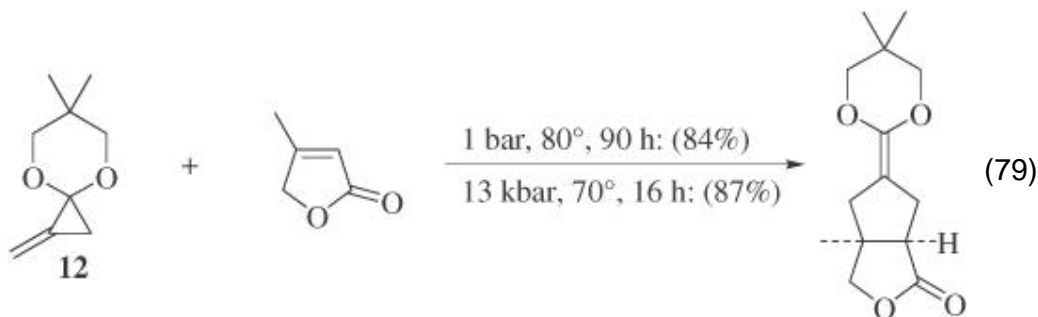
cycloaddition of the dipolar TMMs, such as **3**, to olefins is faster than its reaction with triplet molecular oxygen because of the singlet nature of the dipolar TMM.

The thioacetal derivative **126**, on the other hand, reacts with both electron-deficient and electron-rich alkenes under thermal or photochemical activation (Eq. 78). (107) The reaction usually gives a mixture of the ketene acetal product, such as **129**, and the exomethylene product, such as **130**, but a single isomer can be obtained by the proper choice of the alkene substrates. The reaction proceeds by a single-electron transfer from MCP **126** to electron acceptors, such as tetracyano-ethylene or photo-excited 9,10-dicyanoanthracene (DCA), to generate radical cation **127**. Subsequent ring opening generates TMM radical cation **128**, which undergoes cycloaddition with alkenes.



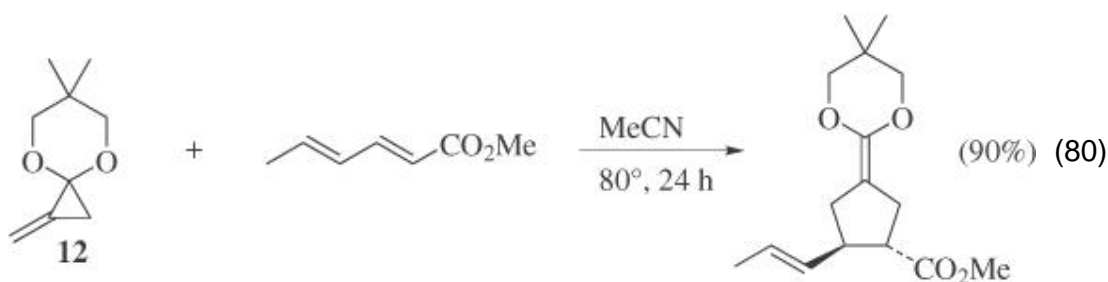
4.1.2.2. Effects of High Pressure

In line with well-known effects of pressure upon cycloadditions, (108) significant rate acceleration under high pressure is observed. For instance, a relatively slow reaction of a 3-methyl-2-butenolide with MCP **12** affords a bridgehead-substituted adduct in 84% yield after being heated for 90 hours at 80° (Eq. 79). (16) The same cycloaddition results in an 87% yield after heating to 70° under 13 kbar for 16 hours. The results also suggest that the rate-limiting step is not TMM generation but C—C bond formation.



4.1.2.3. Cycloaddition to Dienes

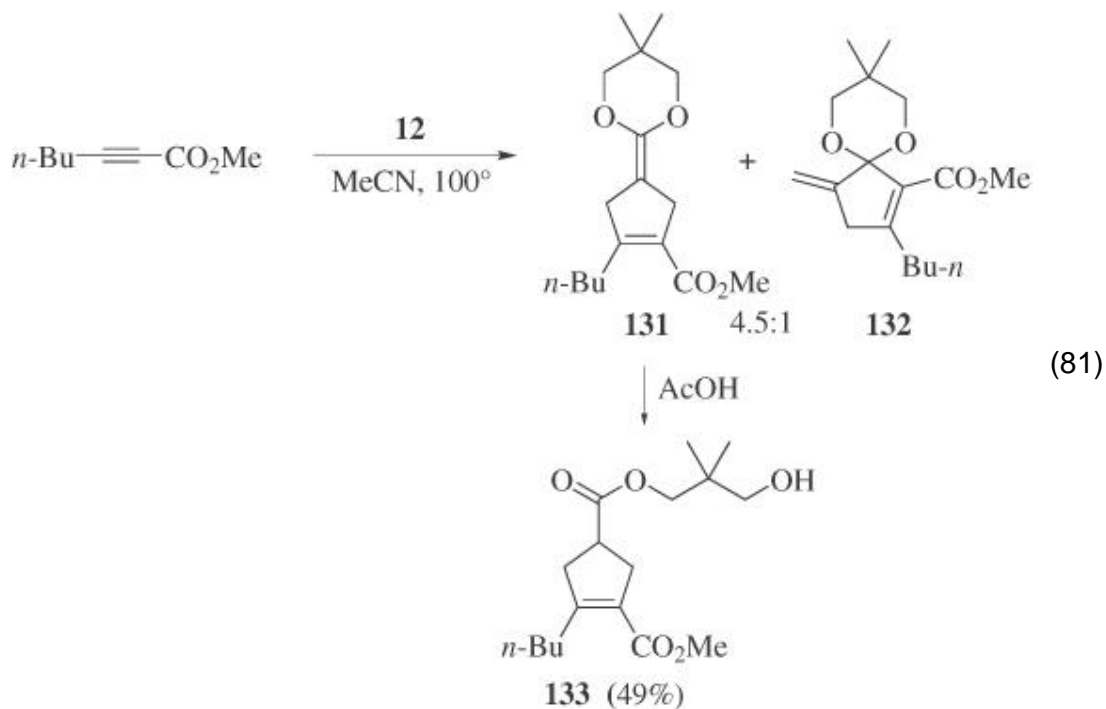
Regio- and periselective reactions take place with acyclic dienes. The reaction of MCP **12** with methyl sorbate occurs selectively at the 2,3-double bond to give a five-membered ring (Eq. 80). (34)



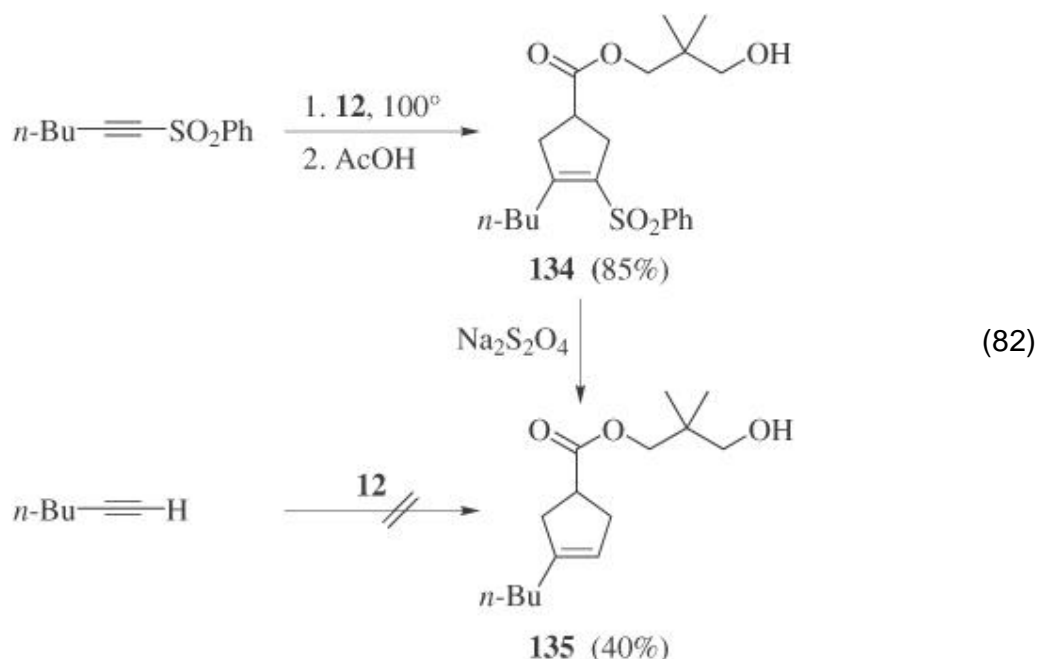
4.1.2.4. Cycloaddition to Alkynes

Unlike the parent TMM, the dipolar TMMs undergo cycloaddition to electron-deficient alkynes in good yields. However, alkynes are indeed less reactive toward TMM **3** than the structurally related alkenyl substrates.

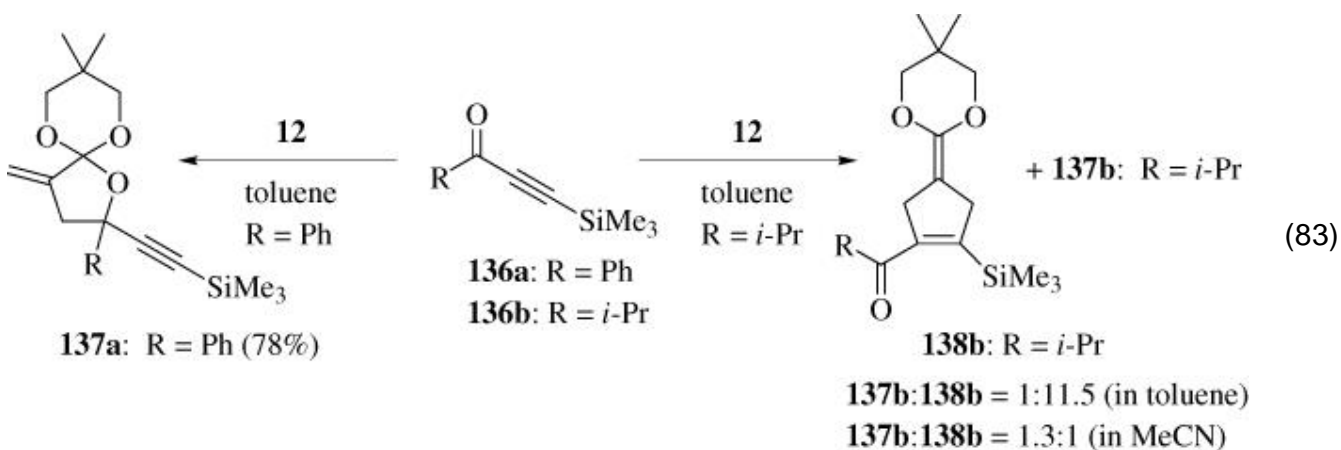
The reaction of precursor **12** with methyl 2-hexynoate in toluene requires 100° (Eq. 81), (109) whereas methyl (*E*)-2-hexenoate reacts at 80°. The cycloaddition proceeds efficiently to afford the cyclopentene **131**, which is isolated as the dicarboxylic ester **133** after acid hydrolysis. A small amount of the exomethylene isomer **132** is also formed, suggesting the intervention of a single electron transfer cycloaddition pathway. The reaction rate also increases as the polarity of the solvent increases, but the ratio of **131**:**132** is not subject to solvent effects.



A variety of alkynes bearing electron-withdrawing groups, such as esters, sulfoxides, and sulfones, undergo cycloaddition with substrate **12**. In consonance with the nucleophilic nature of TMM **3**, the reaction rate increases as the electron demand of the alkyne increases. A synthetic drawback is the failure of unactivated alkynes to act as 2π acceptors. For instance, phenylacetylene and hexyne are inert. Sulfur-substituted alkynes can serve as synthetic surrogates of simple alkynes. Alkynic sulfones and sulfoxides are very reactive TMM acceptors. After the cycloaddition, vinyl sulfone cycloadduct **134** is readily desulfurized under mild conditions to afford cyclopentene **135** (Eq. 82). (109)

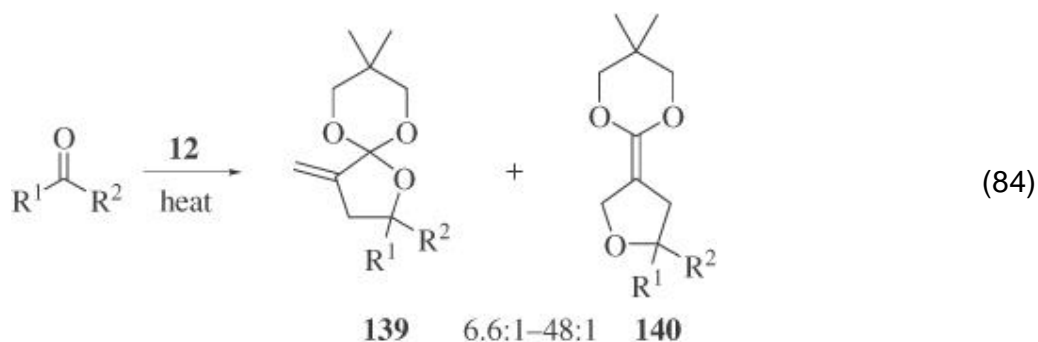


Cycloaddition to alkynyl ketones shows an interesting dichotomy. In the reaction of substrate **12** with ketone **136a** in toluene, the cycloaddition reaction takes place exclusively on the carbonyl group to give the exomethylene product **137a** (Eq. 83). (109) Only when the carbonyl group is deactivated electronically and sterically as in ketone **136b**, and the reaction is performed in toluene, does the cycloaddition take place on the alkyne to give the ketene acetal **138b**. The selectivity toward **138b**, however, erodes in a polar solvent (MeCN), and significant amounts of the exomethylene product **137b** are also formed. This solvent effect suggests that the cycloaddition on the carbonyl group takes place through a polar stepwise reaction pathway, which becomes faster than the concerted-like alkyne cycloaddition reaction in a polar solvent.



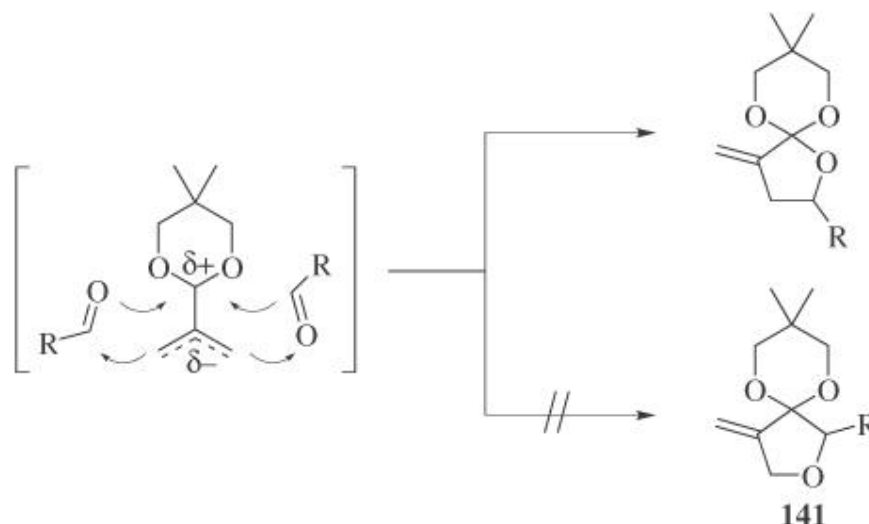
4.1.2.5. Cycloaddition to Carbonyl Compounds

Because of the dipolar and nucleophilic character of TMM **3**, carbonyl compounds also serve as good 2π acceptors. This reactivity is in sharp contrast to the diyl type TMM **2**, which is rather unreactive toward polarized double bonds. Both aromatic and aliphatic aldehydes and ketones react with substrate **12** to give mainly exomethylene products **139** together with a small amount of ketene acetals adducts **140** (Eq. 84). (110)



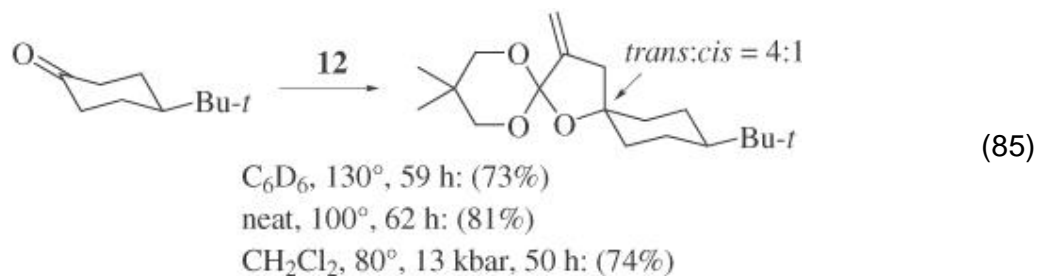
The cycloaddition reactions of the dipolar TMMs are often virtually free of side reactions, and good to excellent yields of cycloadducts are obtained by using stoichiometric amounts of reactants. Because of the inherent polarity of TMM **3**, the regioisomeric exomethylene product **141** is not formed. The reaction rate decreases as the solvent polarity decreases, and the isomer ratio **139:140** increases when a nonpolar solvent is used. The cycloaddition in a nonpolar solvent, such as cyclohexane or benzene, gives about a 24:1–48:1 mixture of **139** and **140** for aliphatic aldehydes and ketones. With some aromatic

aldehydes, the ratio is lower (6.6:1), yet still remains at a synthetically acceptable level.



4.1.2.6. Effects of High Pressure

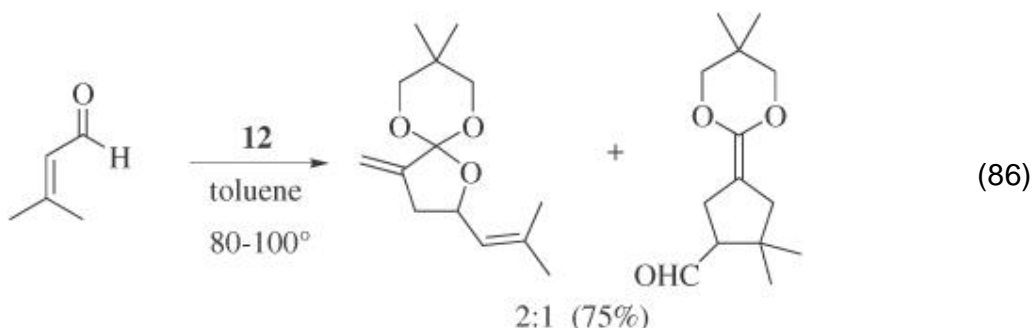
As in cycloadditions to olefins, use of high pressure is particularly advantageous for cycloadditions with aliphatic ketones. The reaction of precursor **12** with 4-*tert*-butylcyclohexanone is complete at 80° under 13–14 kbar of pressure, whereas reaction under 1 bar requires 100–130° (Eq. 85). (110) The process takes place selectively from the electronically favored axial direction, and the stereoselectivity (4:1) remains unchanged under high pressure conditions.



4.1.2.7. Chemoselectivity

Although the cycloaddition of α , β -unsaturated ketones takes place highly regioselectively on the C=C double bond, the cycloaddition of α , β -unsaturated aldehydes gives a mixture from competing cycloadditions to the carbonyl and the alkenyl groups. Even in the cycloaddition with

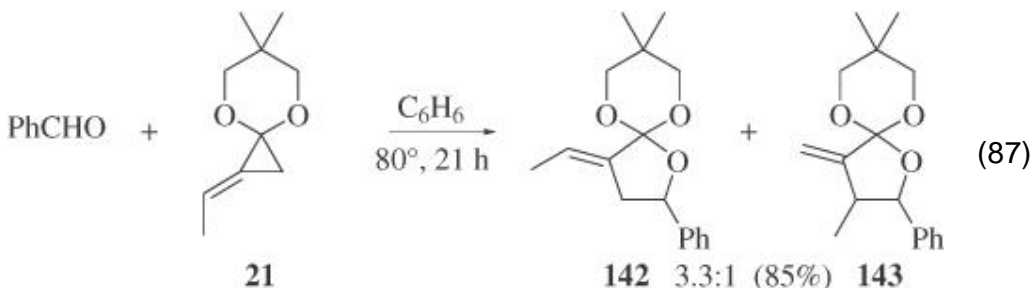
3-methyl-2-butenal whose double bond is sterically encumbered, the two reaction paths compete (Eq. 86). (110)

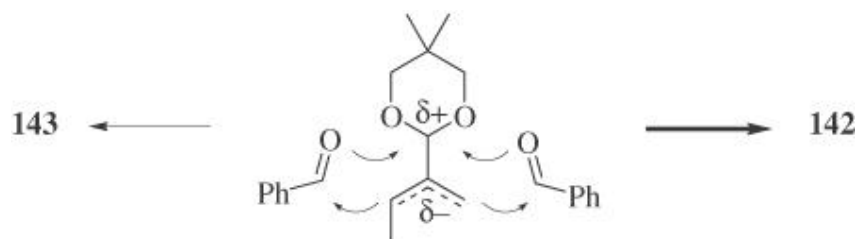


Owing to the low reactivity of alkynes toward TMMs, cycloadditions with α , β -unsaturated alkynyl ketones occur selectively on the ketone group (Eq. 83). Thus, the regioselective cycloaddition to the carbonyl moiety of alkynyl aldehydes or ketones followed by partial hydrogenation of the alkyne moiety to the corresponding alkene provides a useful method for the preparation of the formal carbonyl addition products of α , β -unsaturated aldehydes or ketones.

4.1.2.8. Regioselectivity

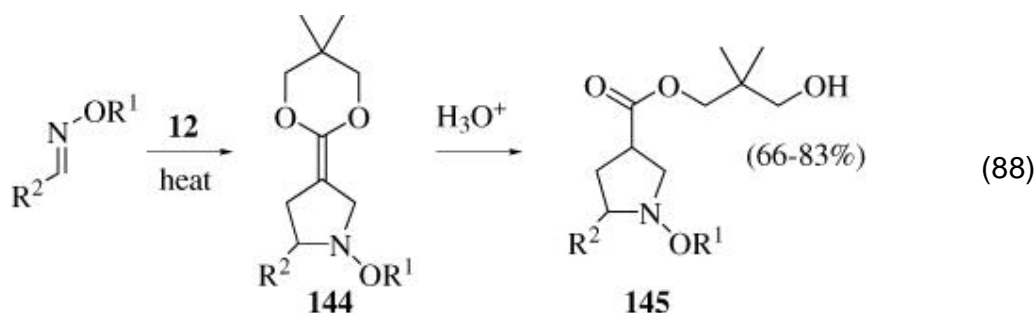
The reaction of the ethylidene compound **21** with benzaldehyde gives predominantly ethylidenelactone acetal **142** together with methylenelactone **143** (Eq. 87). (110) The observed selectivity is rationalized on the basis of steric effects in the asynchronous bond formation. The initial bond formation occurs at the allylic moiety of TMM at the less hindered methylene carbon rather than at the substituted one.





4.1.2.9. Cycloaddition to C = N Double Bonds

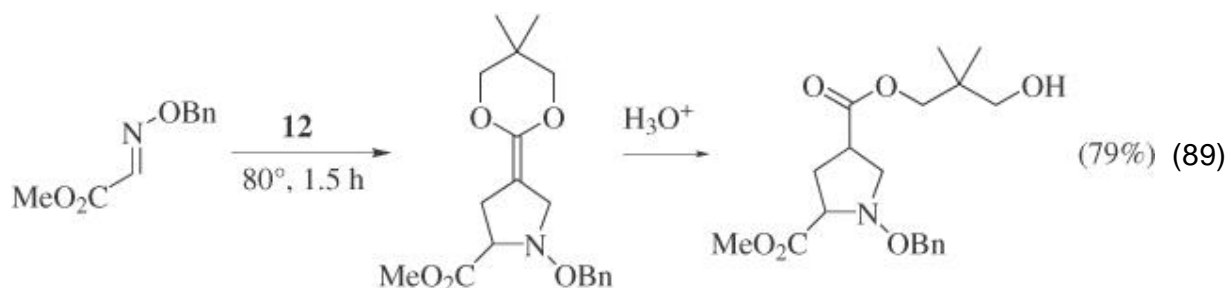
O-Alkyloximes are good acceptors for dipolar TMMs, and cycloaddition with substrate **12** selectively affords ketene acetal product **144**, which can be hydrolyzed by acid to give ester **145** (Eq. 88). (50)



O-Alkyloximes derived from aromatic and heteroaromatic aldehydes give cycloadducts in good to excellent yield by the use of a near equimolar mixture of substrate **12** and the oxime. Oximes derived from aliphatic aldehydes are much less reactive. O-Methoximes and O-benzyloximes can be used with equal success. The configuration of the oximes significantly influences the rate of the reaction, and the anti isomer reacts 67 times faster than the syn isomer in the case of the O-methoxime of 2-furaldehyde in CD₃CN. This marked rate difference provides strong evidence for the concerted character of the cycloaddition. In this respect, O-benzyloximes are superior to O-methoximes, because the former are generally obtained with higher anti selectivity (9:1) than the latter (2.5:1) by the reaction of an aldehyde and the corresponding alkoxyamine.

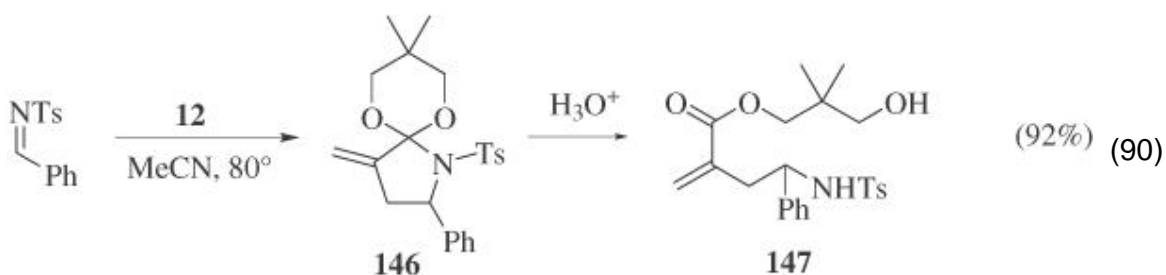
The reaction rate is strongly affected by the electronic nature of the R² group in the oxime. Among various 4-substituted benzaldehyde O-alkyloximes, those bearing an electron-withdrawing group, such as chlorine, react at 100°, whereas benzaldehyde oxime requires higher temperatures (120–130°). The cycloaddition proceeds faster under high pressure, and oximes bearing an electron-donating group, such as a methoxy group, only react under high pressure (10 kbar). On the other hand, the reaction with methyl glyoxylate

O-benzoyloxime occurs within 1.5 hours at 80°, providing a new route to proline derivatives (Eq. 89). (50)

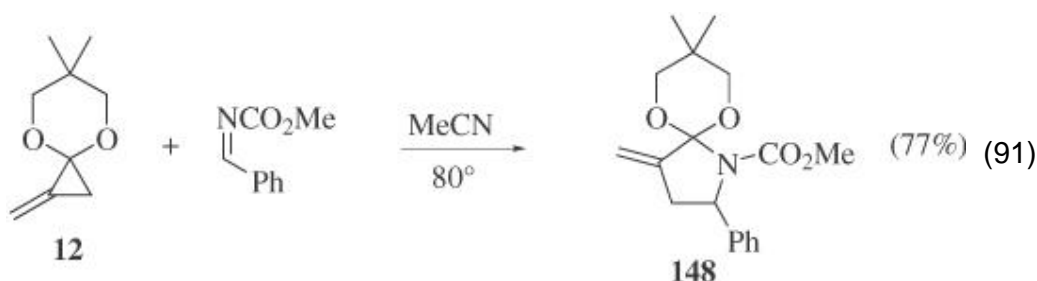


Cycloaddition reactions with more electron-deficient C = N double bonds, such as those in *N*-tosyl and *N*-acylimines, proceed much faster than those with oximes. The reaction of substrate **12** with benzaldehyde *N*-tosylimine affords exclusively the acetal of α -methylene-pyrrolidone **146** instead of the ketene acetal of pyrrolidinone (Eq. 90). (111) Product **146** is sensitive to acid, and is isolated as the corresponding α -alkylidene- γ -amino ester **147**.

Tosylimines from aromatic, vinylic, and aliphatic aldehydes and ketones serve as good acceptors, and in all reactions, acetals of α -methylene-pyrrolidones are formed. However, the reaction fails with tosylimines having enolizable α -hydrogens, and deprotonation of the acidic hydrogen by the dipolar TMM takes place selectively. (111)

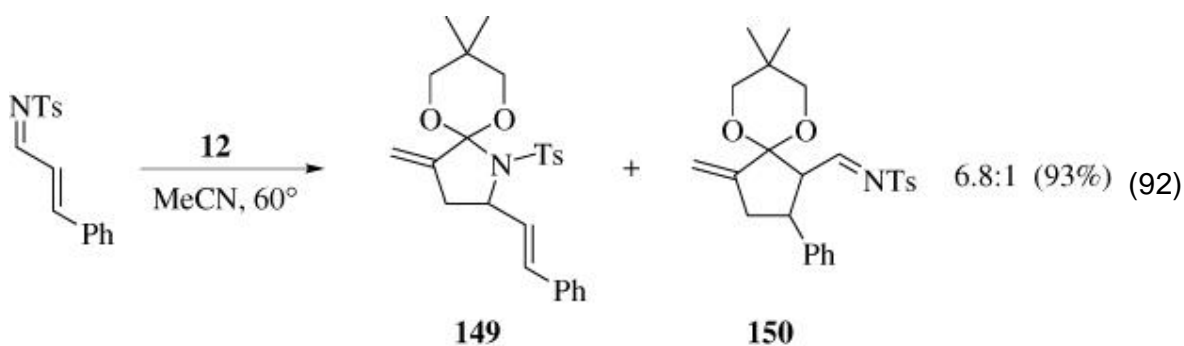


N-Acylimines take part in the cycloaddition, and also give the acetals of α -methylene-pyrrolidone. The reaction of substrate **12** with benzaldehyde methoxycarbonylimine at 80° affords mainly adduct **148**, together with a small amount of the ketene acetal adduct of the pyrrolidine (Eq. 91). (111)



4.1.2.10. Chemoselectivity

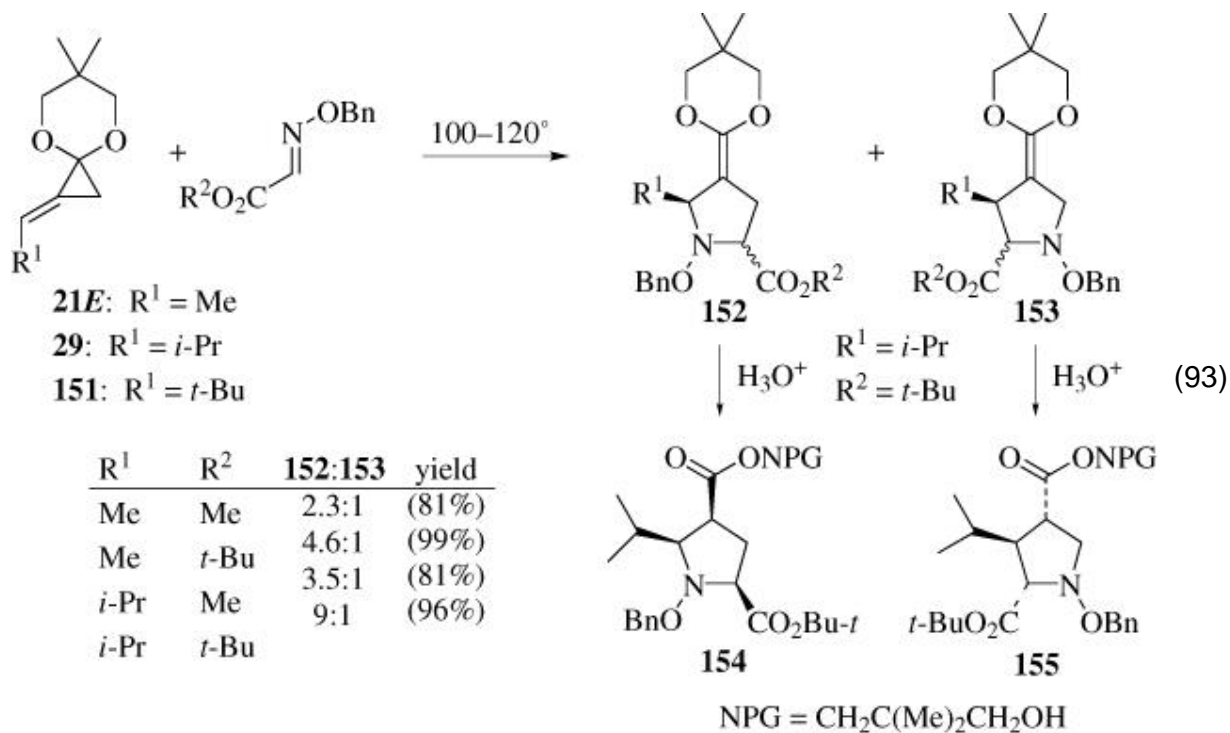
The cycloaddition of substrate **12** with imines of α, β -unsaturated aldehydes occurs preferentially at the imine moiety, but the selectivity is not complete. The reaction of substrate **12** with the tosylimine of cinnamaldehyde gives mainly pyrrolidine cycloadduct **149** (Eq. 92). (111) The carbon-carbon double bond also takes part in the reaction to afford the methylenecyclopentane **150**, and the ratio **149:150** is 6.8:1. This side reaction cannot be suppressed even with the 3-methyl-2-butenal imine, whose double bond is deactivated sterically and electronically, and a mixture of the pyrrolidine and cyclopentane cycloadducts is obtained as a 5.1:1 mixture.



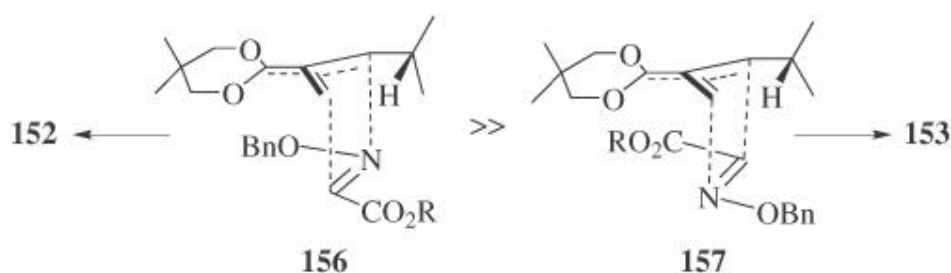
4.1.2.11. Regio- and Stereoselectivity

Steric effects of the substituents both on the TMM (R^1) and on the oxime ester (R^2) influence the regio- and stereoselectivity in the reactions of substituted TMMs (Eq. 93). (50) Thus, a combination of sterically unhindered reactants ($\text{R}^1 = \text{R}^2 = \text{Me}$) affords a 2.3:1 mixture of regioisomers **152** and **153**, both of which are 1:1 mixtures of diastereomers from the disposition of the R^1 and CO_2R^2 groups. When the *tert*-butyl ester of the oxime is employed, the regioselectivity (**152:153**) improves slightly to 4.6:1. The use of an isopropyl

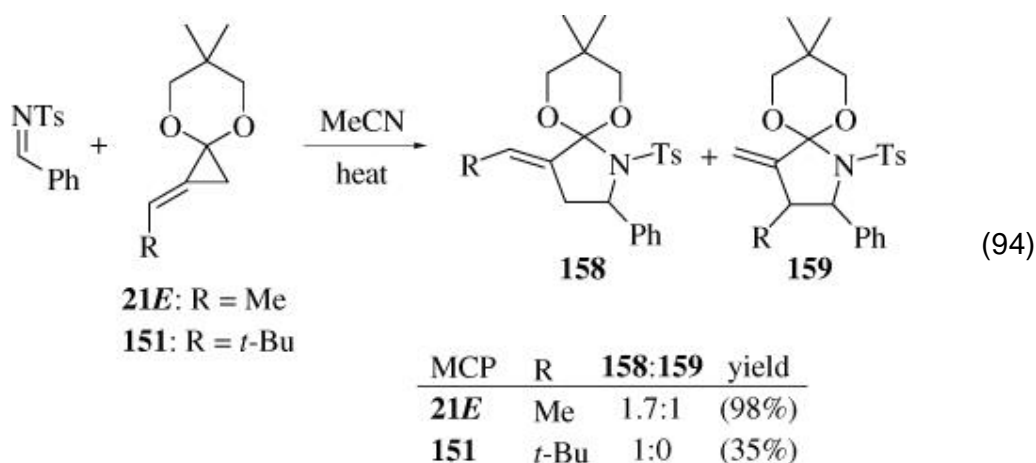
group as the TMM substituent R^1 also improves the regioselectivity. The reaction between a sterically hindered TMM and an *O*-alkyloxime ($R^1 = i\text{-Pr}$ and $R^2 = t\text{-Bu}$) takes place with high selectivity, producing a 9:1 mixture of **152:153**, wherein isomer **152** is >97% pure *cis* and isomer **153** is >96% *trans*. Hydrolysis of the ketene acetals **152** and **153** with acid takes place highly diastereoselectively to give the trisubstituted pyrrolidines **154** and **155** both as single isomers in 79% and 10% isolated yields, respectively.



Stereoselective cycloaddition of the isopropyl-substituted MCP **29** with anti-oximes takes place mainly via a regio- and stereodefined, five-centered transition structure schematically represented as **156** rather than **157**. In these transition states, the oxime ester substrate bearing a bulky R group is oriented so that it avoids interaction with the isopropyl group. The regio- and stereochemical course of the reaction is controlled by the steric bulk of the benzyloxy group and the ester groups, and neither the benzyloxy nor the ester group acts as an electronic stereochemistry-directing group. This behavior is in sharp contrast to the solvent polarity sensitive endo selectivity in the addition of the same TMM **29** to substituted acrylic acid esters. The sensitivity of the selectivities to the steric bulk of the benzyloxy group and the R^1 and R^2 groups is consistent with a highly ordered transition state, wherein formation of the two new σ bonds takes place concurrently.



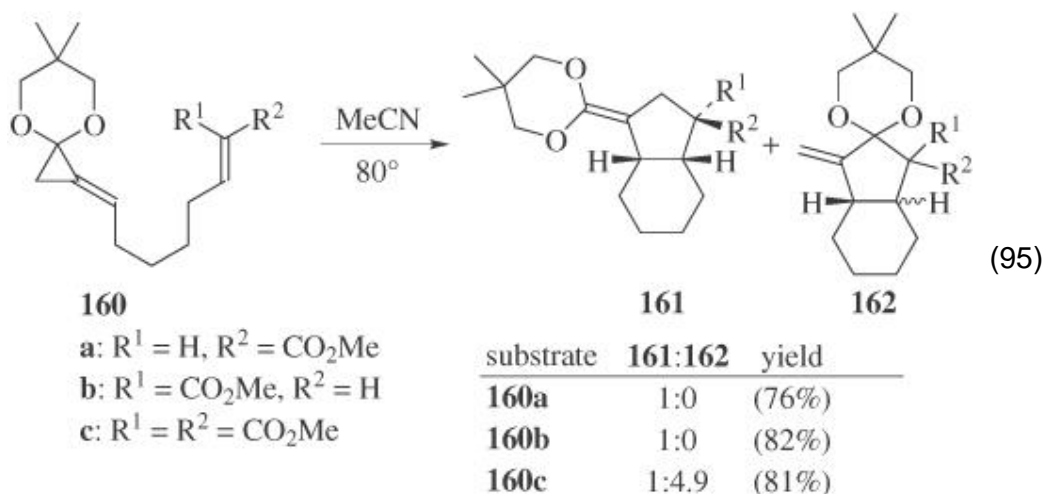
In the cycloaddition of tosylimines with a substituted TMM, two structural isomers, **158** and **159**, can be formed, and steric effects of the substituent on the TMM determine the selectivity (Eq. 94). (111) The cycloaddition of sterically unhindered TMM precursor **21E** with benzaldehyde tosylimine gives a 1.7:1 mixture, whereas the sterically demanding MCP derivative **151** affords the cycloadduct as a single isomer. The alkylidene group in product **158** is exclusively in an *E* geometry, reflecting the geometry of the TMM species.



4.1.3. Intramolecular Applications

Intramolecular cycloaddition of dipolar TMMs provides a method for the synthesis of bicyclo[4.3.0] and [3.3.0] carbo- and heterocycles. MCP **160a** and **160b**, whose carbon-carbon double bonds are activated by single electron-withdrawing groups, selectively and stereospecifically give ketene acetal adduct **161** with high efficiency (Eq. 95). (112, 113), Product **161a** derives from an endo transition state as in the intermolecular reaction, but **161b** derives from an exotransition state because conformational constraints in the transition state override the endo rule. Reaction of MCP **160c**, which possesses a carbon-carbon double bond highly activated by geminal

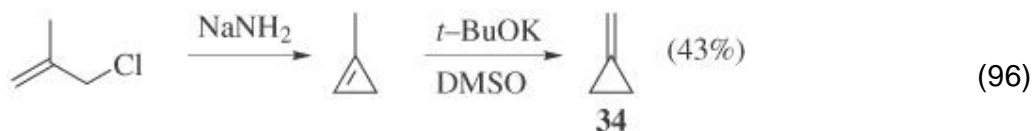
electron-withdrawing groups, gives a mixture of products **161c** and **162c** by way of the single electron transfer pathway.



4.2. Transition Metal Catalyzed Reactions of Methylenecyclopropanes

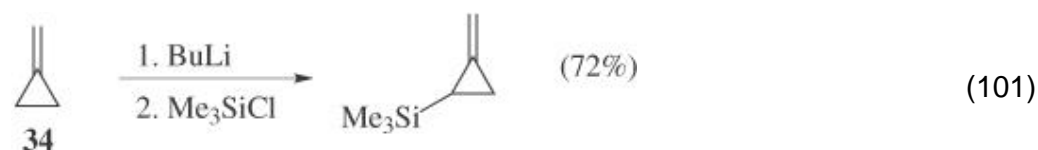
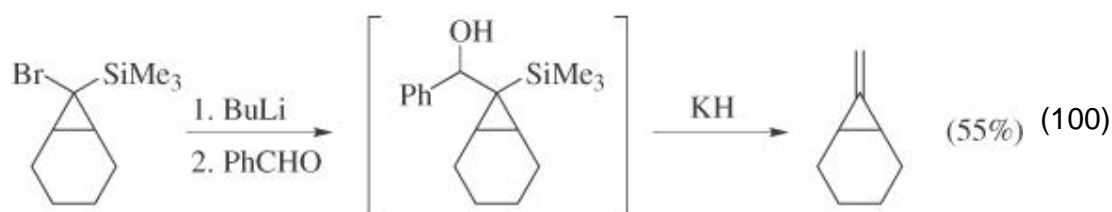
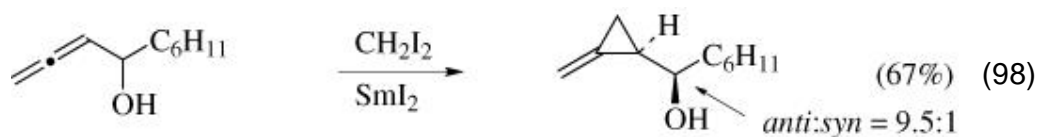
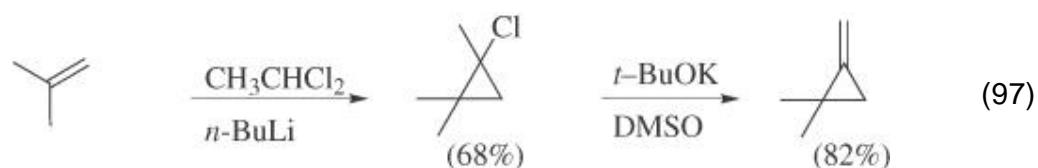
4.2.1. Availability of TMM Precursors

The parent MCP, **34**, is prepared on a large scale in a one-pot, two-step procedure from methallyl chloride by base-promoted cyclization to form methylcyclopropene followed by base-promoted isomerization (Eq. 96). (114) However, extension of this method to substituted MCPs is limited.



Alternatively, substituted MCPs are prepared by various methods, including dehydrochlorination of chloro-substituted cyclopropanes (Eq. 97), (115) carbene or metal carbenoid addition to allenes (Eq. 98), (116-118) Wittig reaction of cyclopropylidene-triphenylphosphorane derivatives with carbonyl compounds (Eq. 99), (119) Peterson olefination of silyl-substituted cyclopropanes (Eq. 100), (120, 121) and nucleophilic addition of lithiated MCPs (Eq. 101). (122) The methods shown in Eqs. 97, 98, and 101 are particularly useful for the preparation of ring-substituted derivatives, and those

in Eqs. 99 and 100 are useful for the olefin-substituted derivatives. The synthesis of MCPs has been reviewed recently. (123)

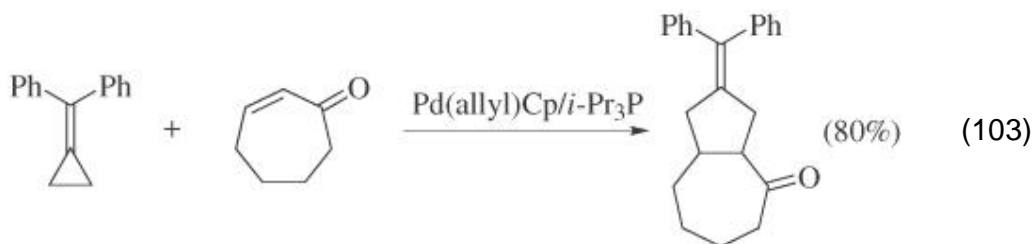
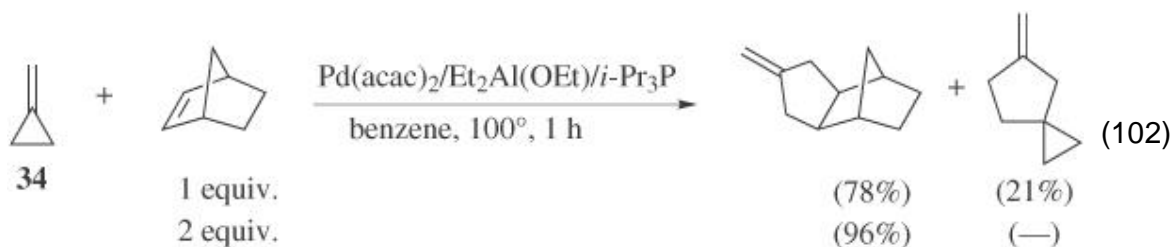


4.2.2. Intermolecular Applications

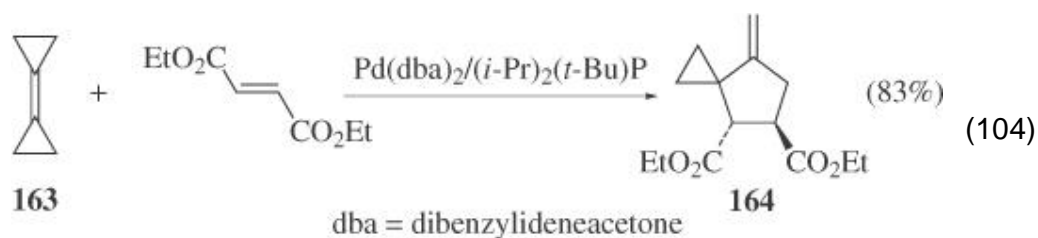
4.2.2.1. Cycloaddition to Alkenes

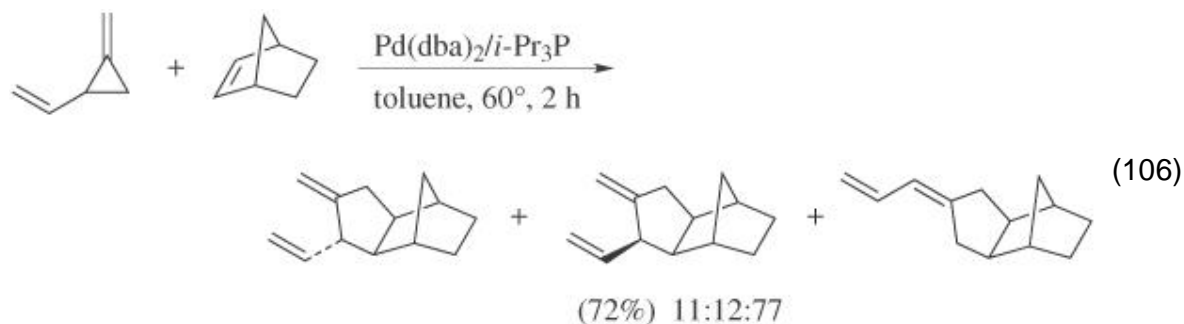
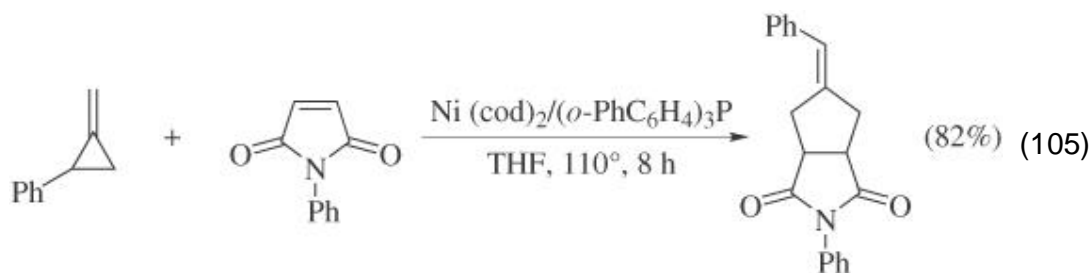
Transition metal mediated cycloadditions of MCPs are generally insensitive to the electronic nature of the acceptors, and unactivated alkenes, such as ethylene and cyclopentene, conjugated alkenes, such as styrene, and

electron-deficient alkenes react equally well with MCP using Ni or Pd catalysts. However, dimerization of MCPs sometimes competes with cycloaddition with unactivated alkenes, and the use of excess alkene is required in such cases (Eq. 102). (22, 124) Enones of medium ring sizes, which are poor acceptors in nucleophilic additions, also serve as good TMM acceptors (Eq. 103). (125)



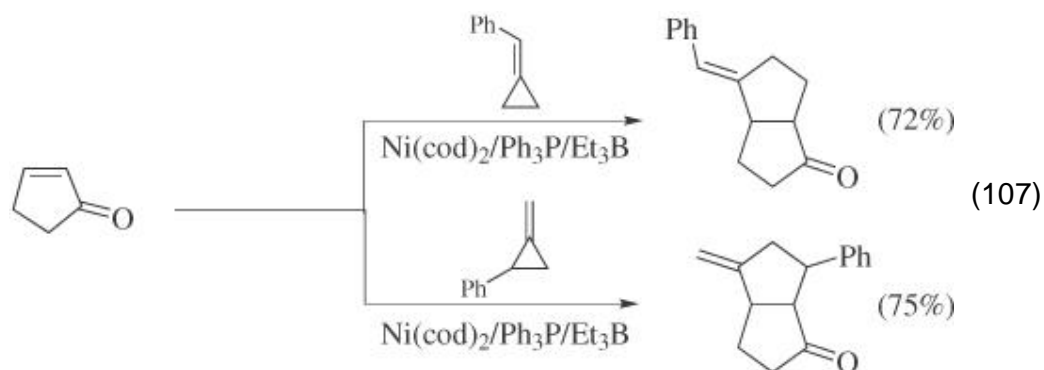
A variety of substituents on both the cyclopropane ring and the alkenes are tolerated, and alkyl- (Eq. 104), (126) aryl- (Eq. 105), (127) vinyl- (Eq. 106), (128) and silyl-substituted MCPs can serve as precursors. The cyclopropyl-substituted MCP **163** selectively affords vinyl-cyclopropane product **164** in the presence of a Pd catalyst (Eq. 104). Although mono- and disubstituted MCPs serve as precursors, tetrasubstituted MCPs do not give the desired [3 + 2] cycloadducts. (129)





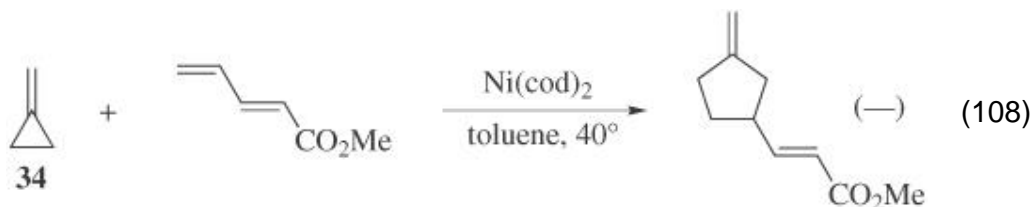
4.2.2.2. Effect of Lewis Acids

Addition of triethylborane as a cocatalyst dramatically improves both the yield and regioselectivity (distal vs. proximal bond cleavage) of the reactions. The products arise through proximal ring opening and, thus, the “memory” of the substituent on the MCP is retained in the product (Eq. 107). (130)



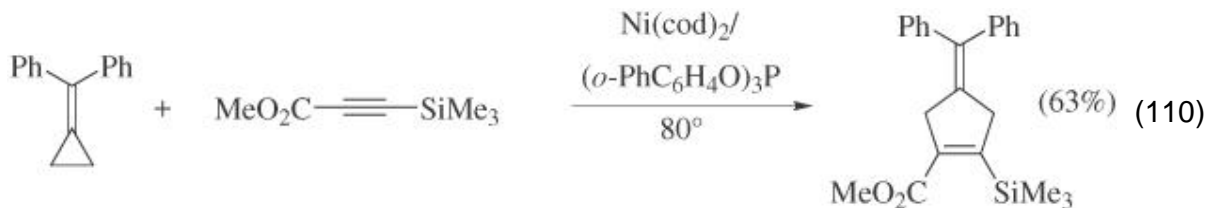
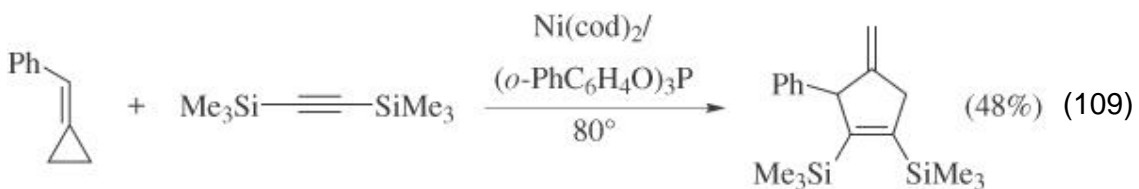
4.2.2.3. Cycloaddition to Dienes

Dienes, such as butadiene and substituted dienes, serve as acceptors and afford [3 + 2] cycloadducts. With substituted dienes, the reaction occurs selectively at the less substituted double bond (Eq. 108). (131)



4.2.2.4. Cycloaddition to Alkynes

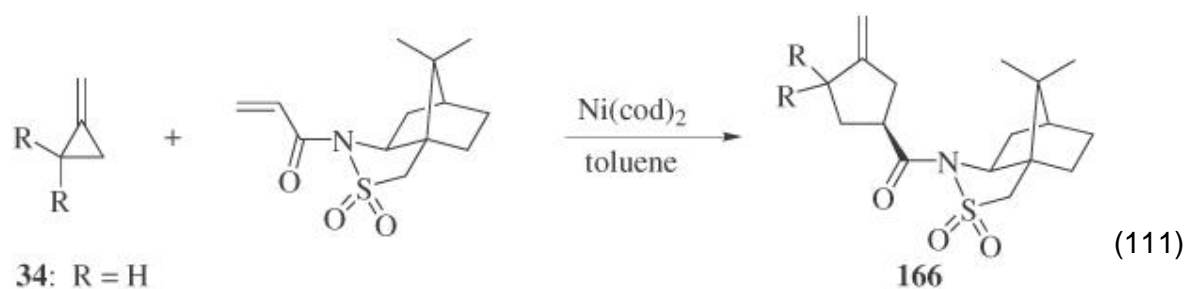
Disubstituted alkynes, especially trimethylsilylacetylene derivatives, are good acceptors. The tris-(2-phenyl)phenyl phosphite modified Ni(0) catalyst is routinely used for this cycloaddition. As in cycloadditions with alkenes, reactions with alkynes usually show low regioselectivity with respect to the ring opening of MCPs, and isomeric mixtures of the cycloadducts are obtained. However, in some specific combinations of substituents on both the MCPs and the alkynes, high regiochemical control can be observed as shown in Eqs. 109 and 110. (132)



4.2.2.5. Asymmetric Induction

High levels of asymmetric induction can be observed using chiral auxiliaries. Although reactions of MCP 34 with menthol- and borneol-derived acrylate

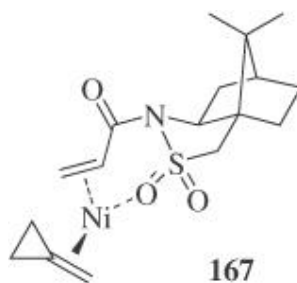
esters show low diastereoselectivity, the reaction with a camphorsultam-derived amide gives cycloadduct **166** with high diastereoselectivity (Eq. 111). (133, 134) The selectivity increases with decreasing reaction temperature at the expense of longer reaction times. Dimethyl-substituted MCP **165** shows higher selectivity than analog **34**, and the reaction at -10° gives a single cycloadduct. The selectivity is believed to be derived from the mode of coordination of the Ni catalyst. As shown in assembly **167**, the Ni catalyst coordinates to the alkenyl moieties of MCP and the acceptor, as well as to the sulfonyl oxygen atoms of the sultam.



34: R = H

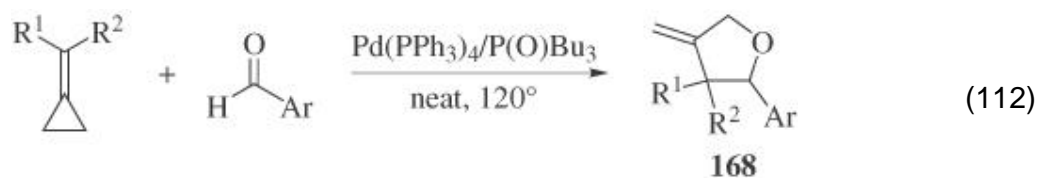
165: R = Me

MCP	temp.	selectivity	yield
34	20°	4.9:1	(80%)
34	-20°	10:1	(72%)
165	20°	49:1	(86%)

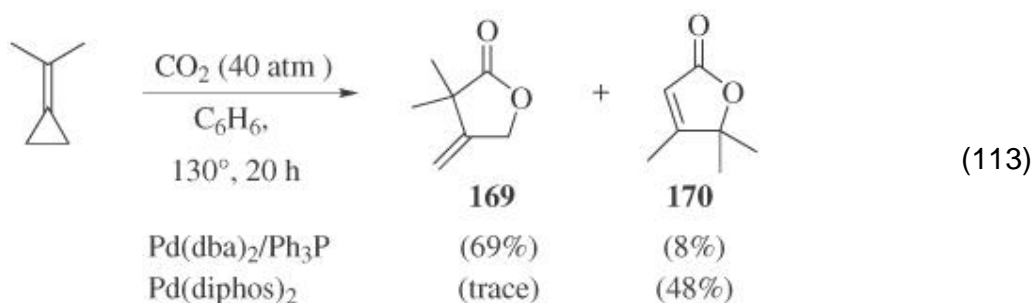


4.2.2.6. Cycloaddition to Carbonyl Compounds and Carbon Dioxide

The cycloaddition of MCPs with carbonyl compounds has been described only recently. Tributylphosphine oxide modified palladium(0) catalysts effect the cycloaddition of various alkylidenecyclopropanes with aromatic aldehydes (Eq. 112). (135) Although the reaction potentially gives three regioisomers, the reaction selectively affords the single isomer **168**. Success of the reaction may be attributed to the high concentration of both substrates.

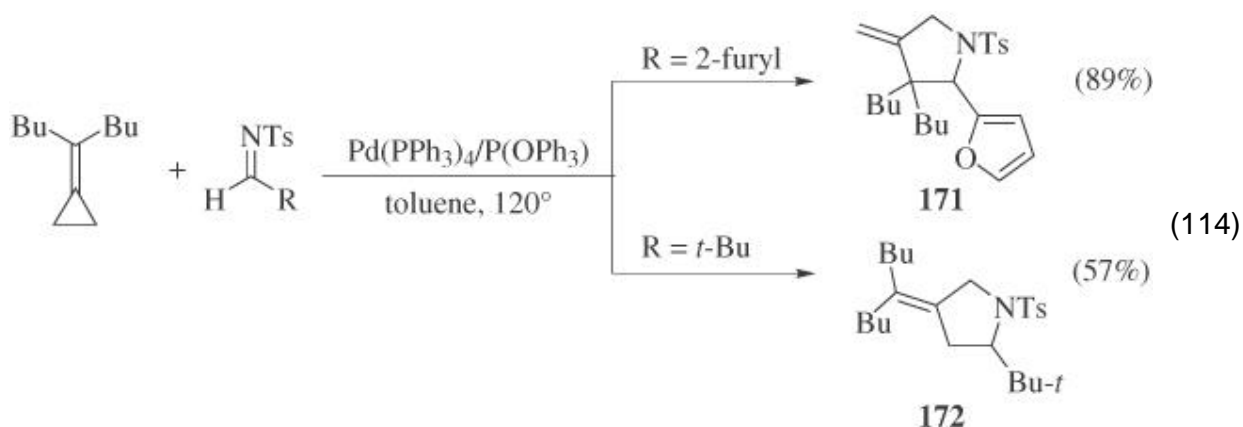


The parent MCP as well as alkyl-substituted MCPs react with carbon dioxide to give γ -lactone derivatives. Palladium(0) catalysts are used for this reaction. With substituted MCPs, both isomers **169** and **170** are selectively formed by proper choice of the phosphine ligand (Eq. 113). (136) Since Pd(0) catalyzes the isomerization of lactone **169** to lactone **170**, formation of isomer **170** most likely involves the initial formation of the regioisomer of adduct **169** followed by the isomerization of the exomethylene to the internal and conjugated alkene.

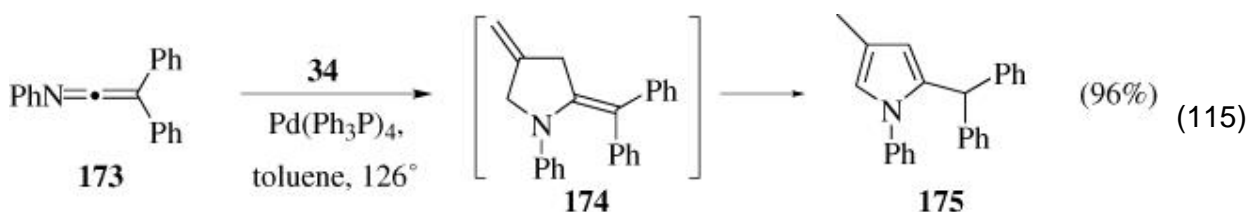


4.2.2.7. Cycloaddition to C = N Double Bonds

The cycloaddition of MCPs with imines has also been recently reported. Alkylidenecyclopropanes undergo cycloaddition with various tosylimines in the presence of a palladium(0) catalyst to give the corresponding pyrrolidines (Eq. 114). (137) The reaction shows a unique substratedependent dichotomy: aryl-substituted imines afford the exomethylene product **171**, and alkyl-substituted imines afford the alkylidene product **172**.



The C = N moiety of ketene imine **173** selectively reacts with MCP **34** under Ni or Pd catalysis, and the adduct is isolated as pyrrolidine **175** by way of intermediate **174** (Eq. 115). (138) Alkyl-substituted MCPs also undergo cycloaddition at the C = N moiety, and the “memory” of the starting structure of the MCPs is lost during the cycloaddition.



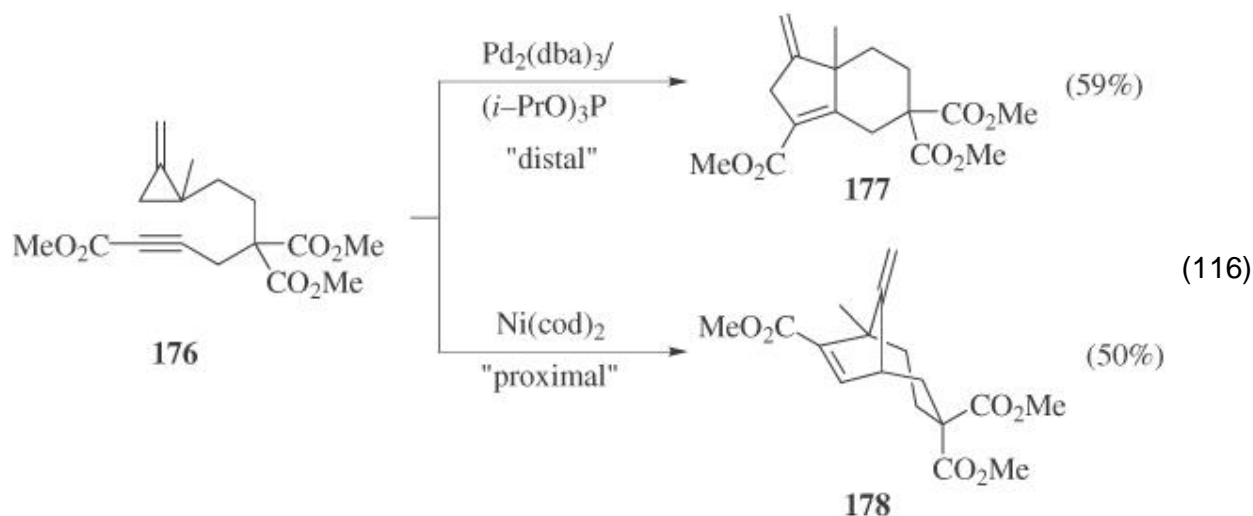
4.2.3. Intramolecular Applications

Regiochemical control can be achieved in the intramolecular reaction, in which many of the undesirable complications can be avoided. Although palladium catalysts have a strong preference for the distal ring opening of substituted MCPs in the intermolecular reaction, the regioselectivity of the ring cleavage in the nickel-catalyzed reaction is strongly affected by the structure of the substrate.

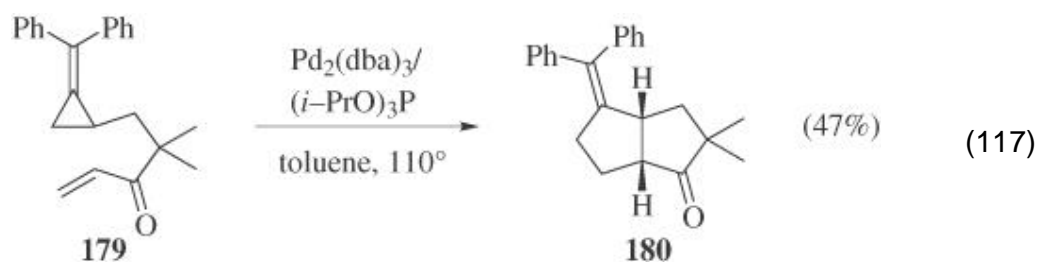
4.2.3.1. Regioselectivity

The Pd(0)-catalyzed reaction of acetylenic MCP **176** gives the substituted hydroindane **177** arising from distal cleavage of the MCP ring, whereas the Ni(0)-catalyzed reaction results in the formation of regioisomer **178** through proximal cleavage (Eq. 116). (139) This result indicates that the selection of

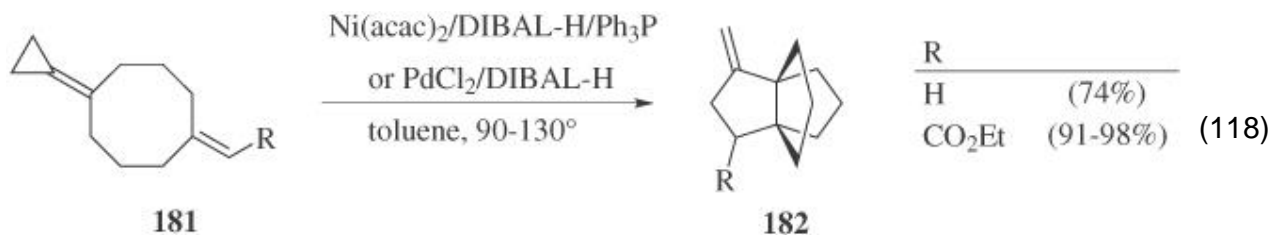
the metal catalyst may be used in a predictable way to govern the regiochemical outcome of certain reactions.



In the presence of Pd(0) catalysts, various acetylenic and olefinic MCPs bearing three-carbon tethers undergo cycloaddition reactions through distal ring opening of MCPs to afford bicyclo[3.3.0]octanes. For example, the olefinic MCP **179** affords *cis*-fused adduct **180** in the presence of Pd(0) catalysts (Eq. 117). (140, 141)

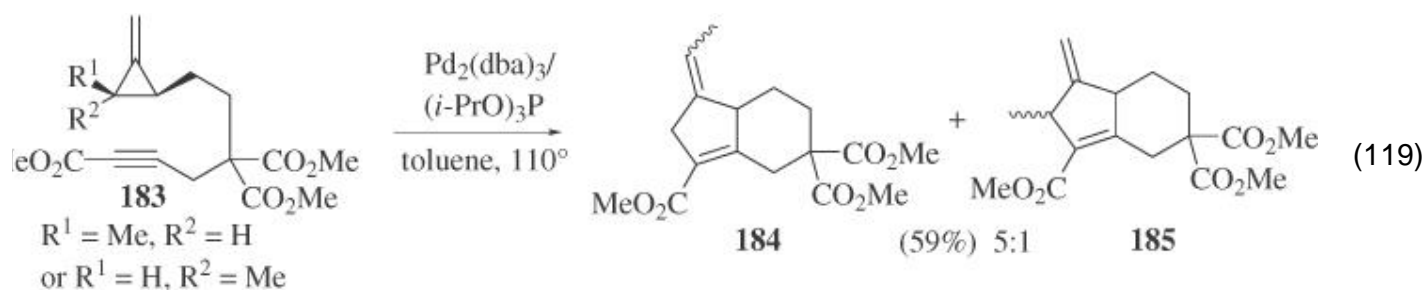


The reaction path is altered by the structure of the substrates, and both the Ni(0)- and Pd(0)-catalyzed reactions of cyclooctane derivative **181** give [3.3.3]propellane **182** as the sole product through distal cleavage of the MCP ring (Eq. 118). (142, 143) The



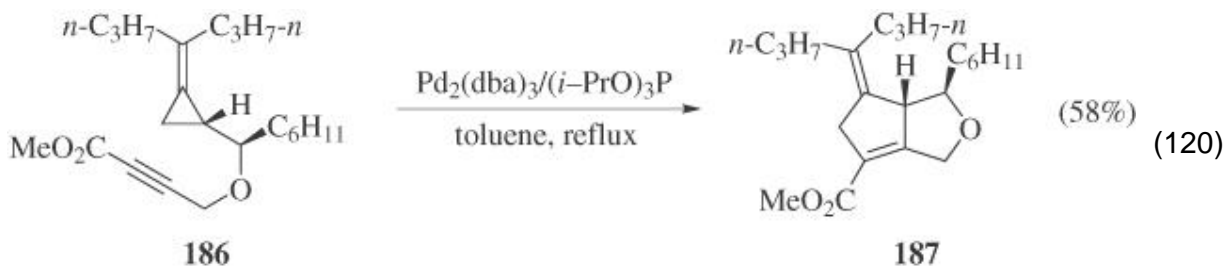
reaction course may be strongly affected by transannular interaction of the MCP and alkenyl moieties, which is well known in medium-ring compounds. The cycloaddition is feasible for both electron-deficient and simple alkenes (R = CO₂Et, H).

The Pd(0)-catalyzed intramolecular cycloaddition of each of the two diastereomers of substrate **183** gives a similar mixture of the two geometric isomers **184** and **185** in a 5:1 ratio (Eq. 119). (144) The observed “memory loss” is initially rationalized



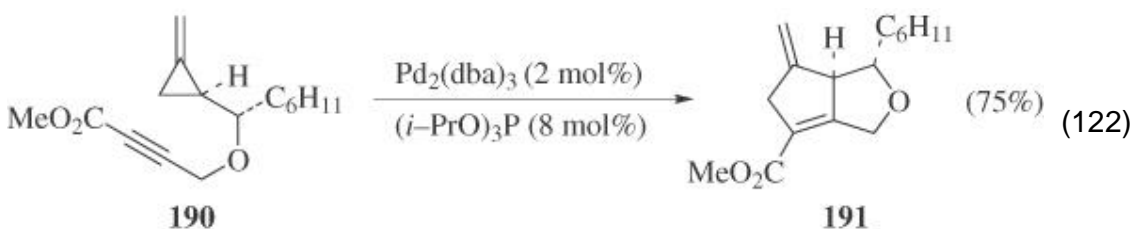
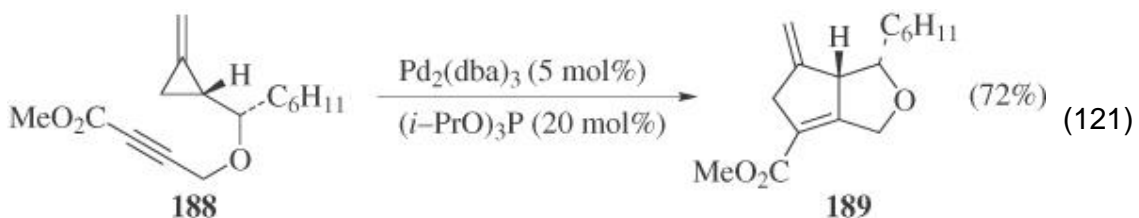
in terms of a relatively long-lived palladium-TMM type intermediate, but a mechanism that involves direct attack of the cyclopropyl group on alkynes as in Eq. 29 can also account for the observed loss of selectivity.

The regiochemical change with respect to the substituents on the MCP is controlled in the reaction of alkylidene MCP **186**, and the cycloaddition selectively affords alkylidenecyclopentene **187** as the sole product (Eq. 120). (57) This result stands in sharp contrast to the intermolecular reaction.



4.2.3.2. Stereospecificity

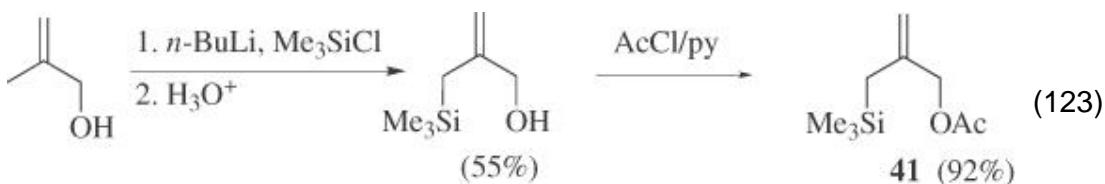
Palladium-catalyzed intramolecular cycloadditions of the diastereomeric acetylenic MCPs **188** and **190** occur stereospecifically (>100:1) with retention of configuration, and give the diastereomeric cycloadducts **189** and **191**, respectively (Eqs. **121** and **122**). (57) This pattern is observed for all the diastereomeric cycloadducts, regardless of the substitution pattern.



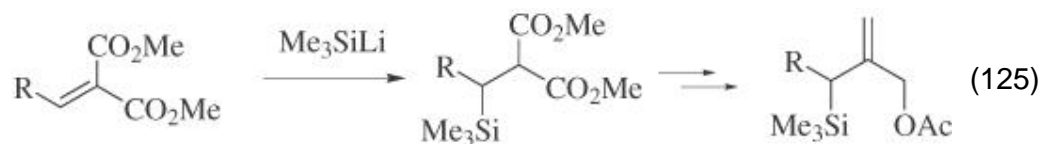
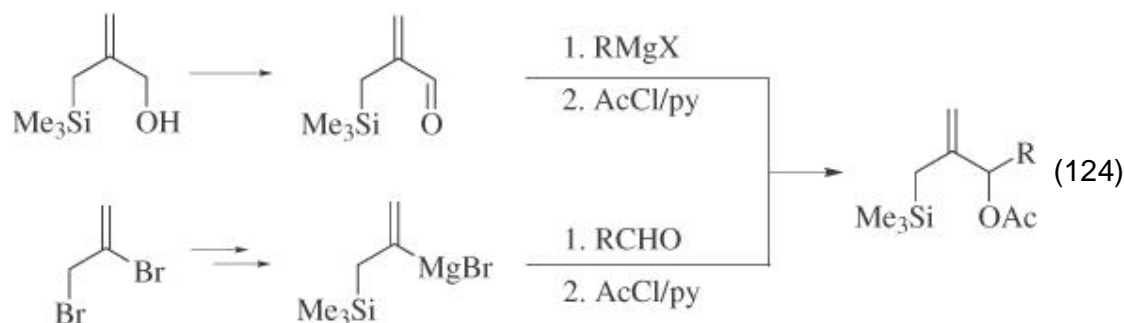
4.3. Transition Metal Mediated Reactions of Silylated Allylic Acetates

4.3.1. Availability of TMM Precursors

2-Acetoxymethyl-3-allyltrimethylsilane (**41**) is the most common precursor of the dipolar TMM-Pd intermediate. This compound can be prepared in 60% overall yield by metalating α -methylallyl alcohol with *n*-BuLi followed by quenching with trimethylsilyl chloride, hydrolysis of the silyl ether, and O-acetylation of the resulting alcohol (Eq. **123**). (69, 145, 146)



The same compound can be also prepared from 2-(chloromethyl)-3-chloropropene or trimethylsilylethyl glycolate. Substituted derivatives can be prepared from the corresponding substituted alcohols. Alternatively, a silyl-substituted allylic acetate or 2,3-dibromopropene can be used as the starting material for substituted derivatives (Eq. 124). (75) The isomeric allylic acetates are also prepared from substituted alkylidenemalonates (Eq. 125). (74)



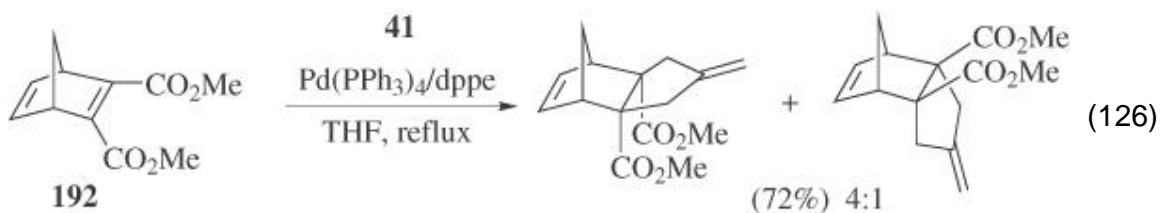
In addition to the acetate, other ester derivatives, including carbonate, benzoate, and mesylate, have been used as TMM precursors. These precursors are prepared by methods similar to those described above. The leaving group sometimes affects the course of the reaction, and specific examples are discussed later. Allylic bromides, however, cannot be used as precursors.

4.3.2. Intermolecular Applications

4.3.2.1. Cycloaddition to Alkenes

The zwitterionic TMM-Pd complex **5** possesses nucleophilic character, and reacts preferentially with alkenes bearing electron-withdrawing groups, such as esters, nitriles, ketones, and sulfones. Simple alkyl-substituted alkenes such as norbornene derivatives or electron-rich olefins such as enamines fail to react. Thus, cycloaddition with norbornadiene **192**, which possesses both an electron-deficient and an unfunctionalized double bond, selectively occurs at the electron-deficient double bond (Eq. 126). (65, 69) However, highly electron-deficient alkenes, such as TCNE, do not give adducts under these

reaction conditions, presumably because electron-transfer processes, such as oxidation of the Pd catalyst, disrupt the cycloaddition.

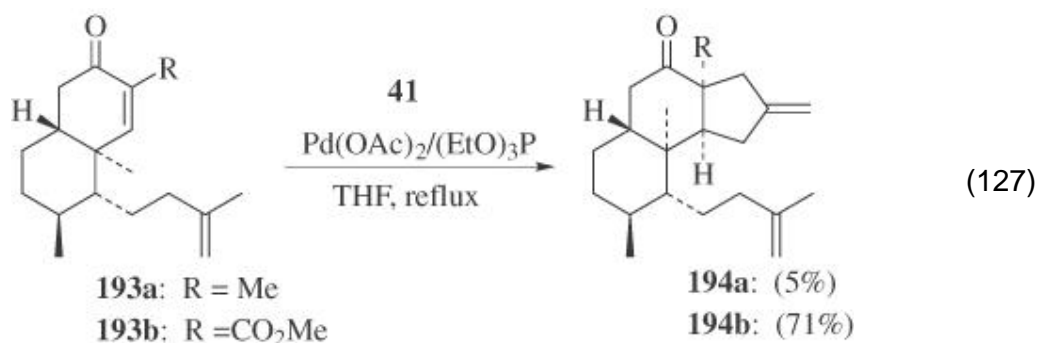


Several Pd(0) and Pd(II) salts can be used in this catalytic system. The reaction proceeds best with a Pd(0) catalyst that bears arylphosphine ligands, normally with a ligand:Pd ratio of 4:1. The typical catalysts used are $(\text{Ph}_3\text{P})_4\text{Pd}$ or a $\text{Pd}(\text{OAc})_2/(\text{i-PrO})_3\text{P}$ combination. When the Pd(II) catalyst is used, it is first reduced to Pd(0) with *n*-BuLi, DIBAL-H, or the alkene reactant. Although there are no significant differences in yields between the Pd(0) and Pd(II) catalysts, the latter does offer a unique advantage of being able to vary the nature of the ligand without preparing the corresponding Pd(0) complex and to avoid handling of air-sensitive complexes.

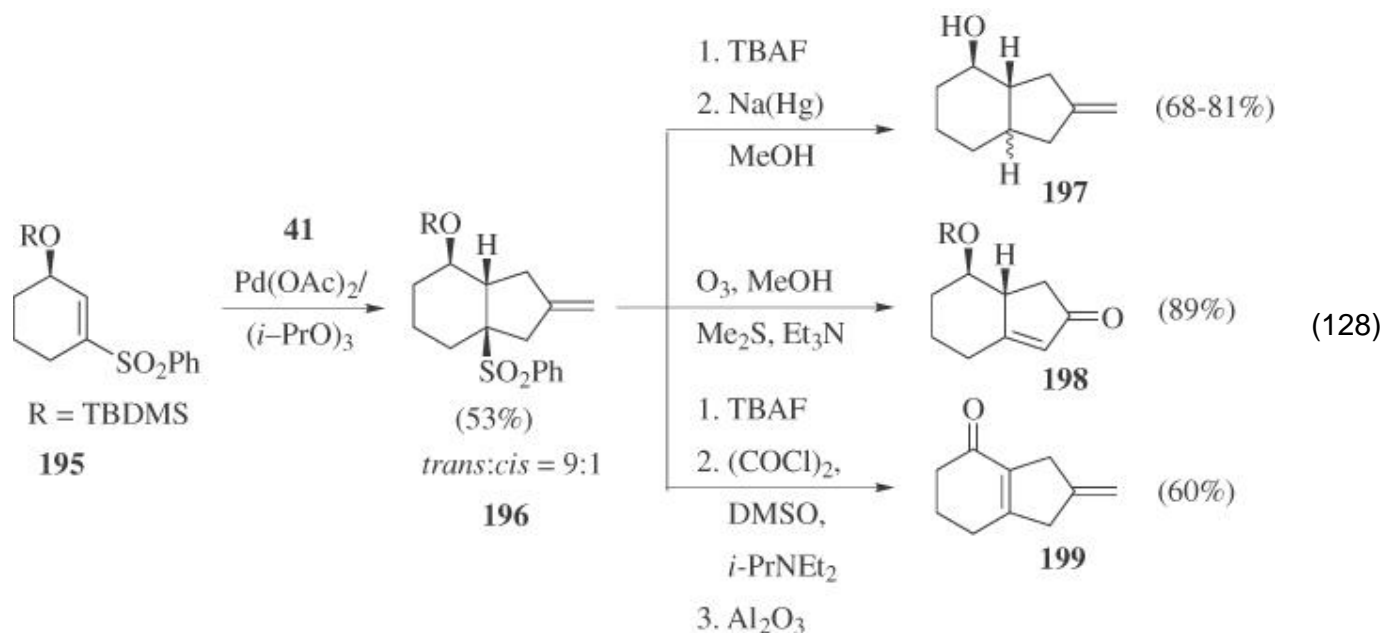
The solvent also plays a very important role. Changing from toluene to THF dramatically shortens the reaction time and enhances the yield of cycloaddition. In dipolar aprotic solvents such as acetonitrile or DMF, the reactions proceed even at room temperature although the yields may be somewhat lower.

The cycloaddition is sensitive to the steric bulk and the structure of the acceptor. Trisubstituted alkenes and enones of medium ring size are usually poor acceptors toward the cycloaddition. For example, the Pd-catalyzed reaction of precursor **41** and substrate **193a** ($\text{R} = \text{Me}$) affords the desired cycloadduct **194a** in only 5% yield (Eq. 127). (147) In such a situation, installation of a 2-carbomethoxy group, such as in enone **193b** ($\text{R} = \text{CO}_2\text{Me}$), enhances the electron-deficiency of the acceptor and increases the yield (71% yield for **194b** with complete stereoselectivity).

2-Carbomethoxy-2-cycloalkenones in medium-size rings also show higher reactivities toward the TMM–Pd complex.

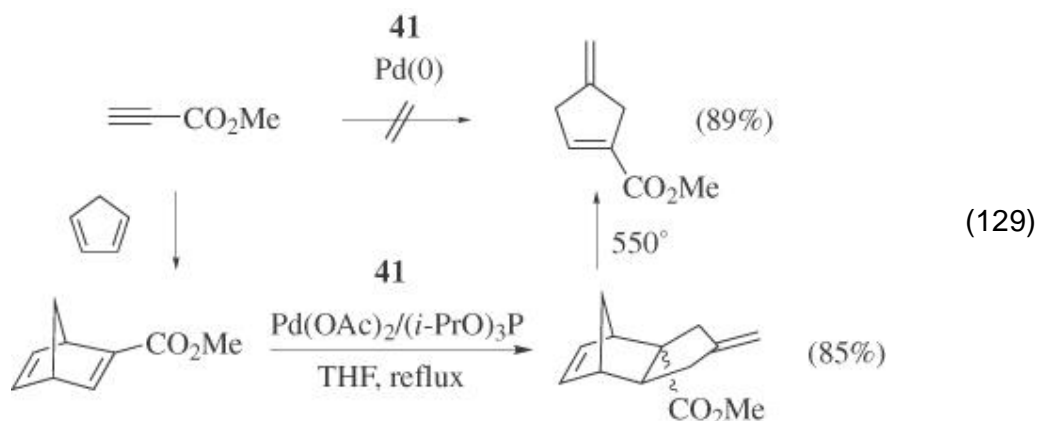


Vinylsulfones are good acceptors for the TMM-Pd complex and serve as masked alkenes by cycloaddition followed by reductive desulfonation. For example, the reaction of precursor **41** with the enantiomerically enriched vinylsulfone **195** affords bicyclic product **196**. Sodium amalgam reduction and deprotection affords alkene **197**. The overall sequence represents the equivalent of a cycloaddition of a cyclohexene derivative (Eq. 128). (148) In addition to desulfonation, other functional group manipulations provide access to a variety of cyclopentane derivatives. Because sulfones are good leaving groups, oxidation of the exomethylene group or alcohol function of intermediate **196** followed by base treatment provides fused enone derivatives **198** and **199**.



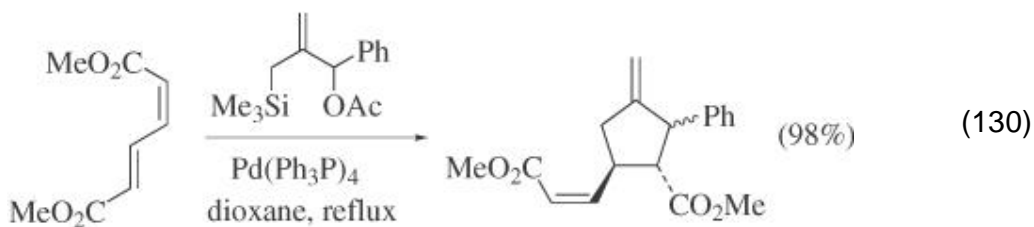
4.3.2.2. Cycloaddition to Alkynes

Cycloaddition of TMM–Pd complexes with alkynes would potentially give methylenecyclopentenes, but this process has not been effective. Alternatively, alkynes are temporarily masked by the Diels-Alder reaction and regenerated after the cycloaddition by flash vacuum pyrolysis (Eq. 129). (149)



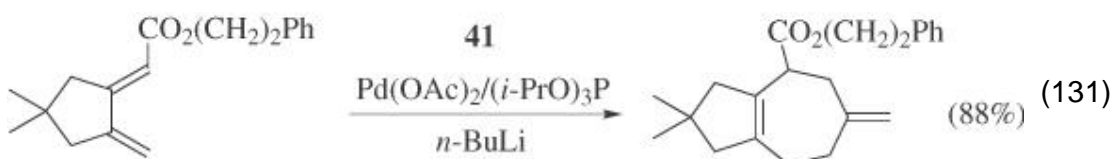
4.3.2.3. Cycloaddition to Dienes and Trienes

In the reaction of precursor 41 with dienes, [3 + 4] cycloaddition competes with [3 + 2] cycloaddition. Selective [3 + 2] cycloaddition takes place when a sterically bulky phenyl-substituted TMM–Pd complex is used with acyclic dienes (Eq. 130). (150) On the other hand, conformational restriction of the diene to its cisoid geometry enhances the formation of the [3 + 4]



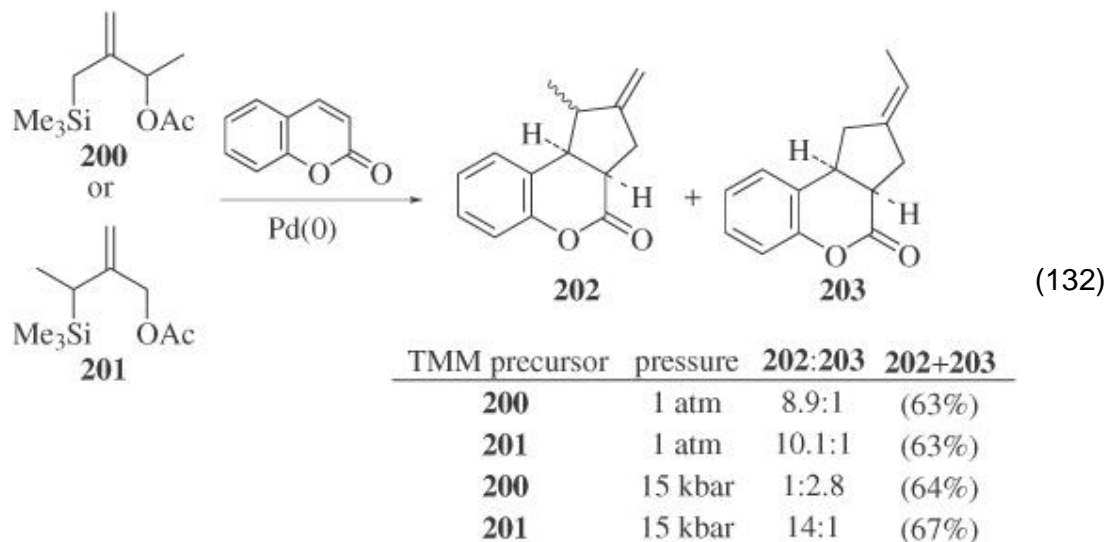
cycloaddition product to afford seven-membered rings (Eq. 131). (151)

Cycloaddition to tropone derivatives, being cyclic trienes, selectively gives the [3 + 6] cycloadducts. (152)



4.3.2.4. Effects of High Pressure

The regioselectivity of cycloaddition of substituted TMM-Pd complexes is pressure dependent (Eq. 132). (153) At ambient pressure, the reaction takes place from a thermodynamically more stable TMM-Pd complex, and under high pressure an initially generated TMM-Pd complex, e.g. 50 and 51 in Eq. 47, reacts preferentially. In the reaction of the isomeric methyl-substituted TMM precursors 200 and 201 with coumarin, the major product under ambient pressure is the same cycloadduct 202. High pressure inverts the regioselectivity of the cycloaddition starting from precursor 200, now favoring cycloadduct 203, whereas the isomeric TMM precursor 201 shows enhanced selectivity for isomer 202 at high pressure.



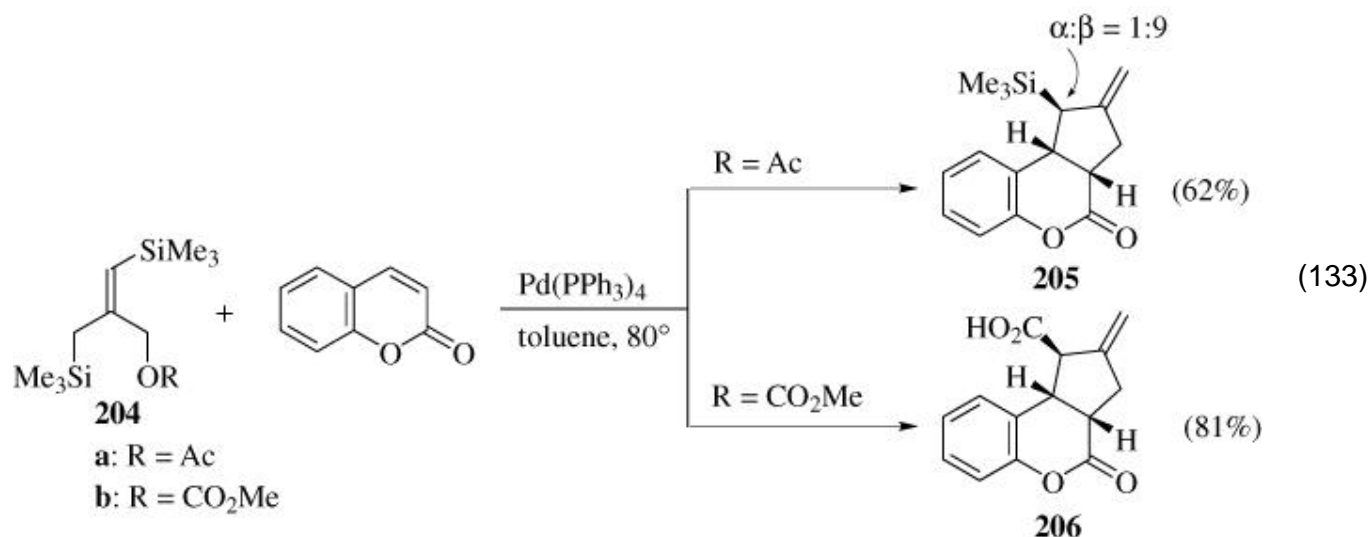
4.3.2.5. Carboxylative Cycloadditions

The silyl-substituted TMM-Pd complex generated from precursor 204 can react directly to give the silyl-substituted methylenecyclopentane 205 or carboxylated methylenecyclopentane 206 depending on the nature of the leaving group (Eq. 133). (154, 155) By the use of acetate 204a, the cycloaddition with coumarin proceeds regioselectively to give product 205. The same reaction with carbonate 204b leads instead to the carboxylic acid 206 as a single diastereomer.

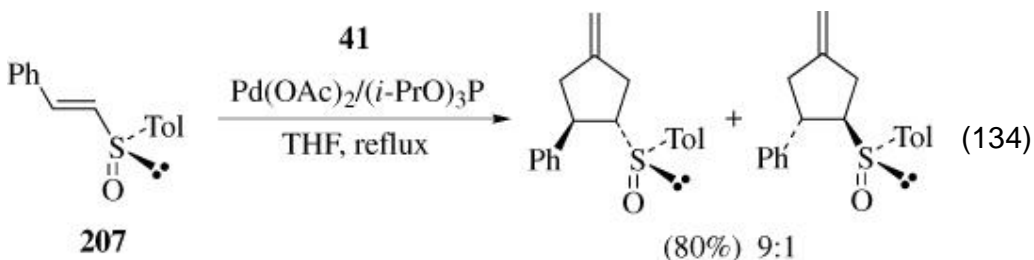
4.3.3. Asymmetric Induction by Chiral Auxiliaries

Asymmetric induction is achieved by the use of conformationally rigid acceptors. Chiral auxiliaries of the type utilized in many Lewis acid catalyzed

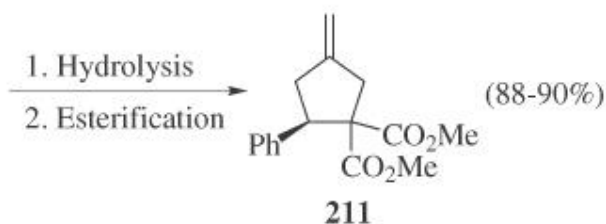
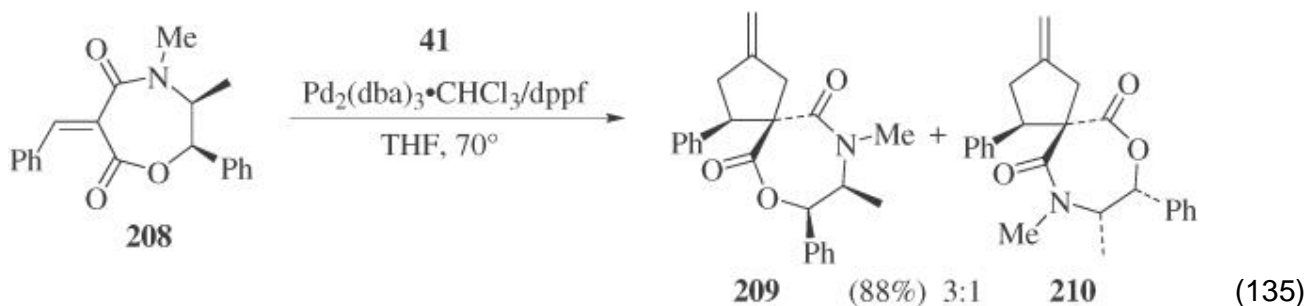
Diels-Alder reactions, such as substituted oxazolidin-2-ones and camphor sultams, have not been successful with the [3 + 2]



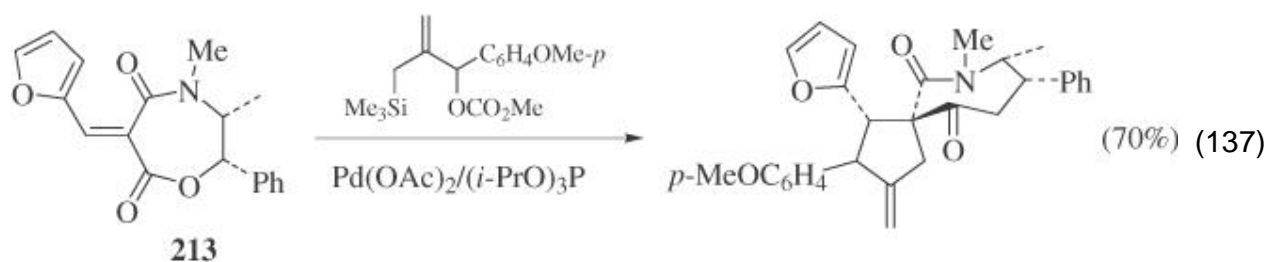
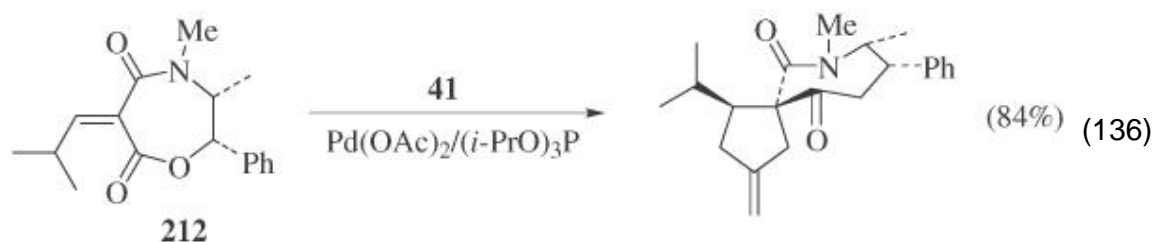
cycloaddition (4–26% diastereofacial selectivity). The use of chiral sulfoxides, such as **207**, as the auxiliary increases diastereofacial selectivity to synthetically acceptable levels (75–90% diastereofacial selectivity) (Eq. **134**). (**156**)



The lack of diastereofacial selectivity may be attributed to the conformational mobility of the acceptors in the absence of a Lewis acid. Therefore, the use of alkenes possessing conformationally rigid chiral auxiliaries, such as **208**, **212**, and **213**, results in high diastereofacial selectivity. Pd(0)-catalyzed cycloaddition of substrate **208** with precursor **41** in THF at 70° gives a 3:1 mixture of two adducts **209** and **210** (Eq. **135**). (**157**) Removal of the chiral auxiliary by basic hydrolysis followed by esterification gives the single product **211**.

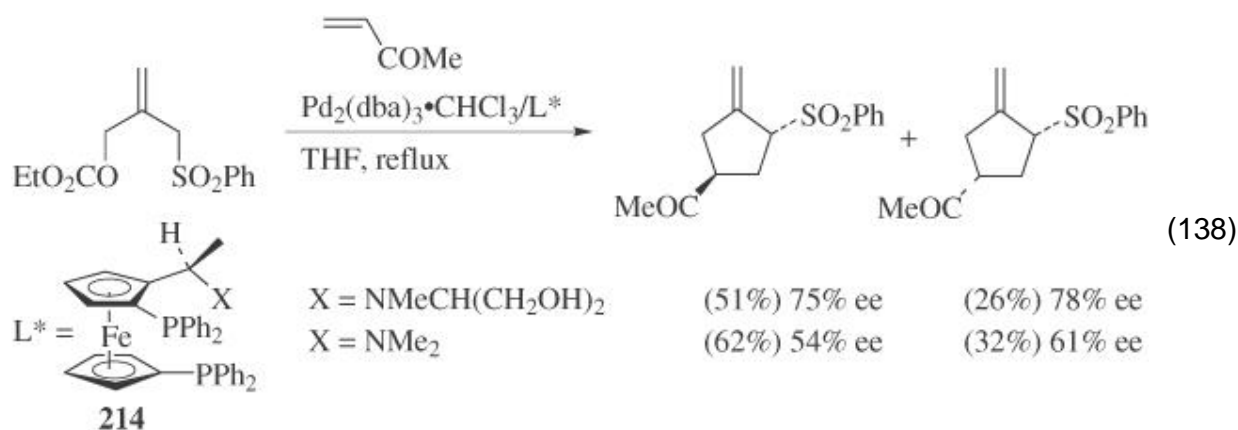


Both enantiomeric series are available either by using the enantiomeric chiral auxiliary or by changing the alkene geometry (Eqs. 136 and 137). (157) In all reactions of the *Z*-alkylidene acceptor, the facial selectivity with respect to the acceptor is >96%. For the *E* acceptor, the facial selectivity drops to 90%.



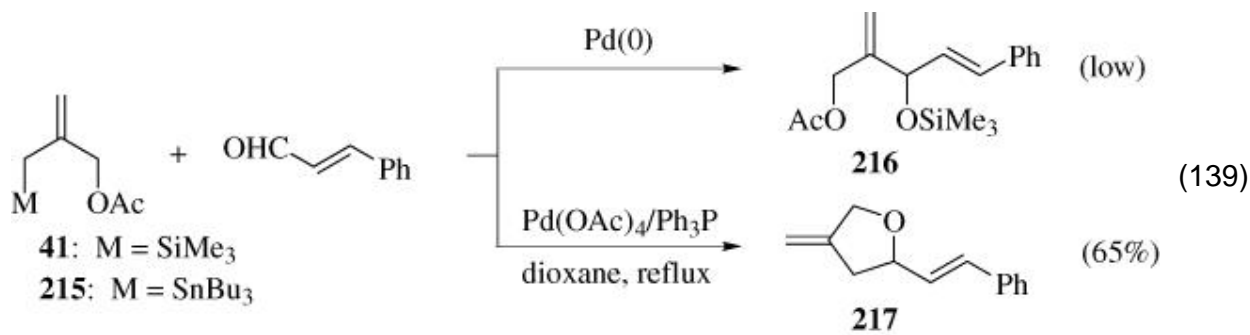
4.3.3.1. Asymmetric Induction with Chiral Catalysts

Asymmetric induction by chiral transition metal complexes has so far met with little success, probably because the bond-making process occurs on the face opposite to that complexed with palladium. (73) The most successful examples employ the chiral ferrocenylphosphine **214**, which affords up to 78% enantiomeric excess (Eq. 138). (158) Other chiral phosphines, such as CHIRAPHOS [bis(diphenylphosphino)butane], BINAP [2,2-*bis*(diphenylphosphino)-1,1-*bis*(naphthyl)], DIOP [2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-*bis*(diphenylphosphino)butane] or CAMP (cyclohexyl-*o*-anisylmethylphosphine) lead to the cycloadduct with low enantioselectivity (4–46% ee). (67)



4.3.4. Cycloaddition to Carbonyl Compounds

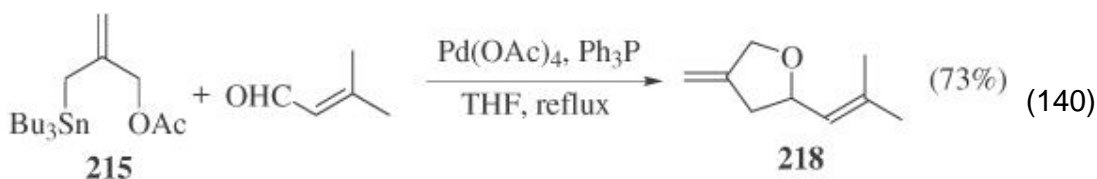
Although the palladium-catalyzed reaction of allylic acetate **41** and an aldehyde gives only the allylated product **216**, addition of a catalytic amount of R₃SnOAc (R = Me, Bu) results in a clean cycloaddition reaction to afford 2-substituted 4-methylenetetrahydrofurans **217** in high yield (Eq. 139). (146, 159) The reaction requires a mixture of approximately equimolar amounts of an aldehyde and precursor **41** in THF with a Pd(0) catalyst and



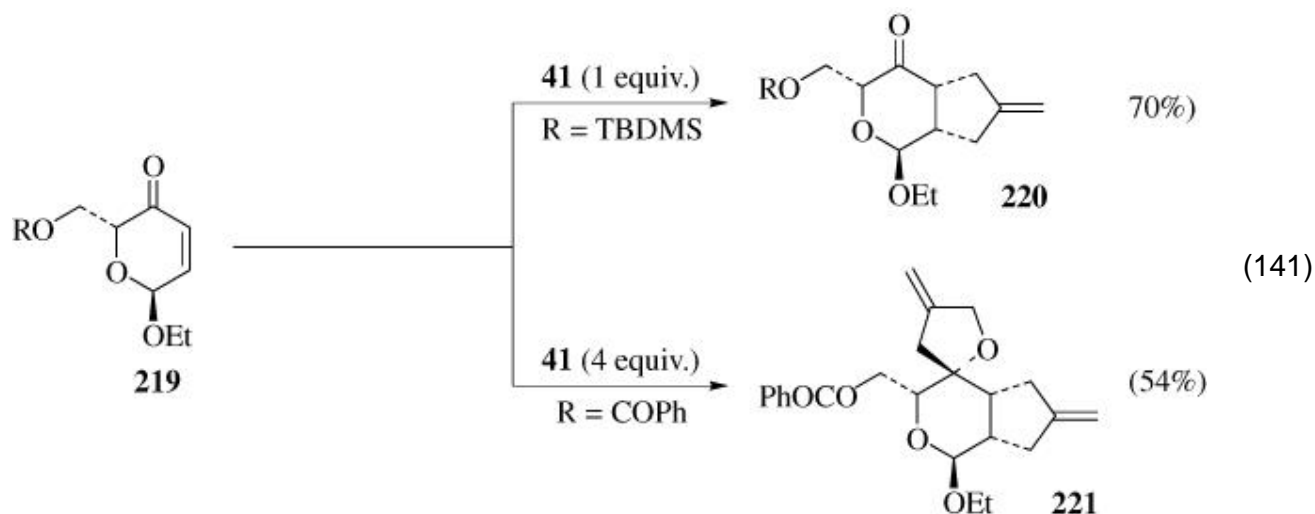
10–25 mol% of R_3SnOAc as a cocatalyst. In both chemical yield and cleanliness of the reaction, trimethyltin acetate is superior to tributyltin acetate. However, the toxicity and high volatility of trimethyltin acetate require careful handling. Allylic acetate **215** also gives a hetero[3 + 2] cycloadduct in the presence of Pd catalysts without an added tin cocatalyst. Although many ketones are unreactive, sterically unencumbered ketones, e.g. 3,5-dioxacyclohexenones, 5-oxacyclohexanones, a 2-acylfuran, and an alkynyl ketone serve as carbonyl acceptors in the cycloaddition.

4.3.4.1. Chemoselectivity

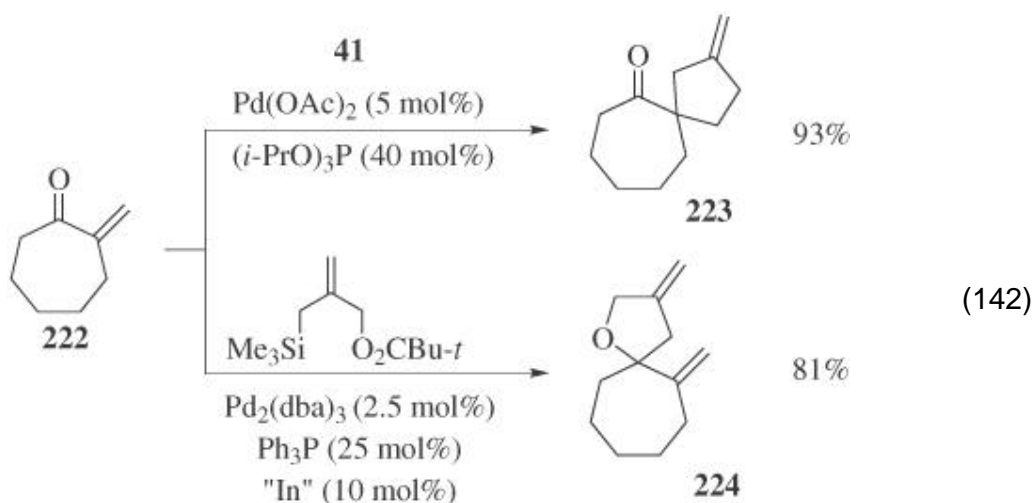
The cycloadditions of enals and enones with TMM-Pd complexes take place with high chemoselectivity. The reaction of enals with precursor **215** occurs exclusively at the aldehyde group to give methylenefuran **218** (Eq. 140). (159)



On the other hand, cycloaddition takes place exclusively at the alkene moiety in the reaction of enones. For example, the reaction of enone **219** with one equivalent of precursor **41** occurs selectively at the alkene to give methylenecyclopentane **220** as the sole product (Eq. 141). (71) The carbonyl groups of compounds **219** and **220** are unreactive, but when there is a benzoyl protecting group, the carbon-oxygen double bond reacts with excess precursor **41** to give the bis-adduct **221** in moderate yield.



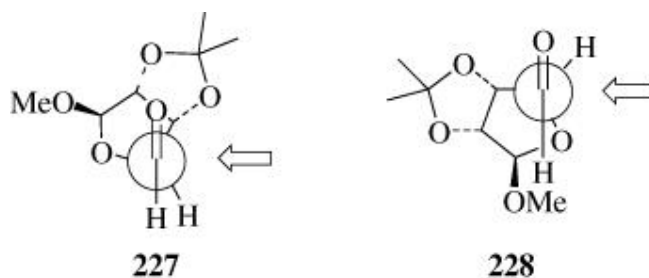
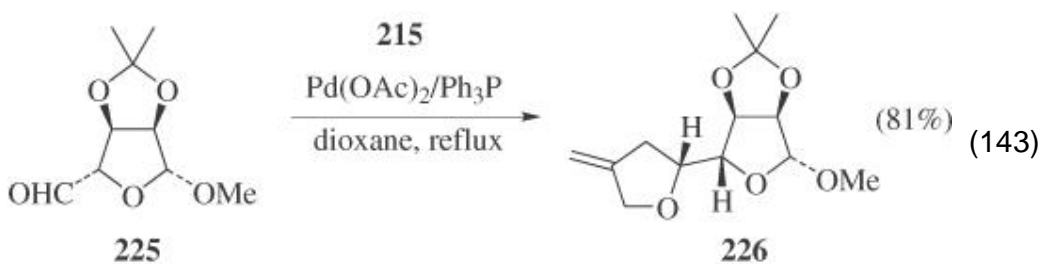
The course of the reaction is altered from cyclopentane formation to tetrahydrofuran formation by the use of an In^{3+} cocatalyst. Both tris(2,4-pentanedionato)indium and its hexafluoro analog direct the reaction course to 1,2-addition (Eq. 142). (160) Exomethylene enones, such as **222**, which are particularly prone to conjugate addition, can be diverted, in the presence of the indium cocatalyst, from exclusive 1,4-addition yielding **223**, to exclusive 1,2-addition yielding isomer **224**.



"In" = tris(2,4-pentanedionato)indium

4.3.4.2. Diastereoselectivity

The 1,2-diastereoselectivity of the reaction of TMM-Pd complexes with α -substituted aldehydes is also excellent, and the cycloaddition with aldehyde **225** affords product **226** as a single diastereomer (Eq. 143). (159) The major pathway followed by the reaction is predicted by the Felkin-Anh model **227**, whereas an alternative model **228**, which better minimizes dipole-dipole and nonbonded interactions, predicts the same diastereoselectivity.

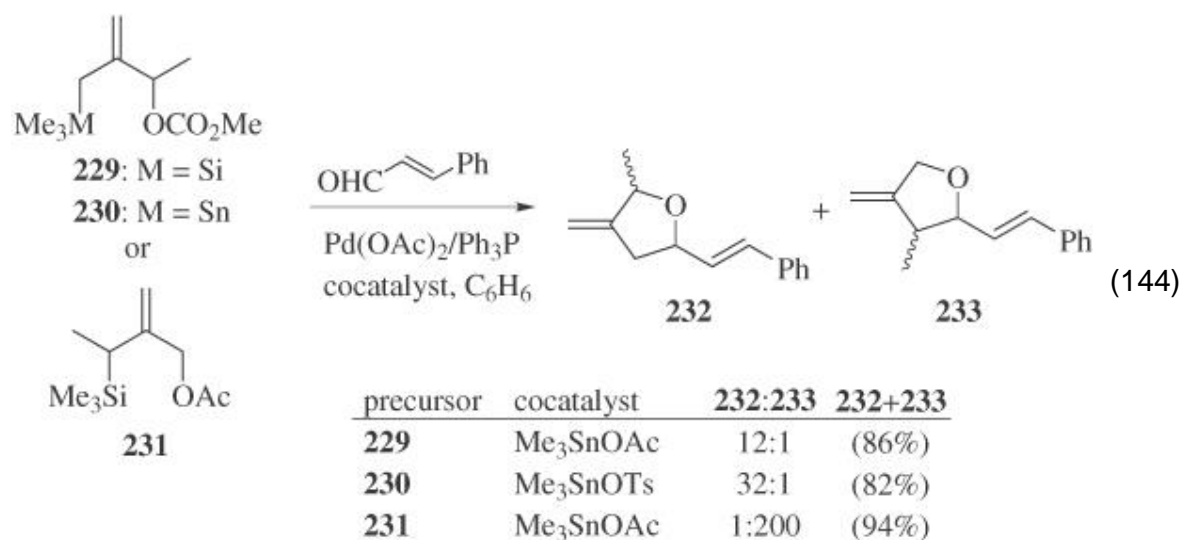


4.3.4.3. Regioselectivity

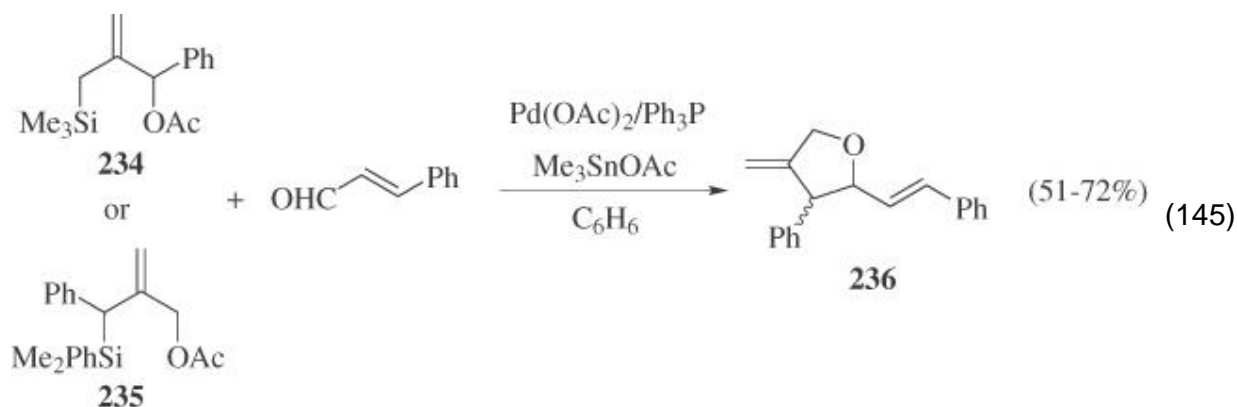
Alkyl-, phenyl-, vinyl-, and acetoxy-substituted TMM-Pd complexes also react with aldehydes in the presence of organotin cocatalysts. In contrast to the cycloaddition of the substituted TMM-Pd complexes with electron-deficient alkenes, the regioselectivity of the hetero [3 + 2] cycloaddition varies depending on the structure of the TMM precursor as well as the reaction conditions.

Reaction of the methyl-substituted TMM, generated from precursor **229** in benzene with palladium acetate/ Ph_3P as the catalyst and Me_3SnOAc as the cocatalyst, with cinnamaldehyde gives a mixture of products **232** and **233** (Eq. 144). (161) The product ratio depends on the concentration of precursor **229**; higher concentration gives a higher **232:233** ratio (1.7:1 at 0.05 M and 8.1:1 at 0.30 M in 91–95% yield). In the presence of Bu_3SnOAc as the cocatalyst, the **232:233** ratio decreases to 1.6:1. On the other hand, the tin reagent **230** reacts well when Me_3SnOTf is used as the cocatalyst yielding a 32:1 mixture of isomers **232** and **233**. Reaction of the isomeric precursor **231** in the presence

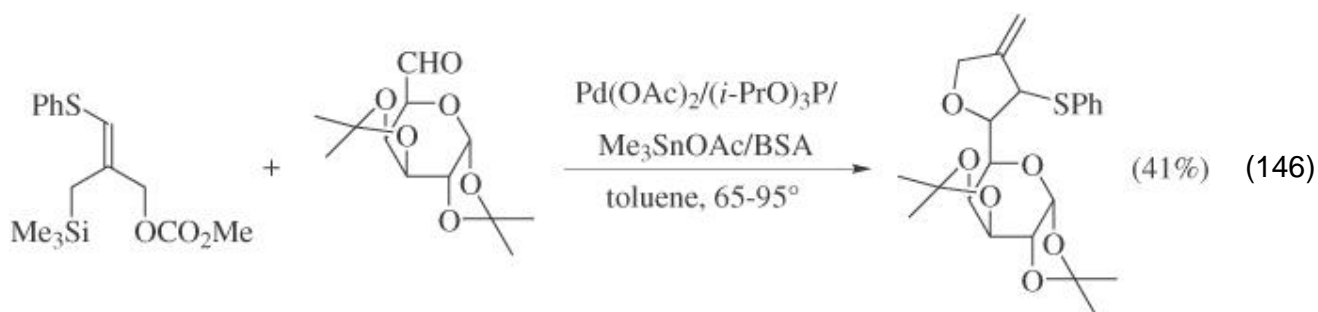
of Me_3SnOAc cocatalyst gives a 1:200 mixture favoring the opposite regioisomer **233**.



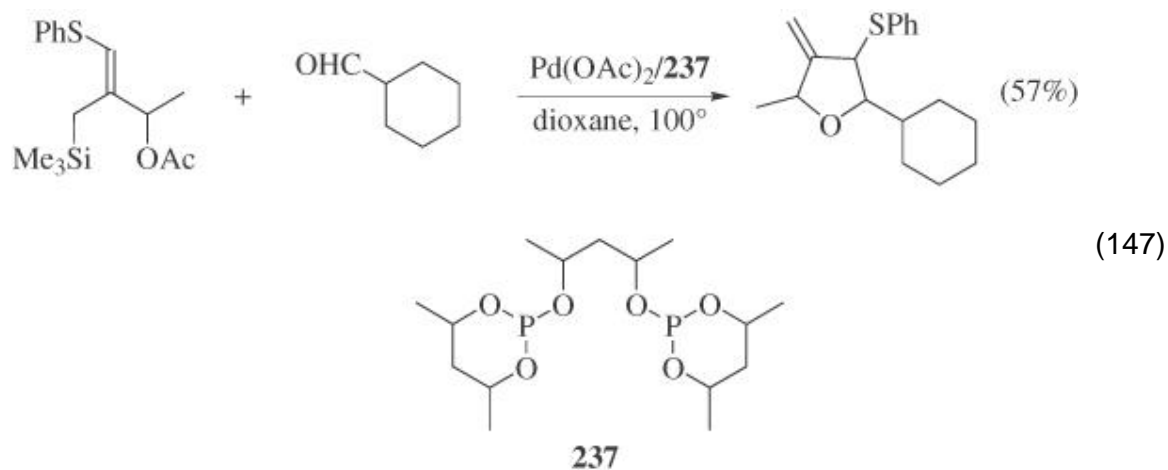
Installation of conjugating groups on the TMM decreases the reactivity of the TMM–Pd complex. Thus, the cycloaddition of phenyl-substituted TMM–complexes generated from either precursors **234** or **235** with cinnamaldehyde selectively gives isomers **236**, which are derived from the thermodynamically more stable TMM complex, regardless of the structure of the precursors (Eq. 145). (161) Electron-withdrawing substituents, such as cyano and carbonyl, as the TMM substituents cause the TMM–Pd complex to be unreactive.



Among various substituents on the TMM–Pd complexes, the phenylthio group serves as an effective regioselectivity control element. In the cycloaddition of mono- and disubstituted TMM–Pd complexes, initial bond formation occurs between the electrophilic terminus of the acceptor and the sulfide-bearing carbon of the TMM intermediate. The subsequent ring closure takes place at the less electron-rich allyl terminus of the intermediate π -allylpalladium complex (Eq. 146). (162)

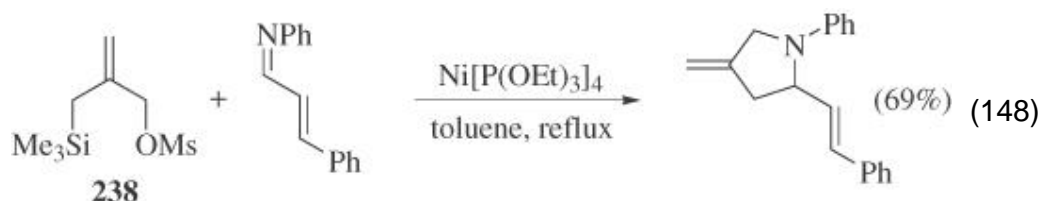


The regioselectivity of the cycloaddition is especially high when 2,4-bis[(4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yl)oxy]pentane (**237**) is used as a ligand. For example, cycloaddition with disubstituted TMM–Pd complexes requires the bidentate phosphite **237**, and affords a single regioisomer (Eq. 147). (162)

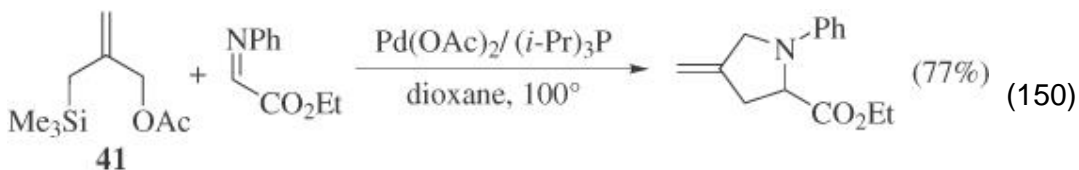
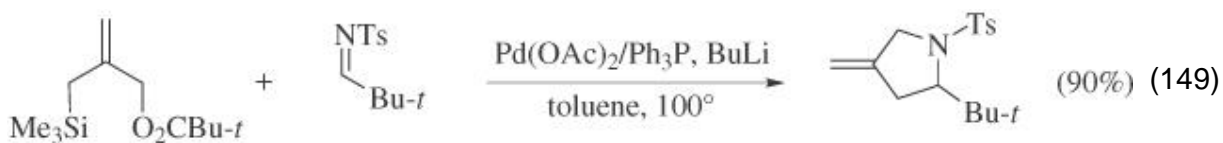


4.3.5. Cycloaddition to C = N Double Bonds

Aryl- and alkyl-substituted imines react with the mesylate precursor **238** in the presence of a Ni(0) catalyst to give 4-methylenepyrrolidines. In the reaction with simple imines, Ni catalysts usually give better results than Pd catalysts. Various imines derived from aromatic, conjugated, and aliphatic aldehydes and ketones participate in the cycloaddition in good to excellent yields. In the reaction with cinnamaldehyde *N*-phenylimine, TMM addition takes place highly chemoselectively and occurs exclusively at the imine moiety (Eq. 148). (88)

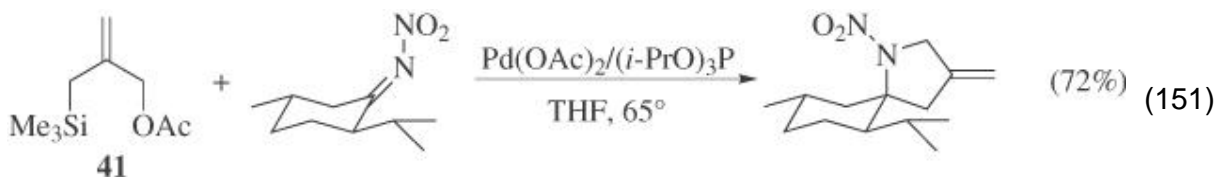


Imines possessing an electron-withdrawing group either on the sp² nitrogen or on the sp² carbon show enhanced reactivity. (163) For example, tosylimines derived from aromatic and aliphatic aldehydes are excellent acceptors and react smoothly with TMM–Pd complexes to give the corresponding methylenepyrrolidines in good to excellent yields (Eq. 149). The *N*-phenylimine of ethyl glyoxylate also reacts with precursor **41** in the presence of a Pd(0) catalyst (Eq. 150).

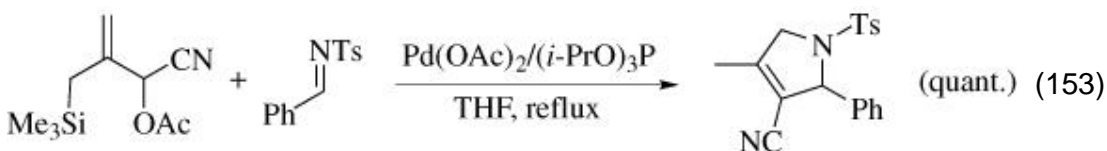
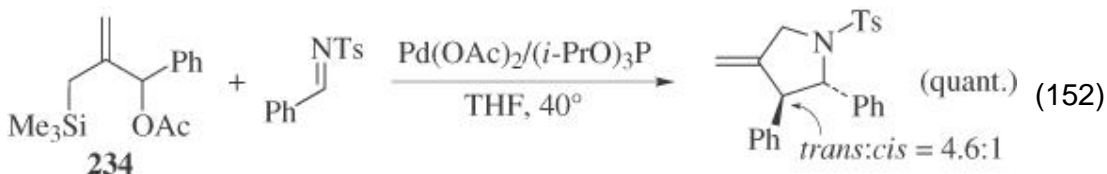


Because of the stronger electron-withdrawing nature of the nitro group, nitrimines derived from relatively hindered ketones participate in the

cycloaddition. The menthone-derived nitrimine affords the cycloadduct with a 17:1 diastereoselectivity (Eq. 151). (163) These hindered acceptors give good yields of cycloadducts, but the unhindered nitrimines bearing an α -hydrogen atom fail to give cycloadducts because of the ease of enolization.

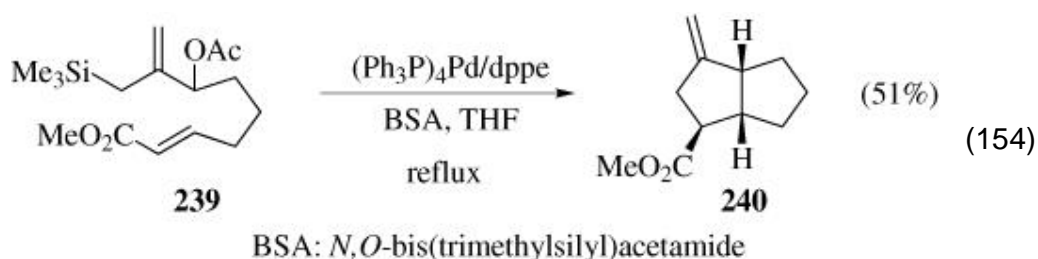


Cycloaddition with both the phenyl- and cyano-substituted TMM units to benzaldehyde *N*-tosylimine proceeds in high yield with excellent regioselectivity. (163) In the former example, the cycloadduct is formed as a 4.6:1 mixture of diastereomers (Eq. 152). In the latter example, the initial cycloadduct is not observed and isomerization of the initial product to the thermodynamically more stable endocyclic conjugated isomer takes place under the reaction conditions (Eq. 153).

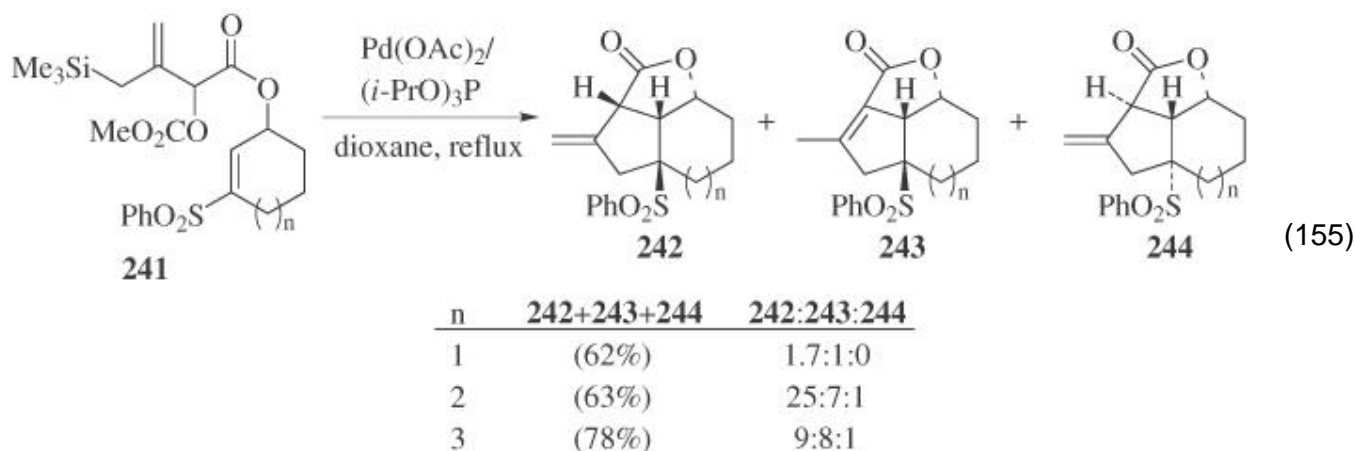


4.3.6. Intramolecular Applications

Intramolecular versions of the reaction provide a valuable synthetic route to bicyclo[3.n.0]alkane ring systems. When TMM precursor **239** tethered to an α , β -unsaturated ester is treated with a Pd(0) catalyst, the cycloaddition occurs selectively via the exo mode to form the cis bicyclo[3.3.0]octane **240** as the sole product (Eq. 154). (164, 165) No product derived from endo cycloaddition to form the seven-membered ring is observed.

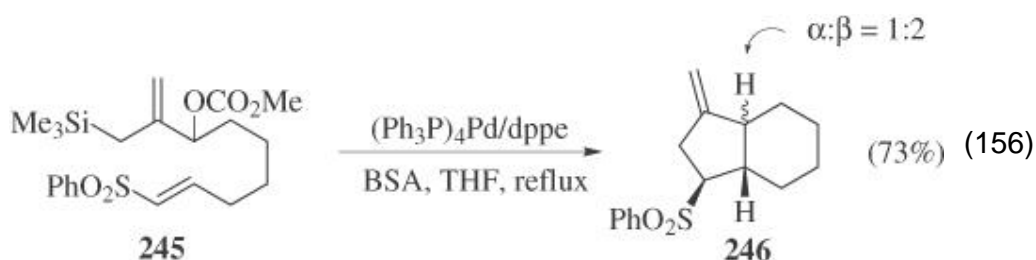


An ester group can serve as a cleavable tether. For example, cycloaddition of the cyclic α , β -unsaturated sulfone **241** followed by hydrolysis of the ester affords the bicyclo[3.4.0]-, [3.5.0]-, and [3.6.0] skeletons with high efficiency. The cycloaddition mainly affords the *cis*-ring-fused products **242**, but small amounts of the isomerized products **243** and *trans*-fused product **244** are formed (Eq. 155). (166) Because the intermolecular cycloaddition to medium ring alkenes often fails, this reaction sequence serves as a convenient alternative for the synthesis of variety of bicyclic carbocycles.

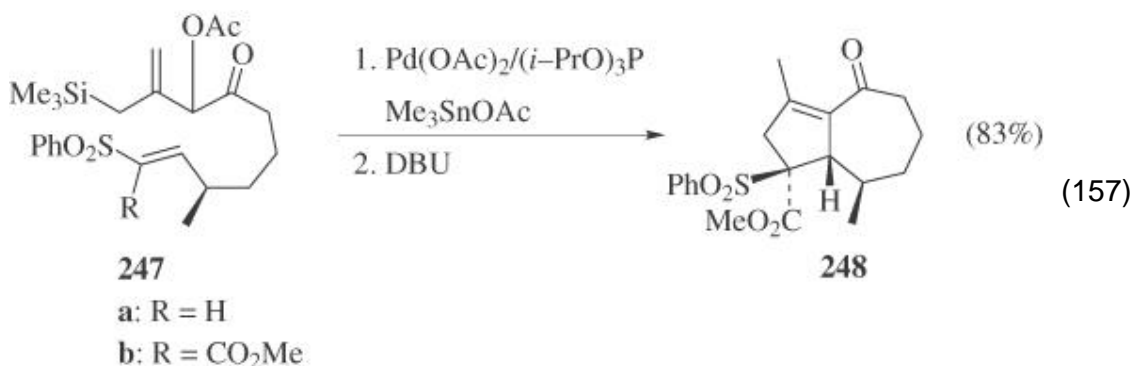


4.3.6.1. Effects of Tether Length

Cycloadditions also proceed with substrates bearing four- and five-carbon tethers, yielding bicyclo[4.3.0]nonane and bicyclo[5.3.0]decane ring systems. The formation of bicyclo[4.3.0]nonanes is less selective with respect to the ring junction, and the reaction of four carbon tethered compound **245** affords a 2:1 mixture of β - and α -adducts **246** (Eq. 156). (165) The configuration of the *trans*-vinylsulfone is retained in the product, but not in the corresponding reaction of the *cis*-vinylsulfone, since the reaction occurs in a stepwise fashion.



The formation of seven-membered rings is less efficient than that of five- and six-membered rings, and the five carbon tethered vinylsulfone **247a** does not give any cycloadduct. In such a case, the use of a highly electron-deficient alkene is effective and the reaction of doubly activated substrate **247b** proceeds smoothly to give adduct **248** as the sole product after isomerization of the exomethylene double bond (Eq. 157). (167)



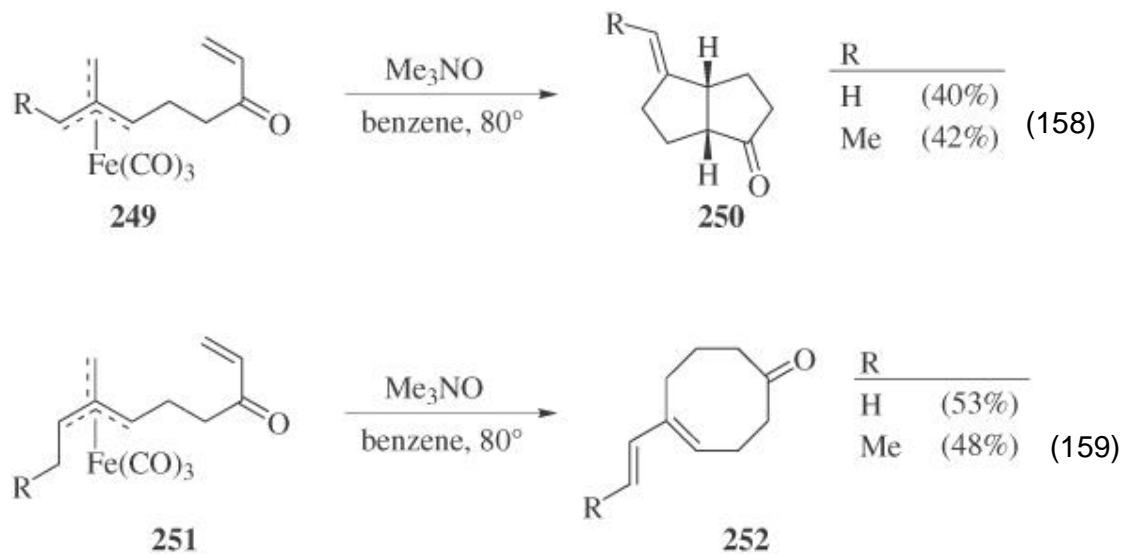
4.3.6.2. Effects of Substituents

Incorporation of an acyl substituent α to the silyl group on the TMM, like the TMM generated from **247**, considerably improves the efficiency of cycloaddition by minimizing the protodesilylation reaction, which is a serious side reaction when the TMM is not acyl-substituted. Intramolecular reaction of a substituted TMM-Pd species permits the synthesis of bicyclo[n.3.0]alkane ($n = 3-5$) ring systems. (168)

4.4. Cycloaddition of Stable TMM-Metal Complexes

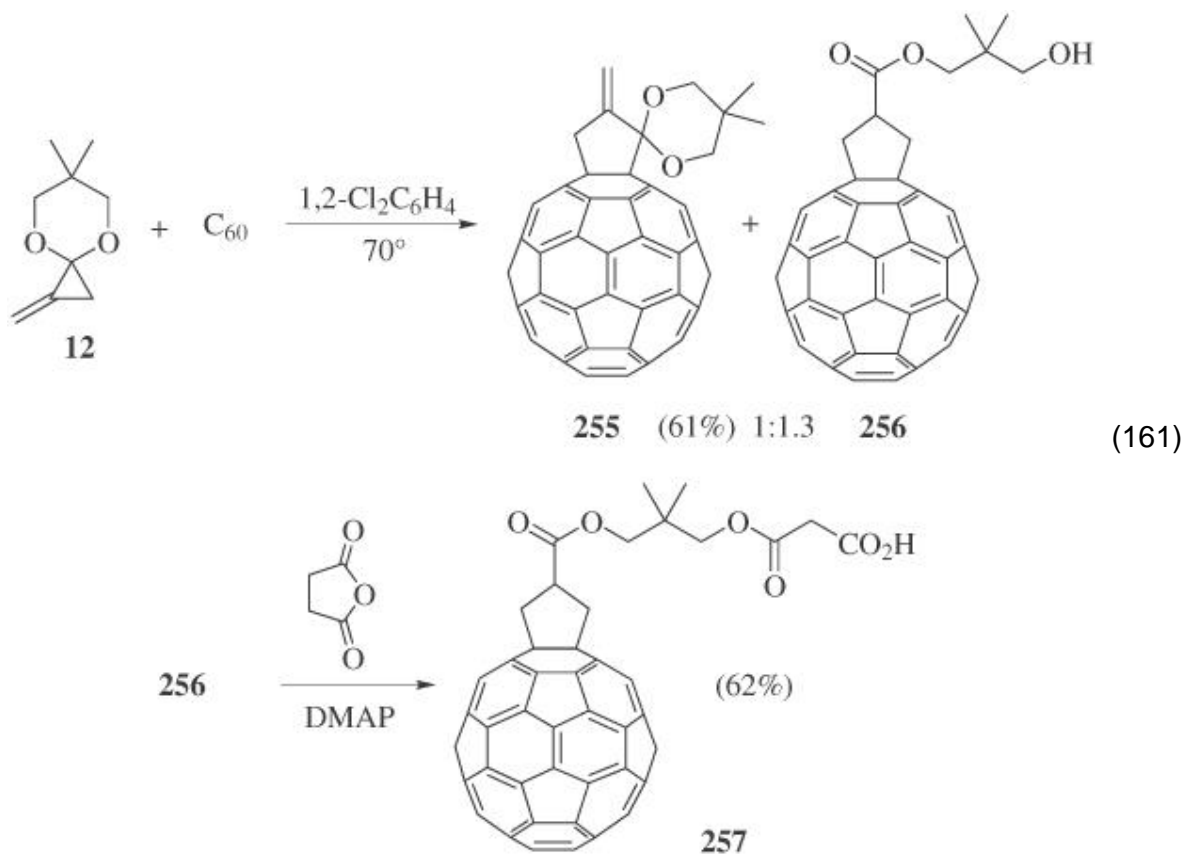
Although the intermolecular cycloadditions of stable η^4 -TMM-Fe(CO)₃ complexes with alkenes are generally not synthetically useful, the intramolecular reactions can be useful with proper choice of substrates. Thus,

the oxidative decomplexation of *E*-substituted TMM-Fe complexes **249** bearing an enone moiety takes place smoothly, and leads solely to the bicyclic methylenediquinane ketones **250** (Eq. 158), whereas the *Z*-substituted TMM complexes **251** are converted exclusively to 5-vinylcyclooctenones **252** (Eq. 159). (169).

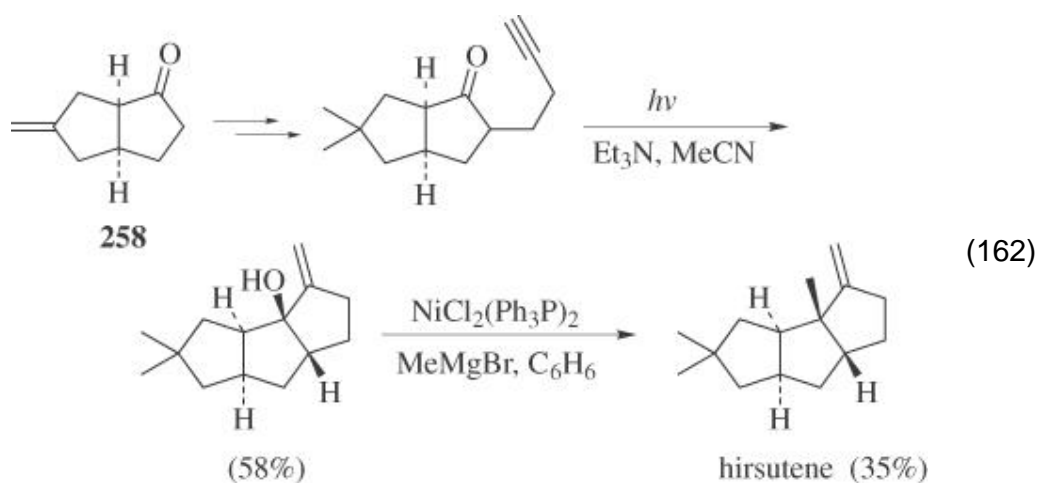




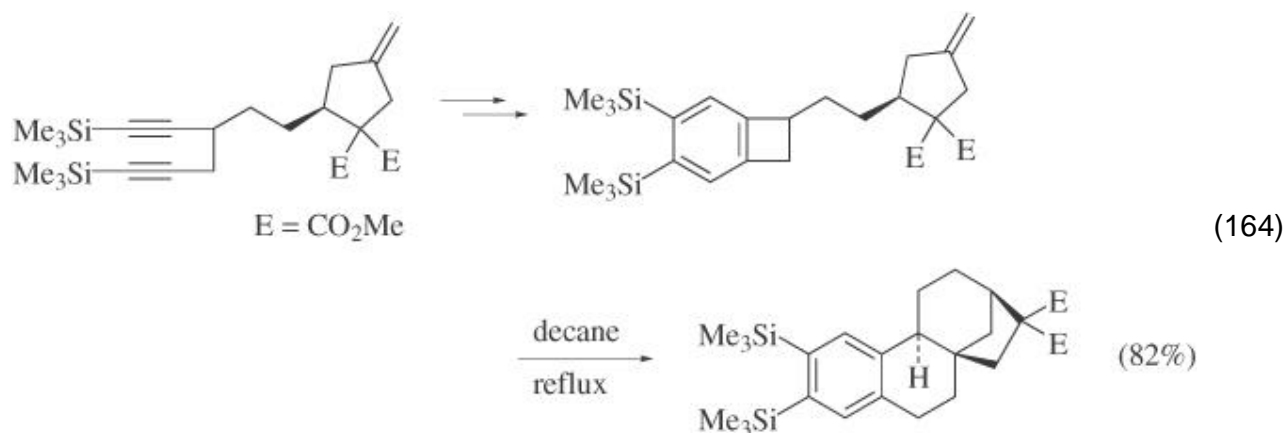
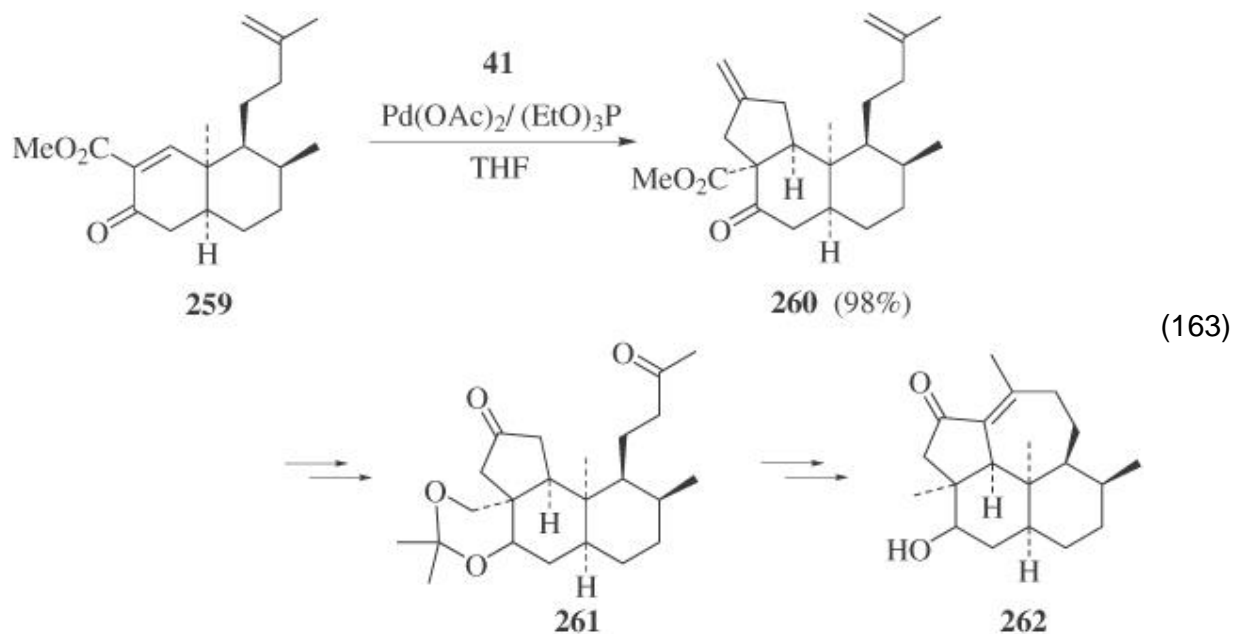
The TMM cycloaddition is useful for the synthesis of not only naturally occurring biologically active compounds, but also unnatural bioactive compounds. For example, the thermal cycloaddition of TMM and buckminsterfullerene (C_{60}) gives isomeric cycloadducts **255** and **256** (Eq. 161). (173) Further functionalization of the hydroxyl group of isomer **256** allows the synthesis of the water-soluble derivative **257**, which shows distinct photo-induced biological activities including cytotoxicity, DNA cleavage, and inhibition of enzymes. (174-177) The use of a ^{14}C -labeled TMM allowed the synthesis of the first radio-labeled water-soluble fullerene derivative and revealed the first pharmacokinetic behavior of an organofullerene. (178)



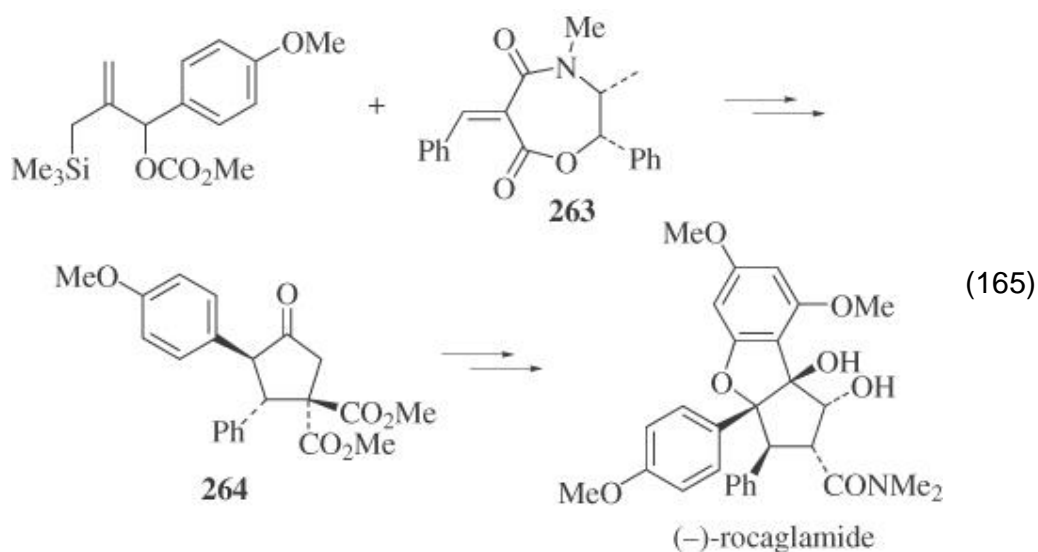
The diversity of functional groups on the cycloadducts of TMM species is useful for further elaboration to complex structures. For example, the exomethylene moiety of the TMM-cyclopentenone adduct **258** serves as a precursor of a gem-dimethyl group, and the ketone moiety derived from cyclopentenone serves as a directing group for the subsequent construction of an additional methylenecyclopentane ring (Eq. 162). (179) The Pd-catalyzed cycloaddition of TMM to activated bicyclooctane **259**



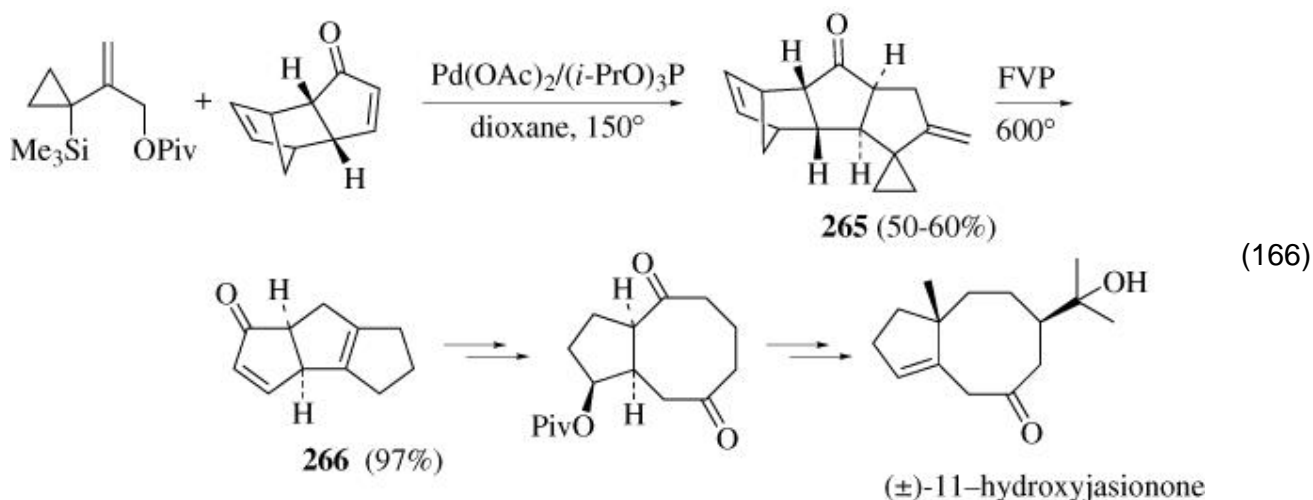
sets two stereogenic centers with complete selectivity to give product **260**, and the subsequent intermolecular aldol condensation of the diketone **261** provides a straightforward construction of hydroxykempenone skeleton **262** with high efficiency (Eq. 163). (180) The exomethylene group of the cycloadduct is also used as the dienophile in the Diels-Alder reaction. A sequence of [3 + 2] cycloaddition, cobalt mediated [2 + 2 + 2] cycloaddition, and [4 + 2] cycloaddition provides stereoselective and straightforward access to the phyllocladane skeleton in eight, high-yielding steps starting from 1,5-hexadiyne (Eq. 164). (181)



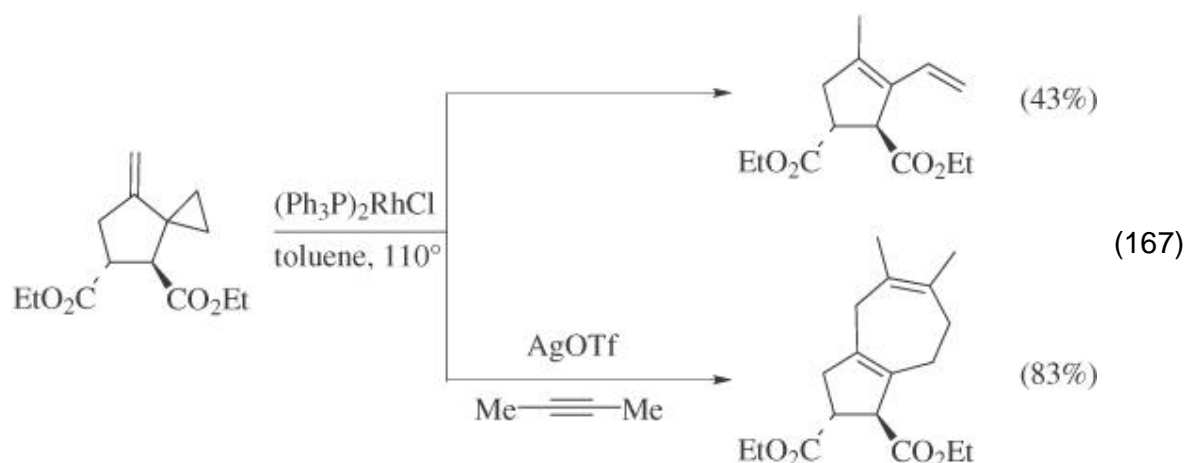
The enantiomerically enriched cyclopentanone **264** is formed by the stereoselective Pd-catalyzed [3 + 2] cycloaddition of the 4-methoxyphenyl-substituted TMM with enantiomerically enriched substrate **263** followed by hydrolysis, esterification, and ozonolysis. Carbon-carbon bond formation with the carbonyl moiety of intermediate **264** and subsequent cyclization provides a synthetic route to (–)-rocaglamide (Eq. 165). (182)



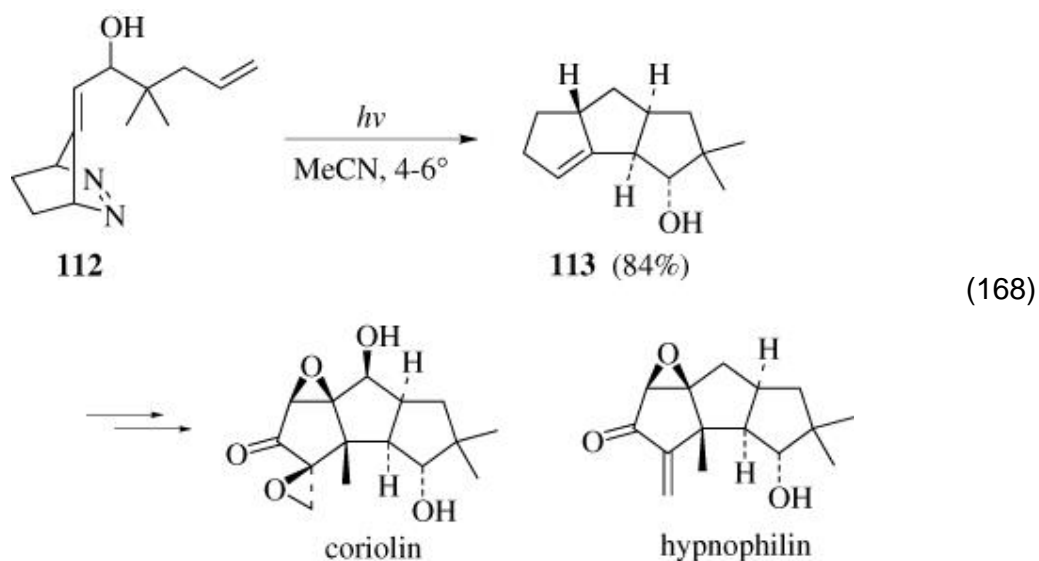
Cyclopropyl-substituted methylenecyclopentanes are formed by the cycloaddition of cyclopropyl-substituted TMM derivatives. The vinylcyclopropane moiety in the cycloadduct rearranges to the cyclopentene upon thermolysis. For example, cycloadduct **265** undergoes vinylcyclopropane rearrangement and retro Diels–Alder reaction to form product **266** by flash vacuum pyrolysis (FVP). Functionalization of the enone moiety and subsequent oxidative cleavage of the internal double bond provides a synthetic route to 11-hydroxyjasione (Eq. 166). (183) In addition to

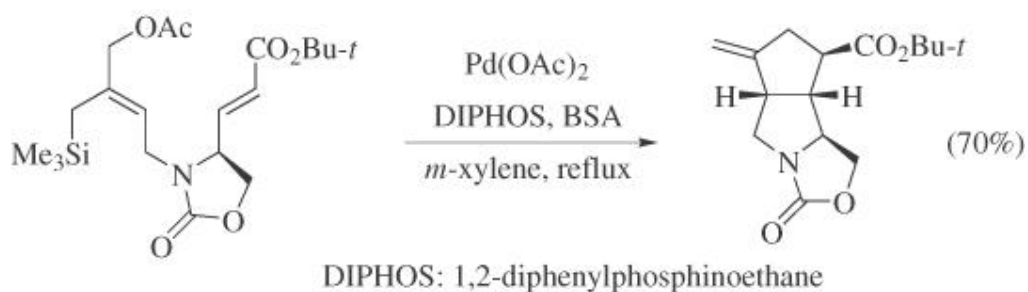


thermal rearrangements, transformation of vinylcyclopropanes to substituted dienes followed by coupling with an alkyne in the presence of a Rh catalyst has also been reported (Eq. 167). (126)

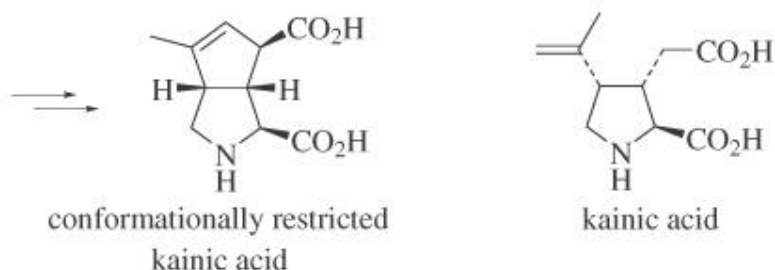


Intramolecular cycloaddition also provides a single-step construction of a variety of fused and bridged ring systems. The cycloaddition of the cyclic TMM derived from diazene **112** gives linearly fused triquinane **113**, which is easily converted into coriolin and hypnophilin (Eq. 168). (99) Pd-catalyzed intramolecular reaction is also useful for the synthesis of conformationally restricted kainic acid derivatives (Eq. 169). (184)





(169)

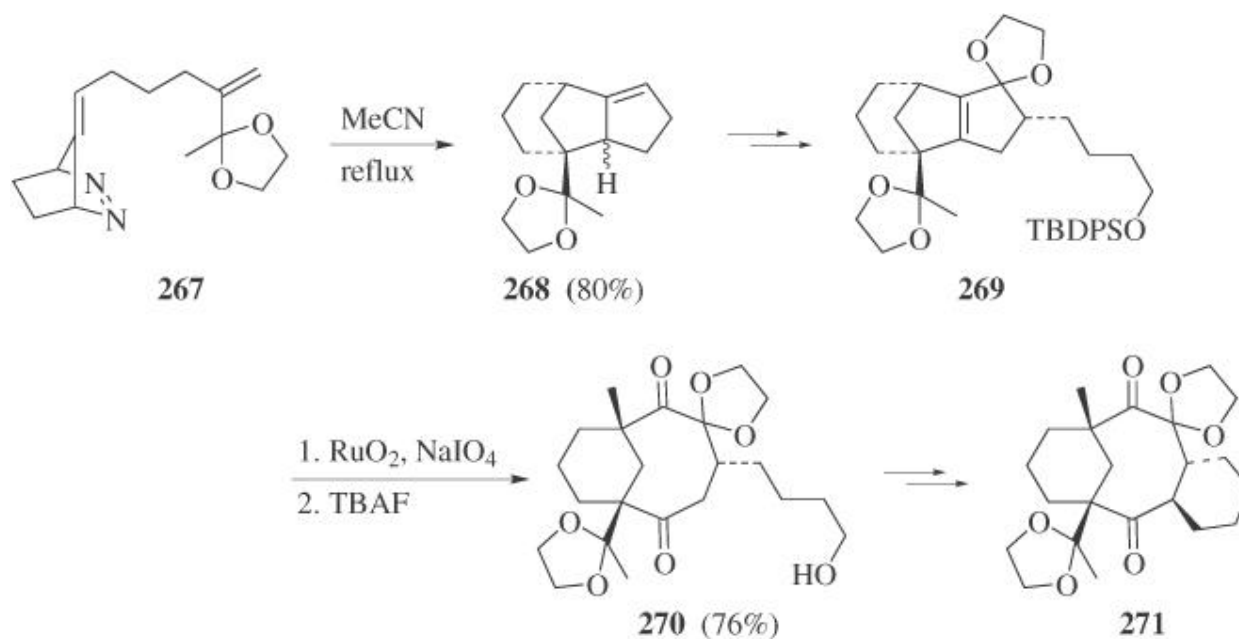


Cycloaddition/oxidative ring enlargement is a useful method for the synthesis of medium-sized ring compounds. For example, tricyclic compound **271** is prepared starting from diazene **267** followed by several chemical transformations on the [3 + 2] cycloadduct **268**. Oxidative cleavage of the double bond of product **269** provides the cyclooctane **270**, which is a precursor of the taxol skeleton **271** (Eq. 170). (185)

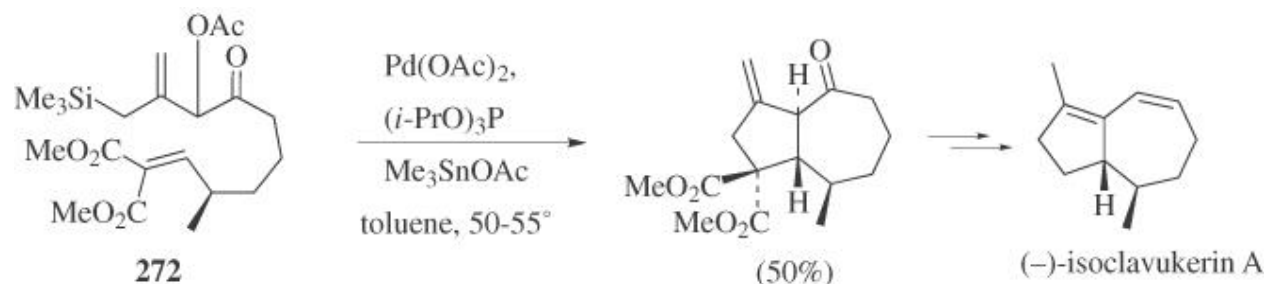
Direct formation of medium-sized rings is also possible. The intramolecular cycloaddition of substrate **272** gives a seven-membered product which is converted into (–)-isoclavukerin A (Eq. 171). (167)

6. Comparison with Other Methods

While 1,3-dipolar cycloaddition is a well-known [3 + 2] cycloaddition for the synthesis of heterocycles, there are few reported methods for single-step construction of five-membered carbocycles besides TMM cycloadditions. (186, 187) This section covers the single-step or the one-pot construction of five-membered rings by cycloaddition or annulation. Sequential multi-step cycloaddition reactions are not covered, as they have already been reviewed. (188, 189)

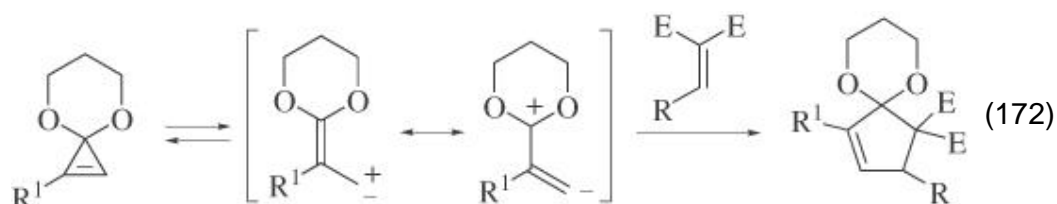


(170)

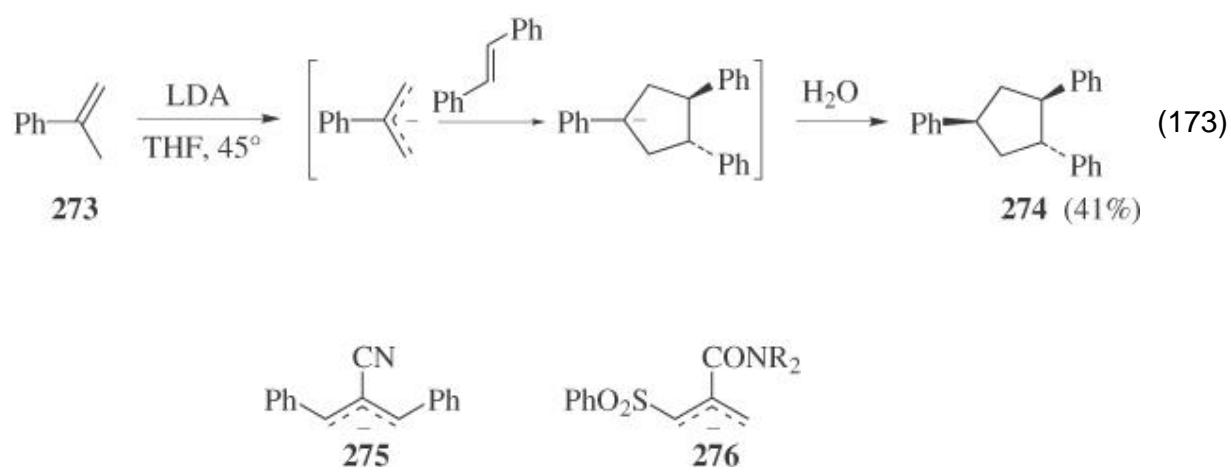


(171)

Vinylcarbene possesses four π electrons on its 1,3-dipole skeleton, and a dipolar vinylcarbene thermally generated from cyclopropenone acetal reacts with highly electron-deficient olefins to give cyclopentenone acetal derivatives (Eq. 172). (190-192) Recent advances in the synthesis of various substituted derivatives of cyclopropenone acetal (R^1 H) greatly expand the utility of this method. (193-197)

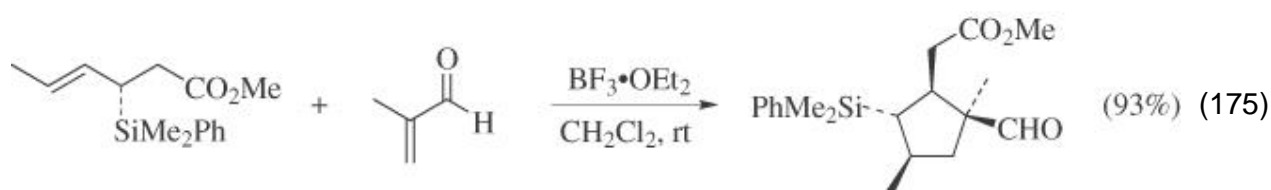
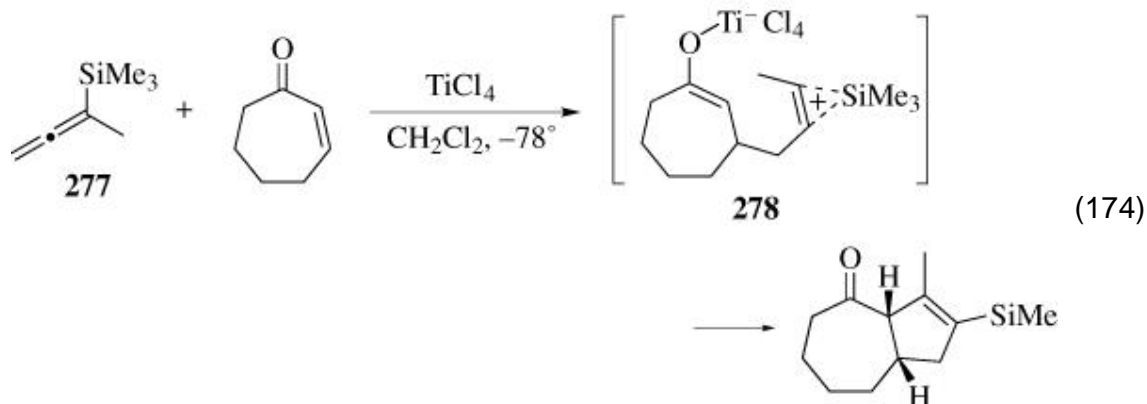


The allyl anion also possesses a 4 π -electron system that is potentially suitable for the concerted [3 + 2] cycloaddition reaction to form a cyclopentane anion. The allylic lithium reagent generated by deprotonation of α -methylstyrene (273) undergoes stereospecific cyclization with *trans*-stilbene to give product 274 after protonation (Eq. 173). (198) Allylic lithium reagents possessing anion-stabilizing groups, such as cyano (275) (199, 200) and SO_2R (276), (201) also react with olefins to give cyclopentane derivatives. A stepwise mechanism has been proposed for the annulation of anion 276 with alkenes.

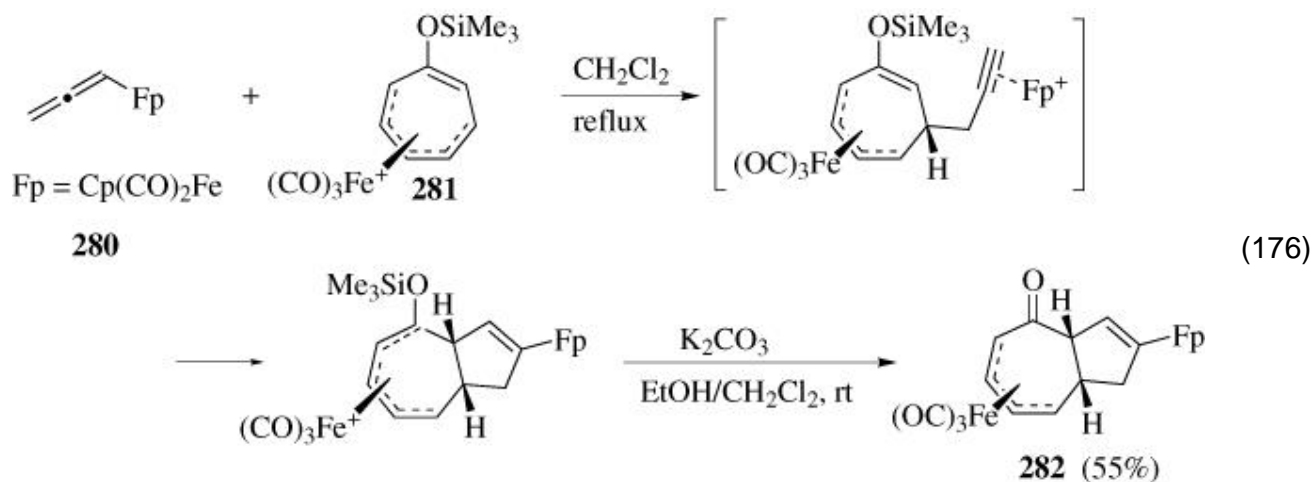


Several σ -allyl- and σ -allenylmetal compounds have been employed for the cyclopentane annulation reactions. For example, allenic silane 277 reacts with

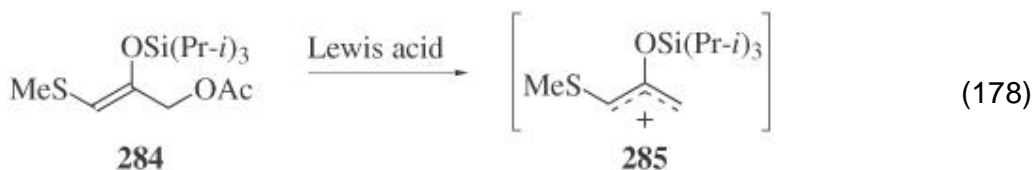
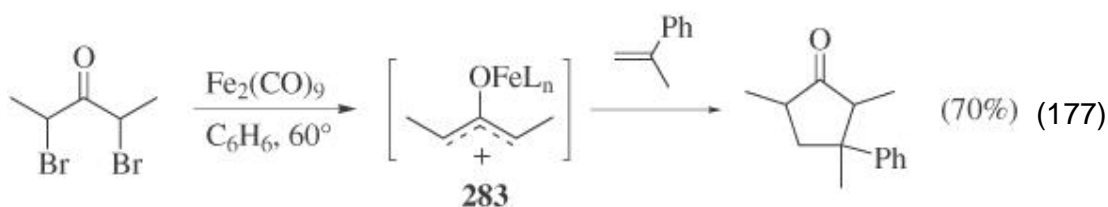
an electron-deficient olefin in the presence of a Lewis acid to form substituted cyclopentene **279** (Eq. 174). (202, 203) 1,2-Cationic shift of the trimethylsilyl group as represented in intermediate **278** gives a [3 + 2] annulation product. Allylic and propargyl silanes and allylic stannanes also undergo similar types of [3 + 2] annulations which involve 1,2-cationic silyl and stannyl migration. (204-208) Enantiomerically enriched cyclopentane products are formed when enantiomerically enriched allylic silanes are employed (Eq. 175). (209)

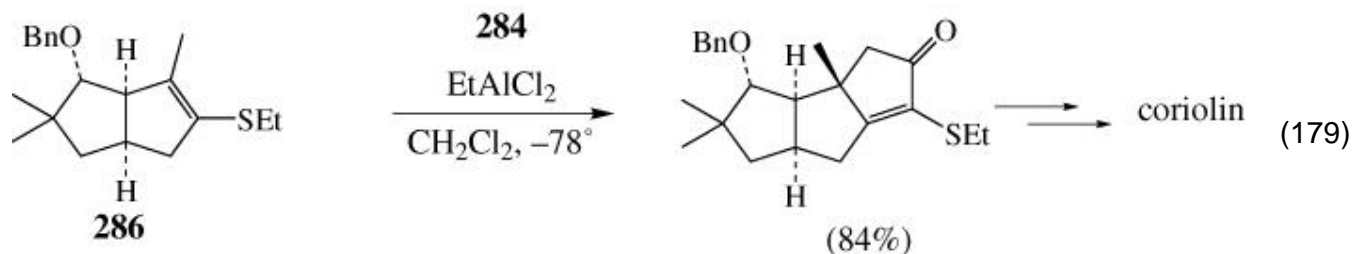


Several σ -allyl-, σ -propargyl-, and σ -allenyl transition metal species, derived from Fe, W, and Cr, also react with highly electron-deficient olefins. (210-212) This type of reaction also involves a 1,2-cationic shift of the metal group. The annulation of allenyliron complex **280** has been applied to the synthesis of azulene **282** by using tropylium iron complex **281** as an acceptor (Eq. 176). (213)

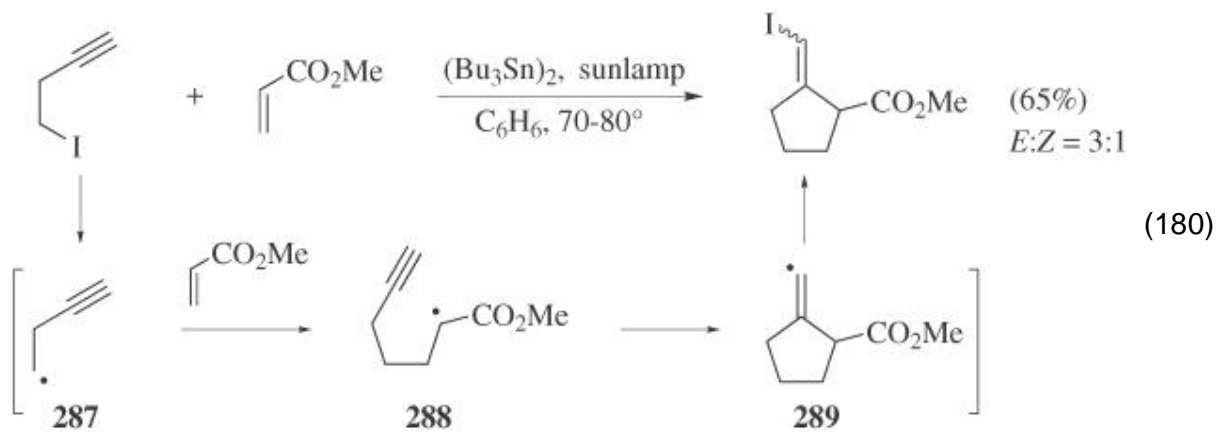


Although allyl cations possess a 2π electronic system that is electronically unsuitable for $[3 + 2]$ cycloaddition reactions, they undergo stepwise $[3 + 2]$ annulation with proper choice of substituents. For example, oxyallyl cation **283**, which is generated from 1,3-dibromoacetone and $\text{Fe}_2(\text{CO})_9$, reacts with conjugated or electron-rich alkenes to afford cyclopentane derivatives (Eq. 177). (214-216) Organosulfur groups are good reaction-controlling groups, and sulfur-substituted allyl cation **285** generated from precursor **284** reacts with a variety of electron-rich and unactivated alkenes (Eq. 178). (217) The reaction of cation **285** with **286** is the key step in the synthesis of coriolin (Eq. 179). (218)

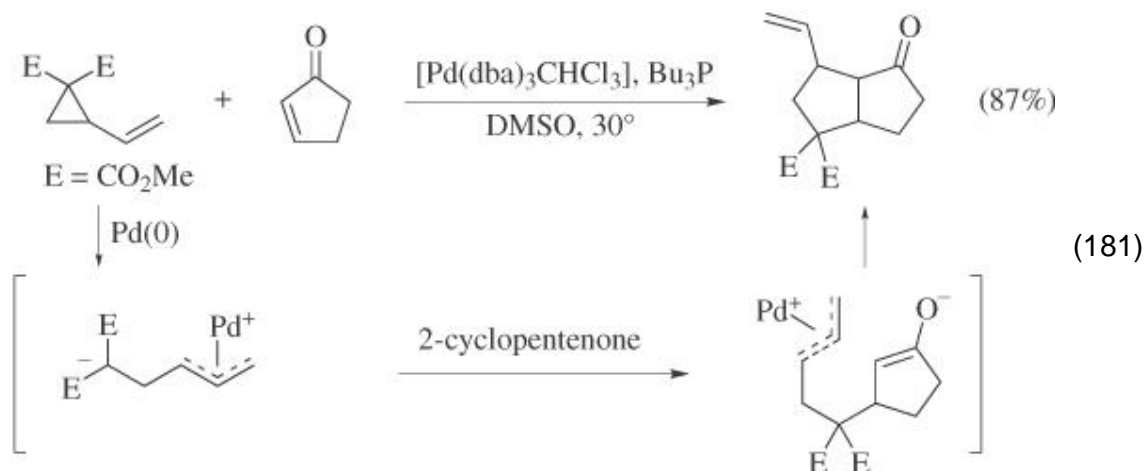




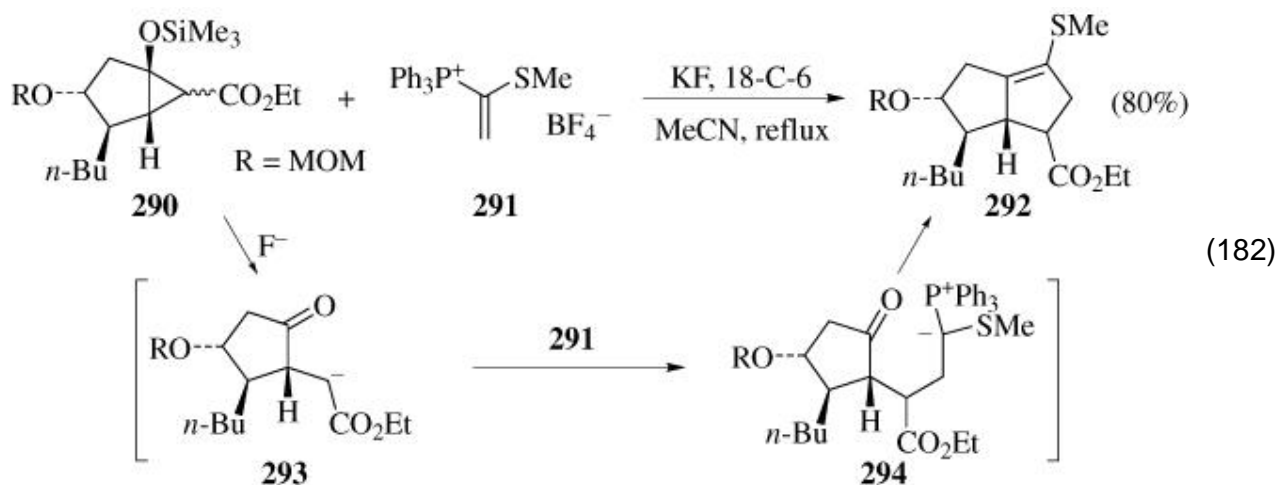
Tandem radical cyclizations of homopropargyl radicals with alkenes also give cyclopentanes (Eq. 180). (219, 220) The reaction involves generation of homopropargyl radical **287** from homopropargyl iodide followed by consecutive C — C bond formation of **287** with methyl acrylate and intramolecular addition of the alkyne moiety of the resulting radical **288** to form the five-membered ring radical **289**.



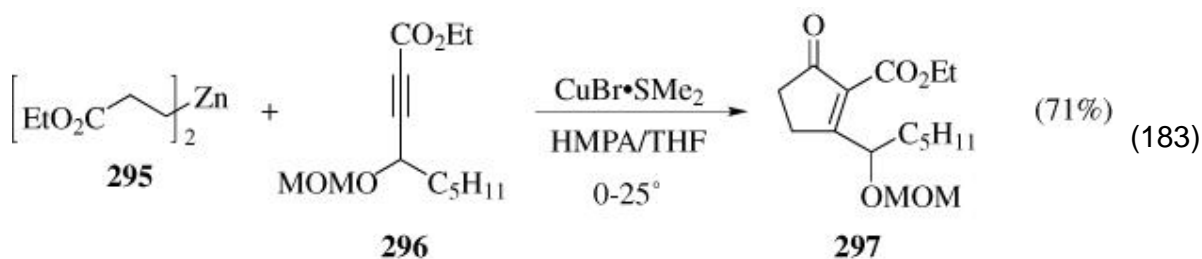
Various cyclopropane derivatives serve as three-carbon units for [3 + 2] annulation. Electron-poor (221) and electron-rich cyclopropanes (222) serve as three-carbon units, but their synthetic utilities are rather limited. Vinylcyclopropanes undergo cyclopropane ring opening and subsequent annulation with alkenes in the presence of a metal catalyst (Eq. 181) (223) or a thiyl radical catalyst. (224, 225) Addition of the catalyst to



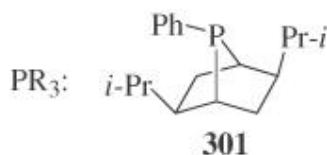
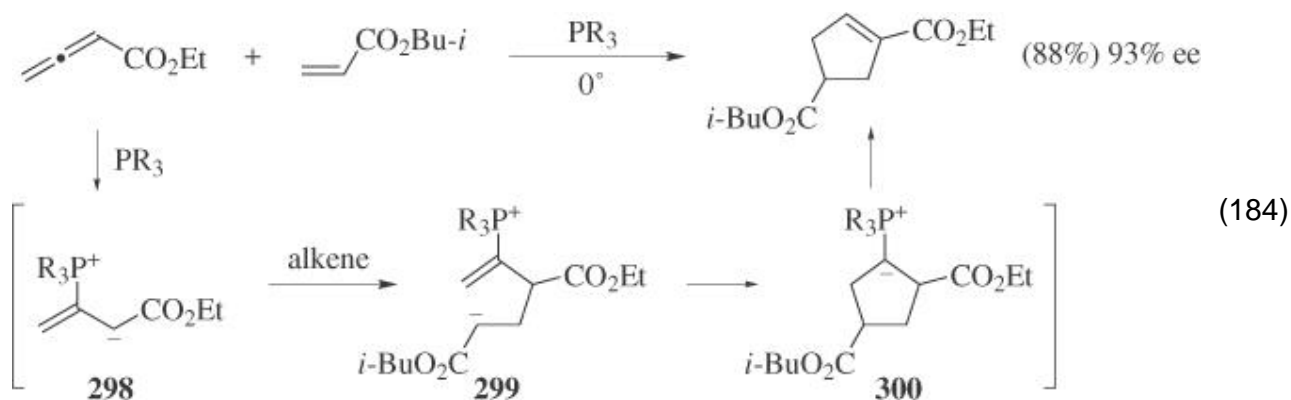
the double bond of the vinylcyclopropane triggers the ring opening. Cyclopropanes bearing electron-donating and accepting groups also react with alkenes in the presence of fluoride ion or Lewis acid. (226, 227) Fluoride ion induced desilylation of siloxycyclopropane ester **290** and concomitant ring opening generate homoenolate system **293**. The successive trapping of **293** with activated alkenes such as vinylphosphonium salt **291**, followed by intramolecular Wittig reaction of the resulting ylide **294**, gives rise to product **292** (Eq. 182). (226)



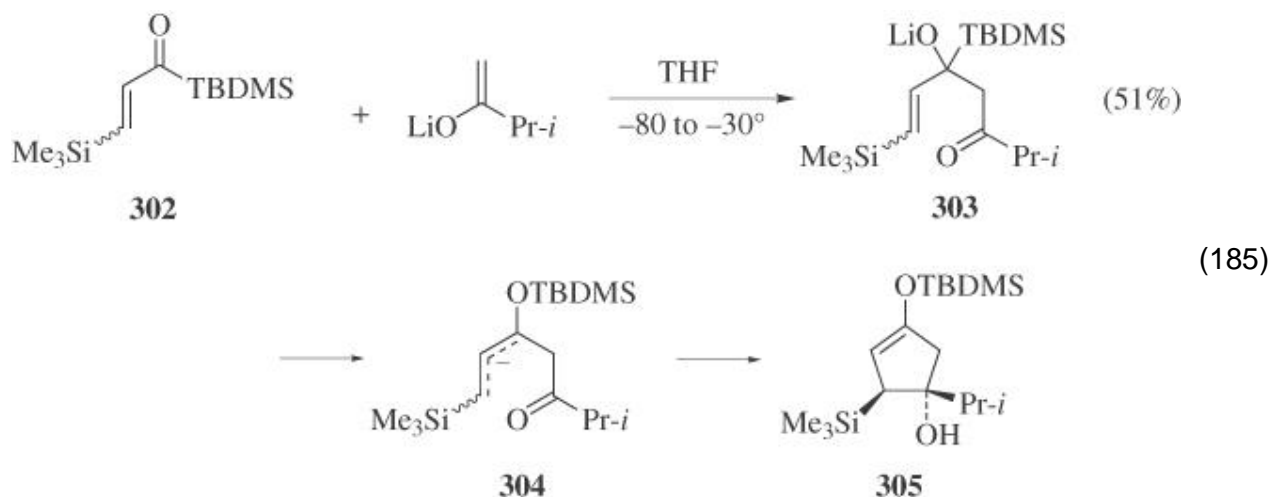
Zinc homoenolates also serve as three-carbon units. For example, the reaction of zinc homoenolate **295** and activated alkyne **296** affords cyclopentene **297** through conjugate addition, intramolecular aldol condensation, and dehydration (Eq. 183). (228, 229)



Allenic esters and electron-deficient alkenes undergo [3 + 2] annulation in the presence of a phosphine catalyst (Eq. 184). (230) The reaction is initiated by addition of phosphine to the allenic ester to give zwitterionic intermediate **298**, which reacts with electron-deficient alkenes to give ylide **300** via zwitterion **299**. Subsequent phosphine elimination gives rise to the product. When enantiomerically enriched phosphine **301** is used as the catalyst, high asymmetric induction is observed. (231)

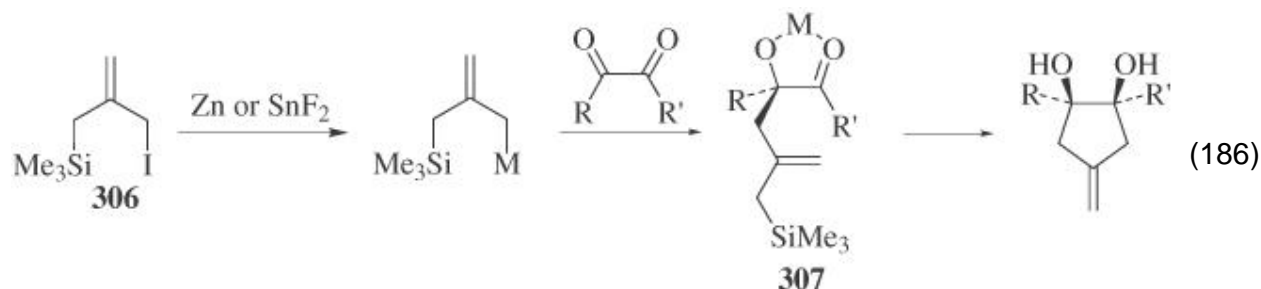


α , β -Unsaturated acylsilanes also serve as three-carbon units in [3 + 2] annulations with ketone enolates (Eq. 185). (232) The reaction involves addition of a ketone enolate



to an acylsilane such as **302** followed by the Brook rearrangement of intermediate **303** to allylic lithium agent **304**. Subsequent intramolecular addition of the latter to the carbonyl group gives rise to the formation of product **305** after hydrolysis.

A functionalized allylic halide serves as a dianion in the presence of a reducing agent. (**233**, **234**) Thus the allylic metal species generated from precursor **306** with zinc or tin(II) fluoride reacts with a 1,2-dione to generate the ketolate intermediate **307**. Its carbonyl group, which is activated by the neighboring metal alkoxide, is then attacked stereoselectively by the allylic silane to give a 4-methylenecyclopentane-1,2-diol derivative (Eq. **186**).



7. Experimental Conditions

The optimal conditions for the cycloaddition are highly dependent on the TMM precursors and 2 π -acceptors. Therefore, only a few general considerations, e.g. solvent, temperature, and catalysts, are given below.

7.1. Free Trimethylenemethane from Diazene

The majority of the intramolecular reactions are carried out in acetonitrile or THF solution at the reflux temperature. The use of degassed solvents is preferable to avoid undesirable side reactions with dioxygen. High dilution or slow addition of the diazene is required to avoid intermolecular side reactions. The reaction can be also carried out at low temperature by photolysis, and these conditions are especially useful for achieving high stereoselectivity. (98, 99)

7.2. Dipolar Trimethylenemethane from methylenecyclopropane

Although the reaction requires essentially no solvent, most of the reactions are carried out in an acetonitrile or propionitrile solution at 60–100°, because generation of the TMM takes place much faster in a polar solvent than in a non-polar solvent. Whereas the reaction does not require rigorous exclusion of moisture or air because of the singlet nature of the dipolar TMM, the use of an anhydrous solvent under an inert atmosphere is generally preferred.

7.3. Transition Metal Catalyzed Reactions of Methylenecyclopropanes

The choice of the metal catalyst and the phosphine ligand is critical for the reaction. Palladium catalysts are used more often than nickel catalysts because the reaction pathways are more predictable. The latter tends to be more reactive than the former. Palladium catalysts usually require a phosphine ligand, and *i*-Pr₃P is most commonly used. The catalysts are usually prepared in situ by mixing Pd(dba)₂ or Pd(allyl)Cp with one equivalent of *i*-Pr₃P. The nickel catalyst prepared from Ni(cod)₂ and (2-PhC₆H₄O)₃P is especially useful for cycloaddition with alkynes. (132) The reactions are routinely carried out in toluene or without solvent.

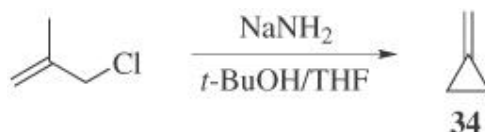
7.4. Transition Metal Catalyzed Reactions of Silylated Allylic Acetates

The most frequently employed catalyst for this reaction is a palladium catalyst generated from Pd(OAc)₂ and (*i*-PrO)₃P. Most of the reactions are carried out in THF or toluene solution at 60–110°, and the solvent choice sometimes affects the results.

Acetate is routinely used as the leaving group, although other ester derivatives, including carbonate, benzoate, and mesylate, can be used as well, and the leaving group sometime affects the course of the reaction.

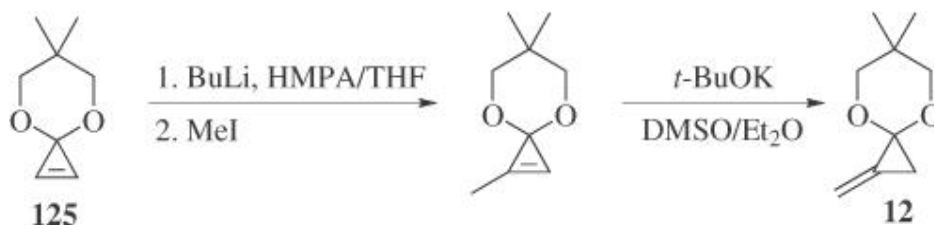
8. Experimental Procedures

8.1. Preparation of TMM precursors



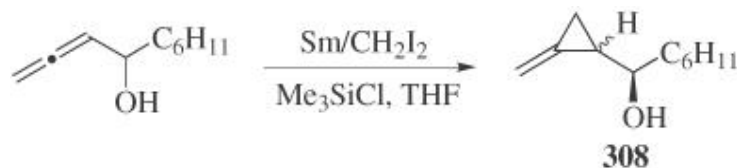
8.1.1. Methylenecyclopropane(34) (114)

A dry, 3-L, three-necked, round-bottomed flask with ground glass fittings was equipped with a sealed stirrer driven by a heavy-duty motor, an efficient condenser fitted with a silica gel drying tube, and a 500-mL, pressure-equalizing dropping funnel connected to a nitrogen inlet. The flask was charged with 450 g (11.50 mol) of sodium amide and 750 mL of anhydrous THF, and the dropping funnel with a solution of 283.5 g (3.83 mol) of anhydrous *tert*-butyl alcohol in 300 mL of anhydrous THF. While the sodium amide suspension was stirred vigorously under a nitrogen atmosphere, the solution of *tert*-butyl alcohol was added dropwise at room temperature over 3 hours. The stirred mixture was heated to 45° in an oil bath for 2 hours. The outlet of the condenser was connected with an adapter to a 250-mL gas-washing bottle containing 100 mL of 5 N sulfuric acid, to trap evolved ammonia. A silica gel drying tube (15-cm long) joined the gas washing bottle to a 300-mL cold trap protected from the atmosphere with a calcium chloride drying tube and cooled in a MeOH/dry ice bath maintained at -80°. A solution of 228 g (2.52 mol) of 3-chloro-2-methyl-1-propene in 500 mL of dry THF was added to the stirred basic mixture, which was then heated to 65° over a period of approximately 8 hours; a light nitrogen stream was used to carry **34** into the cold trap. After the addition was complete, the reaction mixture was stirred and heated to 65° for an additional 3 hours. The trap flask contained 58 g (43%) of methylenecyclopropane. IR (gas) 1789 cm^{-1} ; ^1H NMR (100 MHz, neat, -10°) δ 0.91 (d, $J = 1.8$ Hz, 2 H), 2.12 (d, $J = 1.8$ Hz, 2 H), 6.47 (m, 2 H); MS m/z (%) 54 (M^+ , 77.9), 53 (46.5), 51 (29.1), 39 (100), 28 (38.0), 27 (86.3).



8.1.2. 6,6-Dimethyl-4,8-dioxa-1-methylenespiro[2.5]octane(12) (50)

To a solution of 8.41 g (60.0 mmol) of 6,6-dimethyl-4,8-dioxaspiro[2.5]oct-1-ene (125) and 10.75 g (60.0 mmol) of HMPA in 60 mL of THF was added 36.8 mL (60 mmol) of *n*-BuLi (1.6 M in hexane) at -78° under nitrogen, and the resulting solution was stirred for 30 minutes at this temperature. To this solution was added 9.37 g of CH_3I (66.0 mmol) during 15 minutes. The reaction mixture was gradually warmed to room temperature over 1 hour, and was quenched by addition of saturated aqueous ammonium chloride solution over 5 minutes. The aqueous layer was extracted with Et_2O , and the combined organic extracts were washed with saturated aqueous sodium bicarbonate solution, and brine, dried over sodium sulfate, and concentrated in vacuo to afford an oily product (10.30 g). To a solution of the crude product in 10.3 mL of Et_2O was slowly added a solution of 1.35 g (12.0 mmol) of potassium *tert*-butoxide and 2.80 g (36.0 mmol) of DMSO in 10.0 mL of ether at 0° under nitrogen. After the solution was stirred for 2 hours at room temperature, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride solution. The aqueous phase was extracted with Et_2O , and the combined extracts were washed with saturated aqueous sodium bicarbonate solution, and brine, and dried over sodium sulfate. Concentration in vacuo afforded an oily product (8.90 g). Purification on silica gel (elution with Et_2O :pentane 1:24) followed by distillation under reduced pressure (bp $72\text{--}73^{\circ}/18$ mm Hg) afforded 6.46 g (70% yield) of the title product. IR (neat) 3150(w), 1270, 1255, 1245, 1150, 1140, 1070, 1030, 1015, 970, 905 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 1.04 (s, 3 H), 1.06 (s, 3 H), 1.62 (dd, $J = 3.1, 2.4$ Hz, 2 H), 3.63 (s, 4 H), 5.45 (t, $J = 2.4$ Hz, 1 H), 5.81 (t, $J = 3.1$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 67.5 MHz) δ 18.5 (t), 22.25 (q), 22.3 (q), 30.84 (s), 76.8 (t, two overlapping signals) 84.7 (s), 105.7 (t), 134.6 (s). Anal. Calcd. for $\text{C}_9\text{H}_{14}\text{O}_2$: C, 70.10; H, 9.15. Found: C, 70.02; H, 9.25.



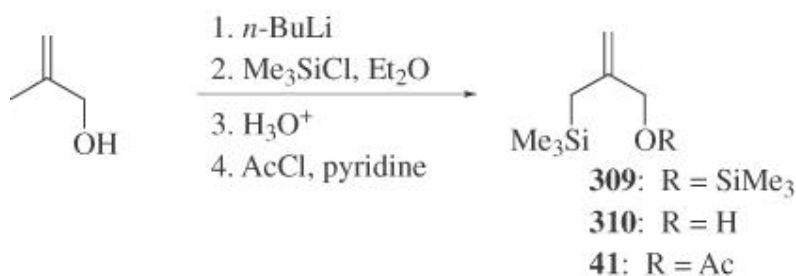
8.1.3. α -(Methylenecyclopropyl)cyclohexanemethanol(308) (116-118)

To a flame-dried round-bottomed flask was added Sm metal (36.0 g, 239 mmol). The flask was flame dried again while being flushed with N_2 . After the flask cooled to room temperature, THF (500 mL) was added, followed by Me_3SiCl (1.50 mL, 11.8 mmol). The suspension was stirred for 30 minutes at room temperature. 1-Cyclohexyl-2,3-butadienol (5.00 g, 29.8 mmol) was dissolved in a small volume of THF and was transferred via cannula to the

flask. The suspension was stirred for 20 minutes at room temperature. The flask was cooled to -78° , and CH_2I_2 (19.0 mL, 236 mmol) was added dropwise. The mixture warmed to room temperature over 3 hours and was stirred overnight. The viscous, dark blue reaction mixture was quenched by addition of a saturated aqueous potassium carbonate solution and was extracted three times with Et_2O . The organic layer was collected, then washed three times with brine, dried over MgSO_4 , filtered, and concentrated in vacuo. The crude mixture was found by GC analysis to be a 1:1.7 mixture of two diastereomers. After flash chromatography, (R^*,S^*)-**308** (1.34 g) and (R^*,R^*)-**308** (2.33 g) were isolated in a combined yield of 67%.

(R^*,S^*)- α -**308**: R_f 0.28 on silica gel (hexane: Et_2O 2:1); IR (neat) 3381 (br s), 3072 (w), 3051 (w), 2924 (s), 2854 (s), 1743 (w), 1448 (s), 1406 (m), 1124 (m), 1089 (m), 1019 (s), 885 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.95 (m, 1 H), 1.30–0.99 (m, 6 H), 1.46 (m, 1 H), 1.50 (d, $J = 3.4$ Hz, 1 H), 1.87–1.58 (m, 6 H), 2.83 (ddd, $J = 8.4, 6.2, 3.4$ Hz, 1 H), 5.37 (m, 1 H), 5.40 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 7.2, 10.8, 26.1, 26.2, 26.5, 28.9, 28.9, 44.0, 78.7, 104.4, 133.3; HRMS Calcd. for $\text{C}_{11}\text{H}_{17}\text{O}$ ($M - \text{H}$) $^+$: 165.1279. Found: 165.1289.

(R^*,R^*)- α -**308**: R_f 0.47 on silica gel (hexane: Et_2O 2:1); IR (neat) 3402 (br s), 3072 (w), 3044 (w), 2924 (s), 2854 (s), 1743 (w), 1448 (s), 1398 (m), 1131 (m), 1103 (m), 1012 (s), 892 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.97 (m, 1 H), 1.30–1.05 (m, 6 H), 1.37 (m, 1 H), 1.48 (m, 1 H), 1.92–1.58 (m, 6 H), 2.94 (ddd, $J = 7.0, 6.2, 5.7$ Hz, 1 H), 5.44 (m, 1 H), 5.50 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 8.2, 19.6, 14.1, 26.3, 26.5, 28.6, 29.0, 44.5, 78.5, 104.2, 133.3.



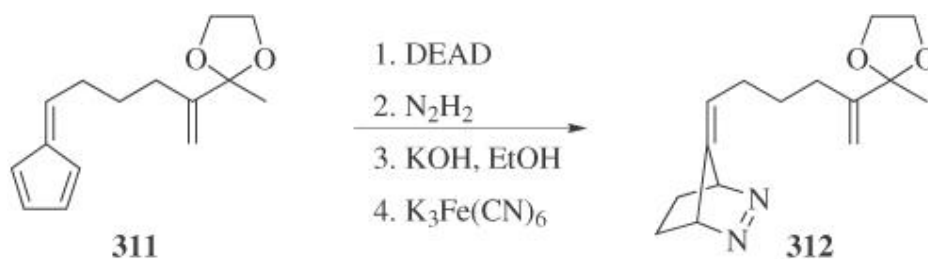
8.1.4. (2-Acetoxyethyl)-3-allyltrimethylsilane(**41**) (**69**)

A three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and septum was charged with $n\text{-BuLi}$ (1.45 M in hexane, 170 mL, 246 mmol). The bulk of hexane was removed in vacuo using a vacuum pump or an aspirator at 15–30 mm Hg. Anhydrous Et_2O (135 mL) and TMEDA (40 mL, 246 mmol) were added at 0° . 2-Methyl-2-propen-1-ol (8.7 g, 121 mmol) was added dropwise over 15 minutes. THF (60 mL) was then introduced, and the mixture turned from cloudy to clear yellowish orange. The reaction mixture was warmed to room temperature over 4–6 hours and then was stirred for 32 hours.

To the dark-red, gummy mixture was added Me_3SiCl (65 mL, 512 mmol) rapidly at 0 to -10° . The reaction mixture was stirred for 10 minutes and then was diluted with 1 g/L of Et_2O . The dark, cloudy mixture was washed with saturated aqueous sodium bicarbonate solution (250 mL), water (250 mL), saturated copper sulfate solution (2×250 mL), water (100 mL), and brine (200 mL), and the extracts were dried over potassium carbonate. The solvent was carefully removed in vacuo, and the orange residue was then distilled through a Vigreux column to give 14.5 g (55%) of 2-[(trimethylsiloxy)methyl]-3-allyltrimethylsilane (**309**) as a colorless oil [bp 67° (5.5 mm Hg)].

To a solution of intermediate **309** (13.5 g, 6 mmol) in 140 mL of THF was added 30 mL of 1 N H_2SO_4 . The mixture was stirred vigorously for ca. 0.5 hour at room temperature. Anhydrous potassium carbonate was added carefully until the bubbling subsided. The mixture was diluted with 500 mL of Et_2O , and the organic phase was washed with saturated aqueous sodium bicarbonate solution (100 mL) and brine (100 mL), and then dried over magnesium sulfate. The solvent was removed in vacuo with care to give 9.3 g (100%) of 2-(hydroxymethyl)-3-allyltrimethylsilane (**310**) as a colorless oil. The crude material was used in the next step without purification.

To a solution of alcohol **310** (7.7 g, 53 mmol) in pyridine (15 mL, 185 mmol) and 60 mL of CH_2Cl_2 at 0° was added acetyl chloride (6.5 mL, 91 mmol) dropwise over 10 minutes. The white, cloudy mixture was stirred for 30 minutes and then was diluted with 500 mL of Et_2O . The mixture was washed with saturated aqueous sodium bicarbonate solution (2×100 mL), saturated copper sulfate solution (3×100 mL), water (100 mL), and brine (100 mL), and the extract was dried (K_2CO_3). The solvent was removed by rotary evaporation and the residue was distilled [bp 95° (7 mm Hg)] to give 9.1 g (92%) of title product **41** as a colorless liquid. IR (neat) 3070, 2945, 2885, 1753, 1643, 1372, 1250, 1044, 840 cm^{-1} ; ^1H NMR (270 MHz) δ 0.05 (s, 9 H), 1.55 (s, 2 H), 2.09 (s, 3 H), 4.44 (br s, 2 H), 4.72 (br s, 1 H), 4.88 (m, 1 H); ^{13}C NMR (25 MHz) δ -1.4, 20.9, 23.6, 67.8, 109.6, 141.7, 170.4; MS m/z (%) M^+ 186 (5), 147 (13), 143 (18), 129 (11), 117 (34), 75 (40), 73 (100). Calcd. for $\text{C}_9\text{H}_{18}\text{O}_2\text{Si}$: 186.1075. Found 186.1075.



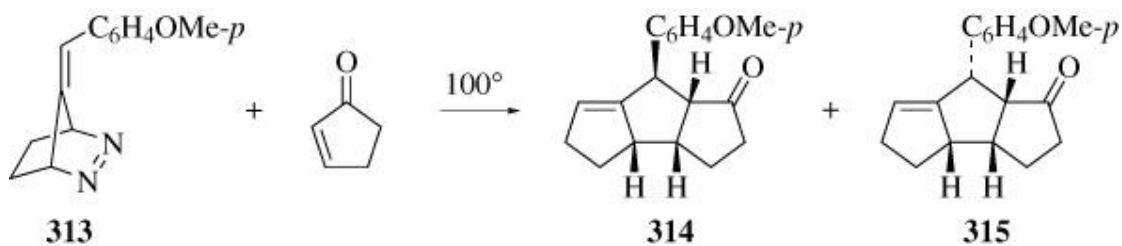
8.1.5. 7-[5[(2-Methyl-1,3-dioxolan-2-yl)hex-5-enylidene]-2,3-diazabicyclo[2.2.1]hept-2-ene(312) (185)

To a solution of

2-[1-(4-cyclopenta-2,4-dienylidenebutyl)vinyl]-2-methyl-1,3-dioxolane (311) (4.90 g, 21.1 mmol) in CH₂Cl₂ (84 mL) was added diethyl azodicarboxylate (3.83 g, 22 mmol) at room temperature. The solution was placed in the refrigerator (4°) for 8 hours. To the solution of crude carbamate was added dipotassium azodicarboxylate (41 g, 211 mmol), and the mixture was stirred with an overhead stirrer. The reaction mixture was cooled to 0°, and glacial acetic acid (18.1 mL, 316 mmol) was added dropwise via an addition funnel over 45 minutes. A vigorous gas evolution took place. After 4 hours, the reaction mixture was filtered through a sintered glass funnel with Et₂O and concentrated in vacuo. The crude reduced carbamate was dissolved in EtOH (192 mL), the solution was degassed with argon for 20 minutes, and potassium hydroxide (21.3 g, 380 mmol) was added. The resulting mixture was heated at reflux for 2.5 hours and then was cooled to 0°. The reflux condenser was removed and replaced with an overhead stirrer. A solution of potassium ferricyanide (21.53 g, 65.41 mmol) in water (172 mL) was added via an addition funnel over 30 minutes. After 2.5 hours, the cloudy brown mixture was poured into a separatory funnel containing water (1 L) and Et₂O (300 mL). The aqueous layer was extracted with Et₂O (7 × 150 mL), and the combined organic layers were dried (MgSO₄) and concentrated in vacuo.

Chromatography on silica gel (Et₂O:pentane 1:1) afforded 5.14 g (19.6 mmol) of the title product (93%). TLC (SiO₂, Et₂O:pentane 1:1, vanillin) *R_f* 0.4; IR (neat/ NaCl) 3092, 2984, 2941, 2888, 1645, 1455, 1039 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.38 (br s, 1 H), 5.26 (d, *J* = 1.0 Hz, 1 H), 5.12 (m, 2 H), 1.70–1.46 (m, 4 H), 1.45 (s, 3 H), 1.10 (d, *J* = 9.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 148.7, 145.0, 117.2, 110.3, 109.4, 76.8, 64.4, 30.1, 28.9, 28.0, 24.4, 21.5, 21.1; HRMS (CI/NH₃) Calcd. for C₁₅H₂₃O₂N₂ [M + H]⁺: 263.1759. Found: 263.1748.

8.2. Cycloaddition Reactions

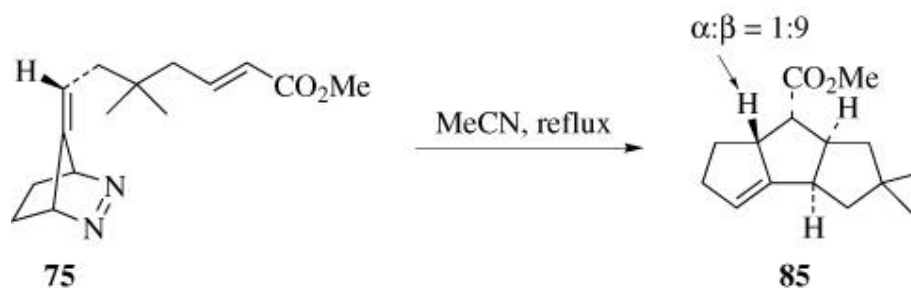


8.2.1. 7-(4-Methoxyphenyl)-2,3,3a,3b,4,5,7,7a-octahydrocyclopenta[a]pentalen-1-one(314 and 315) (84)

In a 100-mL, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and nitrogen inlet tube was placed a solution of 1.0 g (4.67 mmol) of anisyl azo compound **313** dissolved in 33.3 g (406 mmol) of cyclopentenone. The flask was immersed in an oil bath and the reaction mixture was slowly heated to 100° over a period of 1 hour. After an additional 1 hour at 100°, the reaction mixture was cooled to room temperature and the excess enone was recovered by bulb-to-bulb distillation. The resulting oil was dissolved in a minimal amount of CH₂Cl₂ and was purified by medium-pressure liquid chromatography on a 15 × 1000-mm column packed with silica gel. Elution with Et₂O:pentane (1:2.3) afforded 169 mg (13%) of title product **314**, 315 mg (25%) of bridged cycloadduct, 75 mg (6%) of another bridged cycloadduct, and 104 mg (8%) of tricyclopentanoid **315**.

314: mp 91.5–92°; IR (NaCl, film) 1730 cm⁻¹; ¹H NMR (CDCl₃) δ 1.4–2.9 (m, 11 H, aliphatic), 3.65 (br s, 1 H, CHAr), 3.75 (s, 3 H, OCH₃), 4.95 (dd, 1 H, vinyl), 5.15 (dd, 1 H, vinyl), 6.70 (AAϕBBϕ, 2 H, aromatic), 7.15 (AAϕBBϕ, 2 H, aromatic). HRMS Calcd. for C₁₈H₂₀O₂: 268.146. Found 268.148.

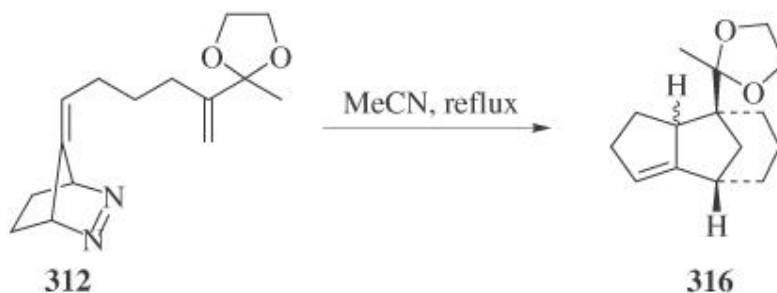
315: mp 81.5–82°; IR (NaCl, film) 1730 cm⁻¹; ¹H NMR (CDCl₃) δ 1.6–2.8 (m, 11 H, aliphatic), 3.20 (m, 1 H), 3.70 (s, 3 H, OCH₃), 3.80 (br s, 1 H, CHAr), 6.80 (AAϕBBϕ, 2 H, aromatic), 6.95 (AAϕBBϕ, 2 H, aromatic). Anal. Calcd. for C₁₈H₂₀O₂: C, 80.56; H, 7.51. Found: C, 80.52; H, 7.42.



8.2.2. (3a α , 6a β , 7 α , 7a α)-2,3,3a,5,6,6a,7,7a-Octahydro-2,2-dimethyl-1H-cyclopenta(a)-pentalene-7-carboxylic acid Methyl Ester(85) (91)

A stirred solution of 300 mg (1.14 mmol) of azo compound **75** in 500 mL of dry MeCN was heated to reflux for 6 hours. The solvent was removed in vacuo to afford an oil, which was purified by medium-pressure liquid chromatography on silica gel to afford 214 mg (85%) of the title product and its epimer, respectively, as a 9:1 mixture. Complete separation of the isomers was accomplished by

further chromatography. **85**: IR (NaCl, film) 3050, 2950, 1735, 1370, 1160 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.92 (s, 3 H), 1.03 (s, 3 H), 2.58 (d, $J = 8$ Hz, 1 H), 3.61 (s, 3 H), 5.20 (dt, $J = 3, 2$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 25.9, 26.7, 28.2, 37.0, 39.9, 40.9, 47.3, 47.6, 50.5, 50.7, 51.4, 175.1. HRMS Calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_2$: 234.16197. Found: 234.15891.



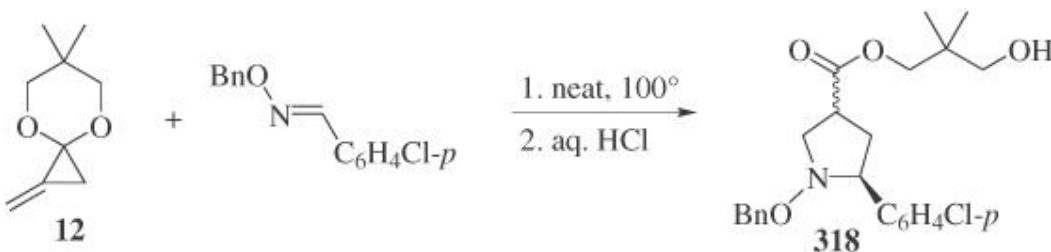
Found: 234.1611.

316b: TLC (SiO₂, Et₂O: pentane 1:10, vanillin) *R_f* 0.34; IR (neat/ NaCl) 3045, 2947, 2874, 1440, 1352, 1210, 1151, 1046 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.85–1.53 (m, 5 H), 2.11 (m, 1 H), 2.50 (m, 1 H), 2.63 (m, 1 H), 2.68(br s, 1 H), 3.05 (br t, *J* = 7.5 Hz, 1 H), 3.93–3.80 (m, 4 H), 5.12 (t, *J* = 1.5 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 18.6, 20.7, 27.1, 27.2, 33.6, 33.7, 37.0, 43.9, 49.0, 56.5, 64.8, 65.0, 112.4, 115.4, 157.7. HRMS (EI) Calcd. for C₁₅H₂₂O₂: 234.1619. Found: 234.1620.



8.2.4. 7-(4',4'-Dimethyl-2',6'-dioxacyclohexylidene)bicyclo[3.3.0]octan-2-one(317) (16)

A mixture of 8.48 g (55 mmol) of 6,6-dimethyl-4,8-dioxa-1-methylenespiro[2.5]octane (12) and 4.52 g (55 mmol) of 2-cyclopentenone in 15 mL of dry MeCN was heated at 60° for 12 hours. The solvent was removed by distillation (ca. 30–120°/ca. 20–1.4 mm Hg) and the residue was distilled under reduced pressure (bp 142–143°, 1.4 mm Hg) to afford 11.32 g (87%) of the title product. ¹H NMR (CD₃CN) δ 1.14 (s, 3 H), 1.15 (s, 3 H), 1.70–1.77 (m, 1 H), 1.89–2.17 (m, 4 H), 2.32–2.53 (m, 4 H), 2.63–2.68 (m, 1 H), 2.78–2.83 (m, 2 H), 3.77 (s, 2 H), 3.78 (s, 2 H); ¹³C NMR (CD₃CN) δ 22.16 (q), 22.18 (q), 24.8 (t), 27.2 (t), 28.6 (t), 31.3 (s), 32.5 (t), 40.1 (t), 43.8 (d), 53.7 (d), 77.4 (t), 77.4 (t), 96.3 (s), 149.2 (s), 213.2 (s).

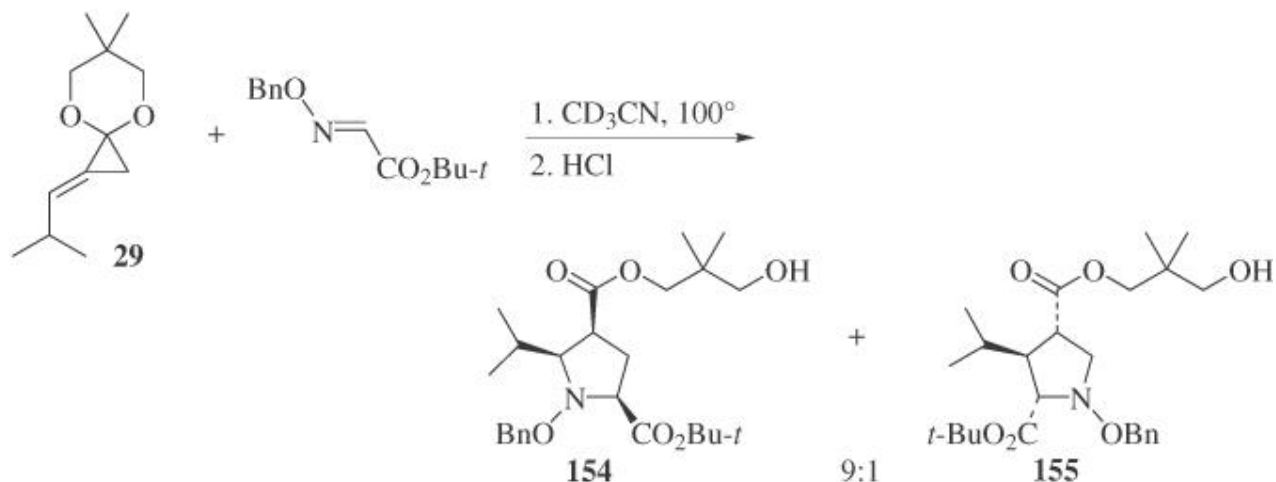


8.2.5. 1-Benzyloxy-2-(4'-chlorophenyl)-4-(2,2-dimethyl-3-hydroxypropoxy carbonyl) pyrrolidine(318) (50)

A mixture of 6,6-dimethyl-4,8-dioxo-1-methylenespiro-[2.5]octane (**12**) (0.79 g, 5.09 mmol) and *p*-chlorobenzaldehyde *O*-benzyloxime (1.02 g, 4.15 mmol, >99.8% anti) was heated for 46 hours at 100° under nitrogen. The reaction mixture was treated with 10% aqueous HCl solution in THF (2 mL) and was stirred for 30 minutes. After usual workup, purification of the resulting crude mixture by silica gel chromatography (EtOAc:hexane 1:3 and 1:1.5) afforded the title product in 98% yield (1.70 g) as a 73:27 diastereomeric mixture.

Major diastereomer of 318: IR (neat) 3450, 1724, 1496, 1373, 1188, 1092, 1050, 1019, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.91 (s, 6 H, CH_3), 2.00 (br dt, $J = 12.7, 9.3$ Hz, 1 H, CH_2), 2.26 (br s, 1 H, OH), 2.46 (ddd, $J = 12.7, 8.8, 5.4$ Hz, 1 H, CH_2), 3.03–3.18 (m, 2 H, CHCO_2 , NCH_2), 3.28 (s, 2 H, CH_2OH), 3.61 (dd, $J = 8.8, 7.8$ Hz, 1 H, NCH_2), 3.93 (d, $J = 11.2$ Hz, 1 H, CO_2CH_2), 3.98 (d, $J = 11.2$ Hz, 1 H, CO_2CH_2), 4.01 (dd, $J = 9.3, 8.8$ Hz, 1 H, NCH), 4.41 (d, $J = 11.2$ Hz, 1 H, OCH_2), 4.46 (d, $J = 11.2$ Hz, 1 H, OCH_2), 7.06–7.16 (m, 2 H, C_6H_5), 7.19–7.27 (m, 3 H, C_6H_5), 7.28 (d, $J = 8.3$ Hz, 2 H, *p*- ClC_6H_4), 7.33 (d, $J = 8.3$ Hz, 2 H, *p*- ClC_6H_4); ^{13}C NMR (100 MHz, CDCl_3) δ 21.4 (CH_3 , 2C), 33.2 (CH_2), 36.4 (C), 39.1 (CHCO_2), 58.4 (NCH_2), 68.1 (CH_2OH), 69.7 (CO_2CH_2), 70.2 (NCH), 75.7 (OCH_2), 127.7 (CH), 128.1 (CH, 2C), 128.3 (CH, 2C), 128.5 (CH, 2C), 129.1 (CH, 2C), 133.1 (C), 137.4 (C), 139.1 (C), 174.8 (C = O). Anal. Calcd. for $\text{C}_{23}\text{H}_{28}\text{NO}_4\text{Cl}$: C, 66.10; H, 6.75; N, 3.35. Found: C, 65.99; H, 6.67; N, 3.16.

Minor diastereomer of 318: IR (neat) 3430, 1735, 1492, 1370, 1192, 1091, 1050, 1017, 728, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.90 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3), 2.06–2.22 (m, 1 H, CH_2), 2.20 (br s, 1 H, OH), 2.36–2.48 (m, 1 H, CH_2), 3.04–3.18 (m, 2 H, CHCO_2 , NCH_2), 3.26 (s, 2 H, CH_2OH), 3.57–3.66 (m, 1 H, NCH_2), 3.94 (d, $J = 9.8, 8.8$ Hz, 1 H, NCH), 3.95 (d, $J = 10.7$ Hz, 1 H, CO_2CH_2), 3.99 (d, $J = 10.7$ Hz, 1 H, CO_2CH_2), 4.42 (d, $J = 11.2$ Hz, 1 H, OCH_2), 4.49 (d, $J = 11.2$ Hz, 1 H, OCH_2), 7.08–7.16 (m, 2 H, Ph), 7.20–7.27 (m, 3 H, Ph), 7.28 (d, $J = 9.1$ Hz, 2 H, *p*- ClC_6H_4), 7.35 (d, $J = 9.1$ Hz, 2 H, *p*- ClC_6H_4); ^{13}C NMR (100 MHz, CDCl_3) δ 21.4 (CH_3 , 2C), 33.5 (CH_2), 36.5 (C), 39.5 (CHCO_2), 58.7 (NCH_2), 68.2 (CH_2OH), 69.8 (CO_2CH_2), 70.9 (NCH), 75.9 (OCH_2), 127.7 (CH), 128.2 (CH, 2C), 128.4 (CH, 2C), 128.6 (CH, 2C), 129.2 (CH, 2C), 133.1 (C), 137.4 (C), 139.3 (C), 174.8 (C = O); Anal. Calcd. for $\text{C}_{23}\text{H}_{28}\text{NO}_4\text{Cl}$: C, 66.10; H, 6.75; N, 3.35. Found: C, 66.14; H, 7.13; N, 3.26.



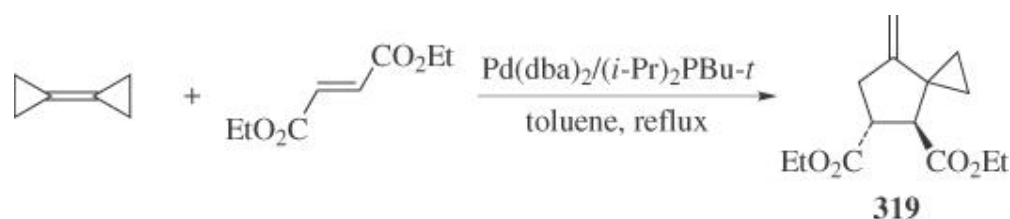
8.2.6. 1-Benzyloxy-*cis*-4-(2,2-dimethyl-3-hydroxypropoxycarbonyl)-*cis*-3-*i*-sopropyl-*r*-2-*tert*-butoxycarbonylpyrrolidine (**154**) (**50**)

A solution of substrate **29** (177 mg, 0.9 mmol) and glyoxalic acid *tert*-butyl ester O-benzyloxime (176 mg, 0.75 mmol, >99% anti) in CD_3CN (0.35 mL) in a sealed NMR tube was heated for 17 hours at 100° . The reaction mixture was treated with 10% aqueous HCl solution in THF (2 mL) and stirred for 5 minutes. After usual workup (addition of saturated aqueous sodium bicarbonate solution, extraction with Et_2O , washing the organic extracts with brine, drying over Na_2SO_4 , and concentration in vacuo), purification by silica gel chromatography (EtOAc :hexane 1:3.2 and 1:2.3) afforded title product **154** in 79% yield (266 mg) and its isomer **155** in 10% yield (34 mg).

154: IR (neat) 3523 (OH), 2962, 2873, 1732 (C =O), 1456, 1369, 1257, 1225, 1157, 1052, 912, 847, 735, 698, 528 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 0.92 (s, 6 H, CCH_3), 0.93 (d, $J = 8.0\text{ Hz}$, 3 H, CHCH_3), 1.00 (d, $J = 8.0\text{ Hz}$, 3 H, CHCH_3), 1.49 (s, 9 H, OCCH_3), 2.00 (dq, $J = 8.0, 8.0\text{ Hz}$, 1 H, CH_3CH), 2.10 (ddd, $J = 13.0, 10.0, 10.0\text{ Hz}$, 1 H, CH_2), 2.27 (ddd, $J = 13.0, 8.0, 5.0\text{ Hz}$, 1 H, CH_2), 2.78 (ddd, $J = 10.0, 8.0, 5.0\text{ Hz}$, 1 H, CHCO_2), 3.30 (dd, $J = 8.0, 4.0\text{ Hz}$, 3 H, NCH , CH_2OH), 3.83 (dd, $J = 10.0, 8.0\text{ Hz}$, 1 H, NCHCO_2), 3.93 (s, 2 H, CO_2CH_2), 4.78 (d, $J = 11\text{ Hz}$, 1 H, OCH_2Ph), 4.95 (d, $J = 11\text{ Hz}$, 1 H, OCH_2Ph), 7.25–7.35 (m, 5 H, C_6H_5); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 17.0 (CH_3), 19.7 (CH_3), 21.5 (CH_3 , 2 C), 28.0 (CH_3 , 3 C), 29.1 (CH_3CH), 30.1 (CH_2), 36.5 (CH_3C), 40.8 (CHCO_2), 68.1 (CH_2OH), 69.4 (NCHCO_2), 69.8 (CO_2CH_2), 75.9 (NCH), 76.5 (OCH_2), 81.2 (OCCH_3), 127.8 (CH), 128.3 (CH, 2 C), 128.6 (CH, 2 C), 137.2 (C), 171.3 (CO_2), 175.5 (CO_2). Anal. Calcd. for $\text{C}_{25}\text{H}_{39}\text{NO}_6$: C, 66.79; H, 8.74; N, 3.12. Found: C, 66.55; H, 8.44; N, 3.35.

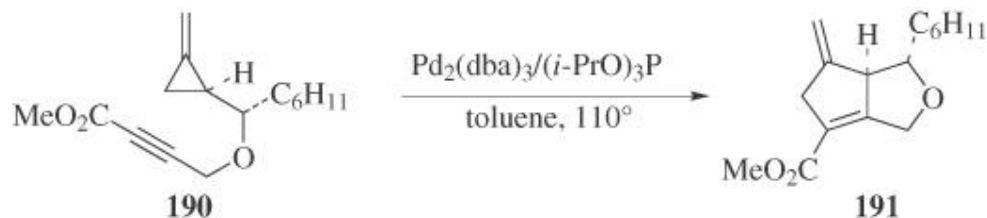
155: IR (neat) 3510, 2962, 2873, 1732 (C =O), 1473, 1456, 1392, 1369, 1255, 1155, 1054, 847, 748, 698 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 0.91 (s, 6 H,

CCH₃), 0.93 (d, *J* = 6.8 Hz, 3 H, CHCH₃), 0.95 (d, *J* = 6.8 Hz, 3 H, CHCH₃), 1.48 (s, 9 H, OCCH₃), 1.81 (dq, *J* = 6.8, 6.8 Hz, 1 H, CH₃CH), 2.52 (m, 1 H, CH₃CHCH), 2.90 (dd, *J* = 8.0, 5.0 Hz, 1 H, CHCO₂), 3.23 (dd, *J* = 11.5, 8.0 Hz, 1 H, CH₂), 3.28 (s, 2 H, CH₂OH), 3.48 (dd, *J* = 11.5, 8.0 Hz, 1 H, CH₂), 3.52 (d, *J* = 6.8 Hz, 1 H, NCHCO₂), 3.94 (s, 2 H, CO₂CH₂), 4.74 (s, 2 H, OCH₂Ph), 7.25–7.35 (m, 5 H, C₆H₅); ¹³C NMR (100 MHz, CDCl₃) δ 20.4 (CHCH₃), 20.5 (CHCH₃), 21.5 (CCH₃, 2 C), 28.0 (OCCH₃, 3 C), 31.6 (CH₃CH), 36.5 (CH₃C), 44.2 (CH₃CHCH), 45.6 (CHCO₂), 59.5 (CH₂), 68.1 (CH₂OH), 69.8 (CO₂CH₂), 74.1 (NCHCO₂), 75.5 (OCH₂Ph), 81.3 (OCCH₃), 127.8 (CH), 128.3 (CH, 2 C), 128.6 (CH, 2C), 137.3 (C), 171.2 (CO₂), 175.6 (CO₂). Anal. Calcd. for C₂₅H₃₉NO₆: C, 66.79; H, 8.74; N, 3.12. Found: C, 66.56; H, 8.49; N, 3.40.



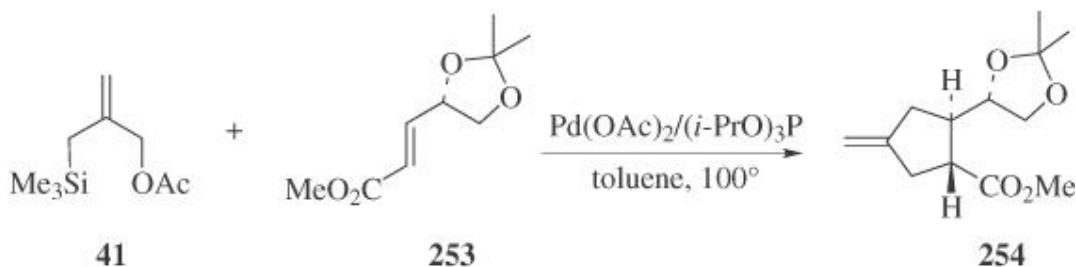
8.2.7. Diethyl 7-Methylenespiro[2.4]heptane-trans-4,5-dicarboxylate (**319**) (126)

A solution of Pd(dba)₂ (600 mg, 1.04 mmol), (*i*-Pr)₂PBu-*t* (180 mg, 1.04 mmol), and diethyl fumarate (8.50 g, 49.4 mmol) in toluene (10 mL) was heated under reflux (110°), and a solution of cyclopropylidene cyclopropane (1.97 g, 24.6 mmol) in toluene (10 mL) was added dropwise over 0.5 hour. The mixture was heated to reflux for another 3 hours until the reaction was complete. Fractional distillation of the reaction mixture yielded the title product (5.44 g, 83% yield); bp 90–95°/1.5 bar; IR (film) 3079, 2983, 2955, 1734, 1653, 1447, 1371, 1345, 1185, 1096, 1031, 962, 865, 796 cm⁻¹; ¹H NMR (200 MHz) δ 0.59–1.06 (m, 4 H), 1.25 (t, *J* = 7.2 Hz, 6 H), 2.71 (ddt, *J* = 16, 8.6, 2 Hz, 1 H), 2.93 (ddt, *J* = 16, 8.6, 2 Hz, 1 H), 3.21 (d, *J* = 8.6 Hz, 1 H), 3.36 (q, *J* = 8.6 Hz, 1 H), 4.15 (m, 4 H), 4.33 (t, *J* = 2 Hz, 1 H), 4.62 (t, *J* = 2 Hz, 1 H); ¹³C NMR (50.3 Hz) δ 15.5, 16.2, 26.8, 35.5, 45.0, 52.2, 60.3, 60.4, 98.9, 153.4, 171.8, 173.3; MS (EI); *m/z* (%) 252 (M⁺, 13), 223 (9), 206 (9), 179 (25), 178 (45), 105 (100). HRMS (EI) Calcd. for C₁₄H₂₀O₄: 252.1362. Found: 252.1361. Anal. Calcd. for C₁₄H₂₀O₄: C, 66.64; H, 7.99. Found C, 66.88; H, 8.21.



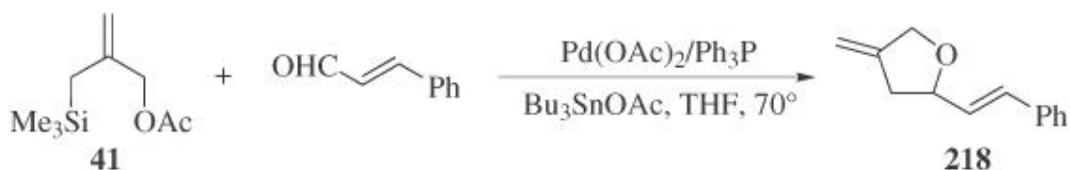
8.2.8. *cis*-1-Cyclohexyl-6-methylene-3,5,6,6a-tetrahydro-1H-cyclopenta[*c*]furan-4-carboxylic Acid Methyl Ester (**191**) (**57**)

A flame-dried round-bottomed flask, equipped with a condenser, was charged with Pd₂(dba)₃ [(1.9 mg, 0.0021 mmol, 3.6 mol% of Pd(0))] and P(OPr-*i*)₃ (2.0 μL, 0.0081 mmol, 7.4 mol%). Toluene (desulfurized and freshly distilled over sodium) was introduced via cannula followed by a solution of substrate **190** (30 mg, 0.11 mmol) in toluene. The mixture was heated to 110° for 1 hour with vigorous stirring. Toluene was removed under vacuum and the crude mixture was purified by column chromatography (EtOAc: hexane, 1:49) to afford the title product (22.6 mg, 75%) as a colorless oil. IR (neat) 2935, 2870, 1724, 1442 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.09-1.28 (m, 5 H), 1.54 (m, 1 H), 1.69 (t, *J* = 12.1 Hz, 3 H), 1.76 (m, 2 H), 1.87 (dd, *J* = 12.8, 1.8 Hz, 1 H), 3.44–3.49 (m, 2 H), 3.65 (ddd, *J* = 19.2, 4.2, 2.5 Hz, 1 H), 3.71 (s, 3 H), 3.74 (br d, *J* = 9.2 Hz, 1 H), 4.40 (dddd, *J* = 15.7, 4.4, 1.8, 1.8 Hz, 1 H), 4.56 (ddd, *J* = 15.7, 4.4, 1.8 Hz, 1 H), 4.84 (m, 1 H), 4.93 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 26.2, 26.6, 27.9, 30.2, 41.9, 44.4, 51.5, 57.8, 65.1, 84.7, 108.7, 122.7, 147.5, 164.1, 164.6. HRMS Calcd. for C₁₆H₂₂O₃: 262.1569. Found: 262.1567.



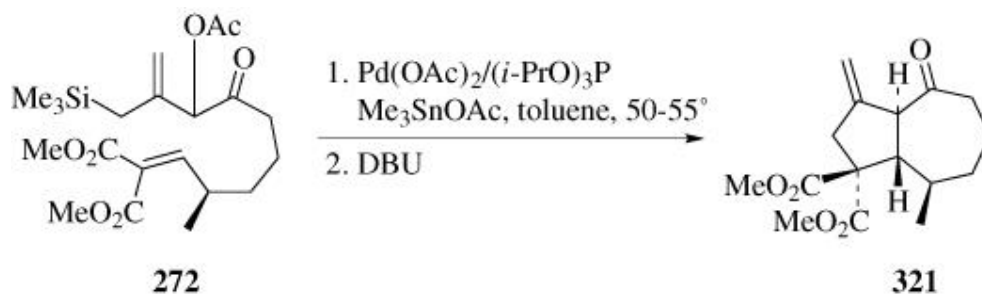
8.2.9. (4*S*,1*c**R*,2*c**R*)-2,2-Dimethyl-4-(2-carbomethoxy-4-methylenecyclopentyl)-1,3-dioxolane (**254**) (**170**)

To 160 mg (0.71 mg) of palladium acetate in 11 mL of dry toluene under nitrogen was added 726 mg (3.48 mmol) of triisopropyl phosphite, 2.00 g (10.7 mmol) of precursor **41**, and 2.00 g (10.7 mmol) of methyl (*S*)-(+)-(*E*)-3-(2,2-dimethyl-1,3-dioxolan-4-yl) propenoate (**253**). The resulting solution was heated at 100° under nitrogen for 16 hours. After cooling, the solution was concentrated. Purification by flash chromatography (hexane:



8.2.11. 2-[(*E*)-2-Phenylethenyl]-4-methylenetetrahydrofuran(**218**) (**159**)

A solution of palladium acetate (5 mg, 22 μmol), triphenylphosphine (30 mg, 114 μmol), and tributyltin acetate (35 mg, 100 μmol) under nitrogen in 1.0 mL of THF was heated at 70° until homogeneous. Cinnamaldehyde (66 mg, 63 μL , 0.50 mmol) and precursor **41** (93 mg, 110 μL , 0.50 mmol) were added and heating was continued at 70° for 4 hours. The reaction mixture was cooled, diluted with hexane: EtOAc, 4:1 (2 mL), and filtered through a silica gel plug. After evaporation of the solvent, the residue was purified by flash chromatography (hexane: EtOAc, 32.3:1) to give 83 mg (89%) of the title product. ^1H NMR (CDCl_3 , 270 MHz) δ 2.45 (dd, $J = 5.4, 7.4$ Hz, 1 H), 2.77 (dd, $J = 15.4, 6.9$ Hz, 1 H), 4.32 (d, $J = 13.0$ Hz, 1 H), 4.46 (d, $J = 13.0$ Hz, 1 H), 4.57 (q, $J = 7.1$ Hz, 1 H), 4.94 (br s, 1 H), 5.02 (br s, 1 H), 6.22 (dd, $J = 15.9, 6.9$ Hz, 1 H), 6.62 (d, $J = 15.9$ Hz, 1 H), 7.40–7.20 (m, 5 H).



8.2.12. (+)-Dimethyl

3,8-Dimethyl-4-oxo-4,5,6,7,8,8a-hexahydro-2H-azulene-1,1-dicarboxylate(**321**) (**167**)

To a suspension of the (+)-isomer of precursor **272** (1.98 g, 4.68 mmol), trimethyltin acetate (51.6 mg, 0.232 mmol), and powdered 3 Å molecular sieves (0.40 g) in 40 mL of toluene was added a catalyst solution consisting of palladium acetate (26.0 mg, 0.116 mmol) and triisopropyl phosphite (145 mg, 0.694 mmol) in 5 mL of toluene. The mixture was heated at reflux for 3 hours, the bath temperature was changed to 90°, and DBU (0.176 g, 1.16 mmol) was added. After 2 hours at 90°, the mixture was filtered through Celite (with 50 mL of Et_2O). The filtrate was partitioned with aqueous 2% sodium bisulfate

solution (50 mL). The organic layers were washed with phosphate buffer (pH 7; 25 mL) and brine (25 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification by silica gel flash chromatography (hexane: EtOAc 4:1) afforded 0.979 g (71%) of the title product as an oil. [α]_D + 67.58° (c 7.6, CHCl₃); IR (neat) 1733 (vs), 1683 (m), 1627 (m), 1435 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.01 (d, *J* = 7.0 Hz, 3 H), 1.44 (dq, *J* = 10.2, 4.3 Hz, 1 H), 1.57–1.72 (m, 2 H), 1.80–2.00 (m, 2 H), 2.10 (s, 3 H), 2.35 (ddd, *J* = 12.8, 7.8, 2.1 Hz, 1 H), 2.72 (dt, *J* = 12.8, 9.5 Hz, 1 H), 2.87 (d, *J* = 18.6 Hz, 1 H), 3.39 (d, *J* = 18.6 Hz, 1 H), 3.67 (d, *J* = 8.5 Hz, 1 H), 3.74 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 16.2, 18.5, 19.4, 30.9, 31.2, 41.4, 46.3, 52.5, 53.0, 56.7, 62.6, 136.0, 149.7, 170.5, 172.3, 200.6. HRMS Calcd. for C₁₆H₂₂O₅ (M⁺): 294.1467. Found: 294.1473. Anal. Calcd. for C₁₆H₂₂O₅: C, 65.29; H, 7.53. Found: C, 65.06; H, 7.65.

9. Tabular Survey

The tabular survey includes all examples found in the literature to the end of 2000. The contents of the tables were derived by searching *Chemical Abstracts* and by direct inspection of the literature.

Table entries are in order of increasing carbon number of the reactant, in order of increasing hydrogen number of the reactant when reactants have the same carbon number, and then in order of increasing carbon number of the product.

The following abbreviations are used in the tables:

Ac	acetyl
acac	acetylacetonato
an	acrylonitrile
BINAP	2,2' -bis(diphenylphosphino)-1,1' - binaphthyl
Boc	<i>N-tert</i> -butoxycarbonyl
BP	biphenyl
BSA	<i>N,O</i> -bis(trimethylsilyl) acetamide
Cp	cyclopentadienyl
Chiraphos	bis(diphenylphosphino)butane
cod	cyclooctadiene
DCA	9,10-dicyanoanthracene
DIBAL-H	diisobutylaluminium hydride
DME	1,2-dimethoxyethane
DMF	<i>N, N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
dba	dibenzylideneacetone
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1' -bis(diphenylphosphino)ferrocene
dppp	1,3-bis(diphenylphosphino)propane
MeCN	acetonitrile
MOM	methoxymethyl
MS	molecular sieves
NMQ ⁺ BF ₄ ⁻	<i>N</i> -methylquinolinium tetrafluoroborate
Piv	pivaloyl
TBDMS	<i>tert</i> -butyldimethylsilyl
TBDPS	<i>tert</i> -butyldiphenylsilyl

TCNB	1,2,4,5-tetracyanobenzene
TIPS	triisopropylsilyl
Tpdp	2,4-bis[(4,6-dimethyl-1,3,2-dioxaphosphorinan-2-yl)oxy]pentane
xs	excess

Table 1. Intermolecular Cycloaddition of Acyclic Alkenes and TMM

[View PDF](#)

Table 2. Intermolecular Cycloaddition of Cyclic Alkenes and TMM

[View PDF](#)

Table 3. Intermolecular Cycloaddition of Alkynes or Allenes and TMM

[View PDF](#)

Table 4. Intramolecular Cycloaddition of Alkenes and TMM

[View PDF](#)

Table 5. Intramolecular Cycloaddition of Alkynes and TMM

[View PDF](#)

Table 6. Intermolecular Cycloaddition of Carbonyl Compounds and TMM

[View PDF](#)

Table 7. Intramolecular Cycloaddition of Aldehydes and TMM

[View PDF](#)

Table 8. Intermolecular Cycloaddition of Imines or Oximes and TMM

[View PDF](#)

Table 9. Intermolecular Cycloaddition of Oxygen and TMM

[View PDF](#)

Table 10. Miscellaneous

[View PDF](#)

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM


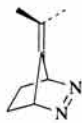
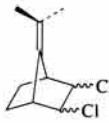
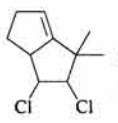









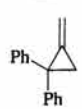
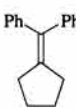


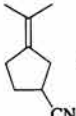
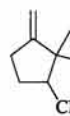
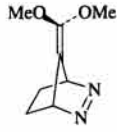
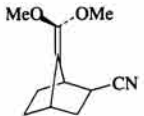
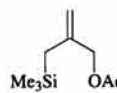




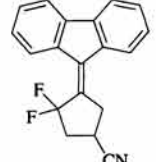
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ 		Alkene (xs), 40-60°	 I +  II I + II (10), I:II = 1:1	8
CH ₂ =CH ₂		Pd(acac) ₂ /Et ₂ Al(OEt)/ <i>i</i> -Pr ₃ P, C ₆ H ₆ , 115°, 6 h	 I +  II I + II (84), I:II = 1:2	124, 22
		Ni(0), 40-60°	 I (>75)	235
		Pd(0), 80-100°	I (>75)	235
		Ni(0), 40-60°	 I (>75)	235
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 100°, 5 h	I (83)	64
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 100°, 8 h	 (77)	64
C ₃ 		Ni(cod) ₂ /Ar ₃ P (1:1), toluene, 130°, 10 h	 I (47) +  II (4)	65
		Et ₂ O, 0°	 (—)	44
		(Ph ₃ P) ₄ Pd/dppe, toluene, 60°, 150 h	 (35)	25, 154
		MeCN, 70°, 6 h	 I +  II +  III I + II + III = (75), I:II:III = 3.8:1:1	51

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Ni(cod) ₂ /Ar ₃ P (1:1), toluene, 120°, 5 h	 (82)	65
		MeCN, 70°, 1.5 h	 I + II I + II (84), I:II = 1:2.2	55
		MeCN, 120°, 2 h	 I + II I + II (42), I:II = 1:10	55
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 100°, 6 h	 (56)	64
C ₃₋₄ 		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 100°, 6 h	 R Me (83) Et (86)	64
C ₄ 		Alkene xs, 40-60°	 (83)	8
		MeCN, 50°	 (>90)	41
		MeCN, 80°, 39 h	 (85)	16
		Pd(dba) ₂ / <i>i</i> -Pr ₃ P (1:1), C ₆ H ₆ , 115°, 16 h	 I (91)	124
		Pd(acac) ₂ /Et ₂ Al(OEt)/ <i>i</i> -Pr ₃ P (1:2:1), C ₆ H ₆ , 100°, 4 h	I (94)	22
		Pd(PPh ₃) ₄	I (4)	22
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 120°, 8 h	 (48)	64

TABLE I. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		(Ph ₃ P) ₄ Pd/dppe, toluene, 78°, 42 h	(30)	25, 69
		[Pd ₂ dba ₃ CHCl ₃], dppe, THF, reflux, 1 h	(89)	70
		(Ph ₃ P) ₄ Pd, toluene, 80°	I + II I + II (37), I:II = 6.1:1	155
		Ni(cod) ₂ /Ph ₃ P (1:1), toluene, 80-100°, 5 h	I + II I + II (54), I:II = 10:1	60
		Ni(an) ₂ , 60°, 48 h	(70)	62
		Pd(dba) ₂ /(<i>i</i> -Pr) ₂ (<i>n</i> -Bu)P, (1:1), 110°, 3 h	I + II I + II (56), I:II = 3:1 I + II (58), I:II = 9:1 I + II (81), I:II = 3:1	126
		R = H R = Me R = Ph		
		Ni(an) ₂ , 60°, 48 h	I (82)	63
	"	Ni(cod) ₂ , -15°	I (>90)	126
	"	Ni(cod) ₂ /Ph ₃ P (1:1), toluene, 80-100°, 5 h	I (55)	60
	"	Pd(dba) ₂ / <i>i</i> -Pr ₃ P (1:1), 100°, 20 h	I (18)	60
	"	Pd(acac) ₂ /Et ₂ Al(OEt)/ <i>i</i> -Pr ₃ P, I (14)	I (14)	61
	"	Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 130°, 2.5 h	I (84)	22
		(Ph ₃ P) ₄ Pd/dppe, toluene, 85-90°, 43 h	I (68)	25, 69
		Ni(cod) ₂	(33-43)	129
		Ni(an) ₂	I (61) + II (0)	63
		Ni(cod) ₂ /Ar ₃ P (1:1), toluene, 100°, 5 h	I (81) + II (14)	65

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.		
		Ni(cod)/Ar ₃ P (1:1), toluene, 50°, 8 h		65		
		[Pd ₂ (dba) ₃ CHCl ₃]/ ligand (1:2), THF, reflux, 38-64 h		158		
<u>R</u>		<u>ligand</u>	<u>I + II</u>	<u>I:II</u>	<u>ee (%) of I</u>	<u>ee (%) of II</u>
CO ₂ Me			(58)	4.6:1	73	58
COMe			(77)	1.9:1	75	78
CO ₂ Me			(76)	3.3:1	66	64
COMe			(86)	2.6:1	54	61
CO ₂ Me		(<i>S,S</i>)-chiraphos	(51)	2.7:1	46	21
CO ₂ Me		(+)-BINAP	(63)	3.5:1	19	4
		MeCN, 50°, 24 h		55		
			I + II (68), I:II = 1:4.9			
<u>C₄₋₆</u>		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 144°, 2-5 h		125		
			<u>R</u>	<u>I:II:III</u>		
			H (78)	1.1:1:0		
			Me (79)	1.3:1:0		
			CO ₂ Me (87)	9:0:1		
<u>C₅</u>		MeCN, 80°, 18 h		16		
		Toluene, 100-120°, 55-75 h		56		
			E = CO ₂ Me I + II (72), I:II = 1:1			
		(Ph ₃ P) ₄ Pd/dppe, toluene, 85°, 67 h		25, 69		
		Pd(dba) ₂ / <i>i</i> -Pr ₃ P (1:1), toluene, 100°, 16 h		61, 22		

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Ni(cod) ₂	I (43) + II (0)	129
		Ni(cod) ₂ /Ph ₃ P (1:1), toluene, 80-100°, 5 h	I + II (55), I:II = 3.5:1	60
		(Ph ₃ P) ₄ Pd/dppe, toluene, 110°, 60 h	I + II (38), I:II = 13:1	25, 69
		Ni(cod) ₂ /Ar ₃ P (1:1), toluene, 110°, 5 h	I (14) + II (46)	65
		Toluene, 100-120°, 55-75 h	I + II (81), I:II = 1:1 E = CO ₂ Me	56
		CD ₃ CN, 100-120°, 55-75 h	I + II (71), I:II = 24:1 E = CO ₂ Me	56
		Ni(cod) ₂ /Ar ₃ P (1:1), toluene, 120°, 5 h	(75)	65
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux, 5.5 h	I + II (35), I:II = 1:1.6	25, 69
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux	(33)	69
		(Ph ₃ P) ₄ Pd, toluene, 80°	I + II (40), I:II = 1:3.2	155

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)


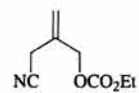
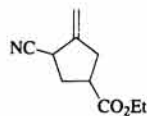
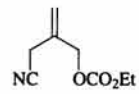
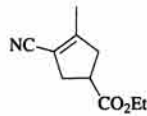
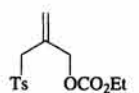
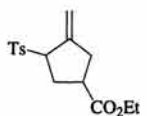

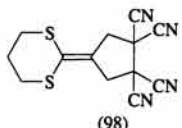
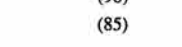
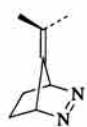
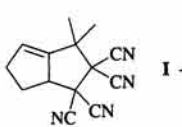
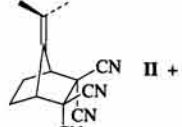
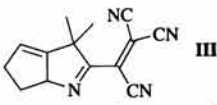
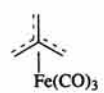
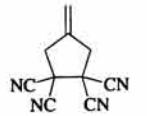

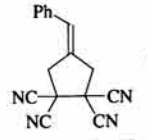
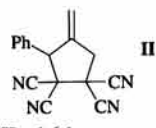
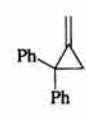
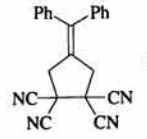
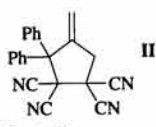
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.																																												
		[Pd ₂ (dba) ₃ CHCl ₃]/ dppe (1:4), THF, reflux, 2 h	 (66)	70																																												
		[Pd ₂ (dba) ₃ CHCl ₃]/ dppe (1:4), THF, reflux, 20 h	 (72)	70																																												
		[Pd ₂ (dba) ₃ CHCl ₃]/ dppe (1:4), THF, reflux, 20 h	 (77)	70																																												
C ₆		MeCN 120°, 15 min hν, 0°, 12 h	 (98)  (85)	107																																												
			 I +  II +  III	236																																												
			<table border="1"> <thead> <tr> <th></th> <th>I</th> <th>II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td><i>hν</i> (> 400 nm), CD₂Cl₂, 0-5°, 10 min</td> <td>(7)</td> <td>(2)</td> <td>(43)</td> </tr> <tr> <td><i>hν</i>, CDCl₃/CD₃CN (97/3), 0-5°, 10 min</td> <td>(5)</td> <td>(2)</td> <td>(39)</td> </tr> <tr> <td><i>hν</i>, CDCl₃/CD₃CN (95/5), 0-5°, 10 min</td> <td>(8)</td> <td>(2)</td> <td>(30)</td> </tr> <tr> <td><i>hν</i>, CDCl₃/CD₃CN (75/25), 0-5°, 10 min</td> <td>(17)</td> <td>(6)</td> <td>(53)</td> </tr> <tr> <td><i>hν</i>, CDCl₃/CD₃CN (50/50), 0-5°, 10 min</td> <td>(19)</td> <td>(6)</td> <td>(29)</td> </tr> <tr> <td><i>hν</i>, CDCl₃/CD₃CN (25/75), 0-5°, 10 min</td> <td>(31)</td> <td>(6)</td> <td>(23)</td> </tr> <tr> <td><i>hν</i>, CD₃CN, 0-5°, 10 min</td> <td>(26)</td> <td>(5)</td> <td>(8)</td> </tr> <tr> <td><i>hν</i>, LiClO₄, CD₃CN, 0-5°, 10 min</td> <td>(16)</td> <td>(3)</td> <td>(4)</td> </tr> <tr> <td>CD₃CN, 60°, 6 h</td> <td>(62)</td> <td>(1)</td> <td>(0)</td> </tr> <tr> <td>CDCl₃/CD₃CN (95/5), 40°, 24 h</td> <td>(65)</td> <td>(trace)</td> <td>(0)</td> </tr> </tbody> </table>		I	II	III	<i>hν</i> (> 400 nm), CD ₂ Cl ₂ , 0-5°, 10 min	(7)	(2)	(43)	<i>hν</i> , CDCl ₃ /CD ₃ CN (97/3), 0-5°, 10 min	(5)	(2)	(39)	<i>hν</i> , CDCl ₃ /CD ₃ CN (95/5), 0-5°, 10 min	(8)	(2)	(30)	<i>hν</i> , CDCl ₃ /CD ₃ CN (75/25), 0-5°, 10 min	(17)	(6)	(53)	<i>hν</i> , CDCl ₃ /CD ₃ CN (50/50), 0-5°, 10 min	(19)	(6)	(29)	<i>hν</i> , CDCl ₃ /CD ₃ CN (25/75), 0-5°, 10 min	(31)	(6)	(23)	<i>hν</i> , CD ₃ CN, 0-5°, 10 min	(26)	(5)	(8)	<i>hν</i> , LiClO ₄ , CD ₃ CN, 0-5°, 10 min	(16)	(3)	(4)	CD ₃ CN, 60°, 6 h	(62)	(1)	(0)	CDCl ₃ /CD ₃ CN (95/5), 40°, 24 h	(65)	(trace)	(0)	
	I	II	III																																													
<i>hν</i> (> 400 nm), CD ₂ Cl ₂ , 0-5°, 10 min	(7)	(2)	(43)																																													
<i>hν</i> , CDCl ₃ /CD ₃ CN (97/3), 0-5°, 10 min	(5)	(2)	(39)																																													
<i>hν</i> , CDCl ₃ /CD ₃ CN (95/5), 0-5°, 10 min	(8)	(2)	(30)																																													
<i>hν</i> , CDCl ₃ /CD ₃ CN (75/25), 0-5°, 10 min	(17)	(6)	(53)																																													
<i>hν</i> , CDCl ₃ /CD ₃ CN (50/50), 0-5°, 10 min	(19)	(6)	(29)																																													
<i>hν</i> , CDCl ₃ /CD ₃ CN (25/75), 0-5°, 10 min	(31)	(6)	(23)																																													
<i>hν</i> , CD ₃ CN, 0-5°, 10 min	(26)	(5)	(8)																																													
<i>hν</i> , LiClO ₄ , CD ₃ CN, 0-5°, 10 min	(16)	(3)	(4)																																													
CD ₃ CN, 60°, 6 h	(62)	(1)	(0)																																													
CDCl ₃ /CD ₃ CN (95/5), 40°, 24 h	(65)	(trace)	(0)																																													
		Ce ⁴⁺	 (4)	78																																												
		C ₆ H ₆ , 100°, 5 d	 I +  II I + II (65), I:II = 1.6:1	237																																												
		C ₆ H ₆ , 100°, 3 d	 I +  II I + II (80), I:II = 1.3:1	237																																												

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		—	(—)	81
		Ni(cod) ₂ , toluene, 40°	(—)	131
		Ni(an) ₂	I + II + III (27), I:II:III = 1.4:2.1:1	62
"	"	Pd(dba) ₂ /i-Pr ₃ P (1:1), toluene, 100°, 16 h	I (76) + II (2)	61
"	"	Pd(dba) ₂ /Et ₂ Al(OEt)/i-Pr ₃ P, (1:2:1), THF, 100°, 16 h	I (19) + II (1)	22
"	"	Pd(acac) ₂ /Et ₂ Al(OEt)/i-Pr ₃ P (1:2:1), toluene, 100°, 16 h	I (59) + II (2)	22
"	"	Pd(allyl)Cp/i-Pr ₃ P (1:1), toluene, 120°, 2 h	I (84) + II (3)	22
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux, 285 h	II (32)	25, 69
		Ni(an) ₂ , benzene, 60°, 2.5 h	I + II I:II = 1:1.6	238
		Ni(cod) ₂ /Ar ₃ P (1:1), toluene, 120°, 5 h	I (56) + II (34)	65
			I + II + III E = CO ₂ Me cis isomer	8, 39
Concentration (M)			I + II + III	I:II:III
6.6		60°, 8 h	(100)	9:1:0
0.515		MeCN, 60°	(100)	89:10:1
0.204		MeCN, 60°	(100)	81:18:1
0.0725		MeCN, 60°	(—)	17:7.5:1
0.035		MeCN, 60°	(—)	9.5:6.2:1
0.017		MeCN, 60°	(99)	7.4:5.9:1
0.007		MeCN, 60°	(96)	6.9:6.4:1
0.298		MeCN, 60°, O ₂ (250 Torr)	(62)	99:1:0
0.224		MeCN, 60°, O ₂ (250 Torr)	(56)	99:1:0
0.149		MeCN, 60°, O ₂ (250 Torr)	(45)	99:1:0
0.075		MeCN, 60°, O ₂ (250 Torr)	(29)	99:1:0
0.037		MeCN, 60°, O ₂ (250 Torr)	(18)	99:1:0

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, 120°, 36 h	 I + II (59), I:II = 1:1.7	107
		Ni(cod) ₂ /Ar ₃ P (1:1), toluene, 100°, 3 h	 (98)	65
		Ni(an) ₂	 I + II + III + IV (20), I:II:III:IV = 1:89:4:6	62
"	"	Ni(cod) ₂	I + II (78), I:II = 1:9	129
"	"	Pd(dba) ₂ / <i>i</i> -Pr ₃ P (1:1), toluene, 100°, 16 h	III (8) + IV (15)	61
"	"	Pd(acac) ₂ /Et ₂ Al(OEt)/ <i>i</i> -Pr ₃ P (1:2:1), toluene, 100°, 16 h	III (18) + IV (13)	22
"	"	Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), toluene, 110°, 8 h	III (25) + IV (20)	22
"	"	Pd(allyl)Cp/(EtO) ₃ P (1:1), toluene, 110°, 8 h	III (61) + IV (18)	22
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux, 210 h	III + IV (60), III:IV = 1.3:1	25, 69
		MeCN, 60°	 I + II + III + IV I:II:III:IV	8, 39
	Concentration (M)			
	6.6	8 h	(95)	15:3:1:6
	3.3	—	(95)	37(I + II):1:13
	1.32	—	(93)	15 (I + II):1:9.3
	0.66	—	(86)	13 (I + II):1:11
	0.33	—	(59)	7.5 (I + II):1:8.2
	0.13	—	(38)	7.2 (I + II):1:8.5
	0.066	—	(24)	9 (I + II):1:10
	0.033	—	(12)	7.2 (I + II):1:8.5
	6.6	O ₂ (250 Torr)	(54)	96:2:1:1
	3.3	O ₂ (250 Torr)	(32)	95:2:2:1
	1.3	O ₂ (250 Torr)	(17)	45:2:1:2.5
	0.66	O ₂ (250 Torr)	(15)	21:1:1:—

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Ni(cod) ₂ /Ar ₃ P (1:1), toluene, 130°, 10 h	 I (57) + II (23)	65
		MeCN, 120°, 72 h	 I + II (46), I:II = 1:1.1	107
		Et ₂ O, 0°	 (—)	44
		Ni(cod) ₂ /Ar ₃ P (1:1), toluene, 120°, 5 h	 I (28) + II (69)	65
		80°, 20-35 h	 I + II	56
		solvent	I + II	I:II
		octane	(77)	32:1
		benzene	(88)	19:1
		toluene	(86)	32:1
		DME	(85)	12:1
		(CH ₂ Cl) ₂	(75)	12:1
		DMF	(72)	4:1
		MeCN	(78)	4:1
		DMSO- <i>d</i> ₆	(73)	2.7:1
C ₇ 		MeCN 80°, 12 h 40°, 60 h	 I + II (84), I:II = 1:1.6 I + II (87), I:II = 1:3.2	55
		Pd(OAc) ₂ /(<i>i</i> -Pr) ₃ P, THF, reflux, 142 h	 (23)	72
		MeCN, 40°, 30 h	 (90)	55
C ₇₋₈ 		Ni(cod) ₂ /Ph ₃ P (1:1), toluene, 80-100°, 5 h	 I + II (50), I:II = 2.7:1 I + II (49), I:II = 2.6:1	76

R = *n*-Pr
R = (CH₂)₂CO₂Me

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)



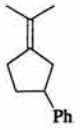


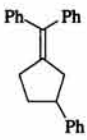


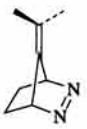
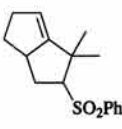
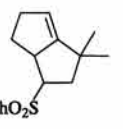
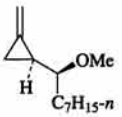
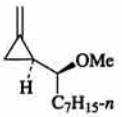
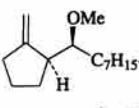
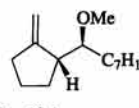
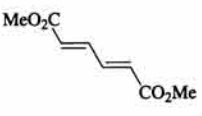
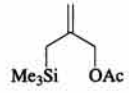
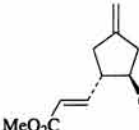
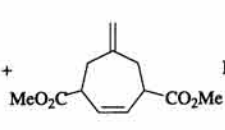
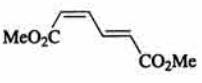
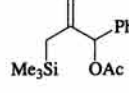
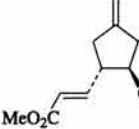
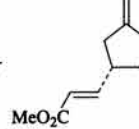
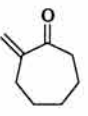
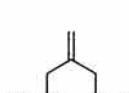
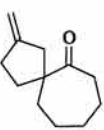
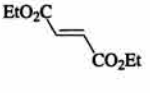

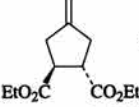
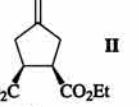
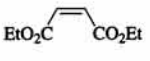

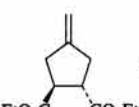
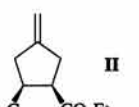
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ 		Ni(0), 40-60°	 I (>75)	235
		Pd(0), 80-100°	I (>75)	235
		Ni(0), 40-60°	 I (>75)	235, 64
		Pd(allyl)(Cp)/i-Pr ₃ P (1:1), 90°, 1.5 h	I (88)	235, 64
		Alkene (4 eq), MeCN, reflux	 I +  II I + II (85)	239
		1. Ni(cod) ₂ /(PhO) ₃ P (1:2), toluene, reflux, 6 h 2. Na/Hg, Na ₂ HPO ₄ , MeOH, 0°	 I +  II I + II (49), I:II = 10:1	240
		(Ph ₃ P) ₄ Pd/dppe Dioxane THF	 I +  II I + II (98), I:II = 3.8:1 I + II (47), I:II = 1.6:1	150, 69
		(Ph ₃ P) ₄ Pd/dppe, dioxane, reflux	 I +  II I:II = 1:1	150
		Pd(OAc) ₂ /(i-PrO) ₃ P (1:8)	 (93)	160
		Ni(cod) ₂ /Ph ₃ P (1:1), toluene, 80-100°, 5 h	 I +  II I + II (72), I:II = 24:1	60
		Ni(cod) ₂ /Ph ₃ P (1:1), toluene, 80-100°, 5 h	 I +  II I + II (42), I:II = 3:1	60

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Ni(cod) ₂ / (2-PhC ₆ H ₄) ₃ P (x:y)	I + II + III	126
		x:y 1:1 1:2 1:3	I (10) + II (31) + III (16) I (12) + II (46) + III (18) I (25) + II (23) + III (9)	
		Pd(dba) ₂ /(<i>i</i> -Pr) ₂ (<i>t</i> -Bu)P (1:1), 110°, 3 h	I (83)	126
		Me ₃ NO, benzene, 60°	I + II + III	79
			I + II + III = (9-19)	
<i>n</i> -Bu 		MeCN, 70°, 26 h	(89)	16
<i>t</i> -Bu 		CD ₃ CN, 100-120°, 55-75 h	(89)	56
<i>n</i> -Bu 		MeCN, 70°, 26 h	(86)	16
		CD ₃ CN, 100-120°, 55-75 h	I + II	56
			I + II (80), I : II = 1:1, E = CO ₂ Me	

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, hexane, reflux	 I + II (94), I:II = 3:1	76, 170
		(Ph ₃ P) ₄ Pd, toluene, 80°	 I + II + III (77), I:II:III = 8:1:1 E = CO ₂ Me	154, 155
		(Ph ₃ P) ₄ Pd, toluene, 80°	 (69)	77
		(Ph ₃ P) ₄ Pd, toluene, 80°	 (66)	154, 155
		MeCN, 40°, 14 h	 I + II (94), I:II = 1:6.7	55
		MeCN 80°, 0.5 h 40°, 14 h	 I + II (88), I:II = 1.3:1 I + II (87), I:II = 1:8.1	55
		MeCN, 120°, 23 h	 I + II (80); I:II = 1:1.2	107
		MeCN, 120°, 4 h	 I + II (72), I:II = 1:5.7	55
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux, 5 h	 (43)	25, 69

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ / <i>i</i> -PrO ₃ P, toluene	 I + I + II (38), I:II = 3:1	153
		(η ³ -C ₃ H ₅ PdCl) ₂ /tpdp, toluene, benzene, 15 kbar	I + II (90), I:II = 1:3.6	153
		[Pd ₂ (dba) ₃ CHCl ₃]/ dppe (1:4), THF, reflux, 1 h		(51)
		(Ph ₃ P) ₄ Pd, toluene, 80°	 I + I + II (61), I:II = 2.7:1	155
		Pd(0)/ <i>i</i> -Pr ₃ P (1:1), 100-140°	 I (40)	61
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux, 4.5 h	I (70)	25, 69
		(<i>i</i> -PrO ₃ P) ₄ Pd, dioxane, 150°	 I + I + II (74), I:II = 2.3:1	241
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux, 3 h	 I + I + II (55), I:II = 1:1.3	25, 69
		(Ph ₃ P) ₄ Pd, toluene, 80°	 I + I + II (70), I:II = 1.4:1	154, 155
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux, 12 h		(51) 25, 69
		—		(64) 76

TABLE I. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

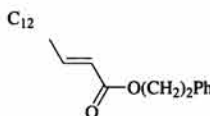

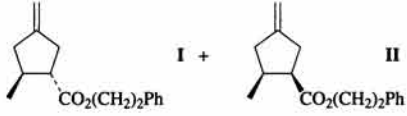
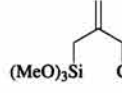
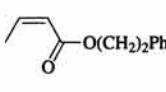
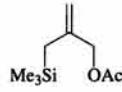
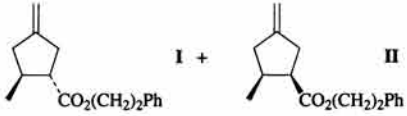
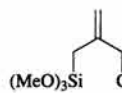
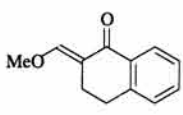
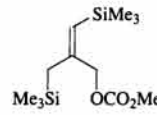
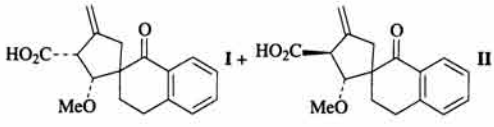
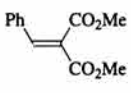
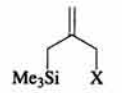
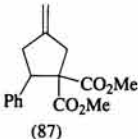
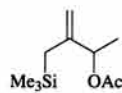
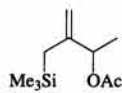
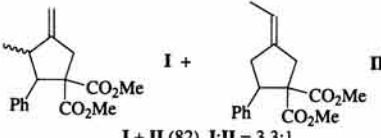
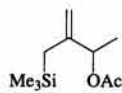
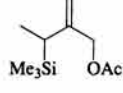
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, <i>n</i> -BuLi, THF, 65-70°	 I + II (95), I:II = 19:1	71
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, <i>n</i> -BuLi, THF, 25°	I + II (59), I:II = >99:<1	71
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, <i>n</i> -BuLi, THF, 65-70°	 I + II (86), I:II = 1:2.3	71
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, <i>n</i> -BuLi, THF, 25°	I + II (57), I:II = 1:7.3	71
		(Ph ₃ P) ₄ Pd, toluene, 80°	 I + II (51), I:II = 2:1	154, 155
	 X = OMs	[(EtO) ₃ P] ₂ Ni, toluene, reflux	 (87)	88
	X = OAc	(Ph ₃ P) ₄ Pd/dppe, toluene, 85-95°, 5 h	(70)	25, 69
	X = OBz	"	(69)	25, 69
	X = OMs	"	(42)	25, 69
	X = Br	"	(0)	25, 69
		Pd(PPh ₃) ₄ , THF, reflux	 I + II (82), I:II = 3.3:1	75, 153
		Pd(OAc) ₂ /(<i>i</i> -Pr) ₃ P, toluene, 10 kbar	II (90)	75, 153
		Pd(PPh ₃) ₄ , THF, reflux	I + II (90), I:II = 6.7:1	75, 153

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ (<i>i</i> -PrO) ₃ P, toluene, 100° (<i>i</i> -PrO) ₃ P, dioxane, 150° tpdp, DMSO, 100° tpdp, neat 100°	 I + II (43), I:II = 1:3.1 I + II (95), I:II = 1:1 I + II (quant.), I:II = 9.3:1 I + II (81), I:II = 18:1	242
		Pd(OAc) ₂ / <i>i</i> -Pr) ₃ P, toluene, 80°	 (69)	241
		(Ph ₃ P) ₄ Pd, toluene, reflux	 (89)	75
		Pd(OAc) ₂ / <i>i</i> -Pr) ₃ P, dioxane, 100°	 (89)	75
		Pd(OAc) ₂ / <i>i</i> -Pr) ₃ P dioxane, 1 atm toluene, 10 kbar	 I + II + III (86), I:II:III = 1:0:0, E = CO ₂ Me I + II + III (69), I:II:III = 0:4:1	75, 153
		Pd(OAc) ₂ / <i>i</i> -Pr) ₃ P, toluene, reflux	 (59)	75
		Pd(OAc) ₂ /ligand, reductant, dioxane, 100°	 I + II (92), I:II = 1:1	155
		(<i>i</i> -PrO) ₃ P, <i>n</i> -BuLi Ph ₃ P, <i>n</i> -BuLi Ph ₃ P, DIBAL-H Ph ₃ P	 I + II + III + IV (62), I:II:III:IV = 1:0:1.4:1.4 I + II + III + IV (62), I:II:III:IV = 4:1:20:20 I + II + III + IV (—), I:II:III:IV = 4:1:20:4 I + II + III + IV (—), I:II:III:IV = 4:1:20:4	
		Pd(OAc) ₂ / <i>i</i> -Pr) ₃ P, toluene, reflux	 (92)	182
		Pd(OAc) ₂ / <i>i</i> -Pr) ₃ P, toluene, 65-95°	 (85)	162

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ , <i>n</i> -BuLi, Ph ₃ P, THF, reflux	 I + II (86), I:II = 4:1	73
		Pd(OAc) ₂ , <i>n</i> -BuLi, Ph ₃ P, THF, reflux	 I:II = 2.3:1	73
C ₁₃		(2,4-pentadionato) ₃ In, Pd(OAc) ₂ , DIBAL-H, (2-MeOC ₆ H ₄) ₃ P, toluene	 (81)	160
		(Ph ₃ P) ₄ Pd, toluene, 80°	 I + II (59), I:II = 1.9:1	155
		MeCN, 60°, 0.1 h	 I + II (8), I:II = 1:2.4, II <i>cis</i> :II <i>trans</i> = 1:2.4	55
		MeCN, 80°, 9.5 h	I + II (96), I:II = 1:2.7, II <i>cis</i> :II <i>trans</i> = 1:1.6	55
		MeCN, 80°, 6.5 h	I + II (97), I:II = 1:2.3, II <i>cis</i> :II <i>trans</i> = 1.5:1	55
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, toluene, 80°	 I + II (80), I:II = 2:1	148
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, 80°, 5 h	 I + II (41), I:II = 1.5:1	148

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, toluene, 50°, 10 h toluene, 80°, 6 h <i>n</i> -BuLi, THF, 80°, 6 h toluene, 80°, 24 h	 I + II (79), I:II = 1.5:1 I + II (76), I:II = 1:1 I + II (61), I:II = 1:2 I + II (80), I:II = 1:2	148
		Pd ₂ (dba) ₃ , CHCl ₃ , (<i>i</i> -PrO) ₃ P, toluene, 80°, 6 h	I + II (81), I:II = 1:1.3	148
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, toluene, 80°, 6 h	 (64)	148
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:4), THF, reflux	 I + II (82), I:II = 4.6:1	156
C ₁₃₋₁₉ 		Ni(cod) ₂ 0°, 20 h -10°, 120 h 20°, 14 h 20°, 20 h	 COR (86), 99:1 >99:1 (55), 3.4:1 (63), 1.6:1	133, 134
C ₁₃₋₂₅ 		Ni(cod) ₂ 25°, 7 h 20°, 24 h 0°, 24 h -20°, 24 h 20°, 48 h 0°, 48 h -20°, 72 h 20°, 20 h 0°, 48 h -20°, 72 h 20°, 72 h	 COR (92) 1.1:1 (91) 5.6:1 (86) 6.7:1 (93) 9.1:1 (73) 2.2:1 (60) 5.1:1 (38) 5.3:1 (58) 1.7:1 (44) 1.6:1 (85) 1.9:1 (47) 2.7:1	245, 134

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Ni(cod) ₂		245, 134
R =	R ¹ = H	-20°, 72 h	(78) 1.7:1	
	R ¹ = H	0°, 20 h	(78) 1.7:1	
	R ¹ = H	25°, 7 h	(85) 1.7:1	
	R ¹ = H	40°, 5 h	(90) 1.5:1	
	R ¹ = Ph	20°, 4 h	(86) 4:1	
	R ¹ = Ph	0°, 18 h	(89) 6.7:1	
	R ¹ = Ph	-20°, 24 h	(59) 8.1:1	
R =		toluene, 20°, 16 h	(69) 11:1	
		0°, 16 h	(-) 13:1	
		-20°, 16 h	(-) 21:1	
		-40°, 140 h	(-) 13:1	
C ₁₄				
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:5), <i>n</i> -BuLi, THF, 65-70°	 I + II I + II (65), I:II = 1:5.3	71
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:5), <i>n</i> -BuLi, THF, 65-70°	 (41)	71
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:5), <i>n</i> -BuLi, THF, 65-70°	 (44)	71
		(Ph ₃ P) ₄ Pd, toluene, 80°	 (60)	155
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:4), THF, reflux	 I + II I + II (62), I:II = 3.3:1	156
		[Pd ₂ (dba) ₃ CHCl ₃]/ dppe (1:4), THF, reflux, 24 h	 (61)	70
		[Pd ₂ (dba) ₃ CHCl ₃]/ dppe (1:4), THF, reflux, 18 h	 (73)	70
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:4), <i>n</i> -BuLi, THF, 65-70°	 I + II I + II (80), I:II = 16:1	71

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		—	 I + II (91), I:II = 2.6:1	76
		—	 I + II (95), I:II = 2.6:1	76
C_{14-15} 		$Pd(OAc)_2/(i-PrO)_3P$, toluene, 110°, 12 h	 I + II (79), I:II = 7.3:1 I + II (81), I:II = 1:0	243
$R = Me$ $R = CH_2CF_3$ 		$Pd(OAc)_2/(i-PrO)_3P$, toluene, 110°, 12 h	 I:II = 3.7:1, I + II (55); I:II = 1:0	243
C_{14} 		—	 I + II (92), I:II = 7.5:1	76
C_{15} 		$Pd(OAc)_2/(i-PrO)_3P$ (1:4), THF, reflux	 I + II (80), I:II = 9:1	156
		$Pd(OAc)_2/(i-PrO)_3P$ (1:4), THF, reflux	 I + II (47), I:II = 3:1	156
		$[(EtO)_3P]_2Ni$, toluene, reflux	 I (50)	88

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		(Ph ₃ P) ₄ Pd/dppe, toluene, 115°, 11 h	I (85)	25
		(Ph ₃ P) ₄ Pd, toluene, 80°	 I + II (77), I:II = 4:1	69, 155
		Pd(OAc) ₂ /(i-PrO) ₃ P (1:5), n-BuLi, THF, 65-70°	 I + II (90), I:II = 32:1	71
		Pd(OAc) ₂ /(i-PrO) ₃ P (1:5), n-BuLi, THF, 65-70°	 I + II (89), I:II = 1:3.5	71
C ₁₇ 		(Ph ₃ P) ₄ Pd, toluene, 80°	 I + II (62), I:II = 2.3:1	155
		Pd(OAc) ₂ /(i-PrO) ₃ P	 (84)	157
		(2,4-Pentadionato) ₃ In, Pd(OAc) ₂ , DIBAL-H, Ph ₃ P	 I + II (78), I:II = 4.2:1	160
C ₁₈ 		Pd(OAc) ₂ /(i-PrO) ₃ P	 (70)	157
		—	 (88)	76

TABLE 1. INTERMOLECULAR CYCLOADDITION OF ACYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, <i>n</i> -BuLi, toluene, 115-120°, 30 h	 I + II (61-67), I:II = 4.2:1	148
C ₂₀ 		[Pd ₂ (dba) ₃ CHCl ₃]/ dppf (1:4), THF, 70°	 I + II (88), I:II = 3:1	157
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, <i>n</i> -BuLi, toluene, dioxane, 110°	I + II (>70), I:II = 1:3.4	157
		—	 (80)	157
		—	 (58)	157
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P	 (76-90)	157
C ₂₂ 		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, toluene, 80-85°, 18 h	 I + II (100), I:II = 7.5:1	148
C ₂₄ 		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P	 (90)	157
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, <i>n</i> -BuLi, toluene, 115-120°, 30 h	 (76)	148, 244

TABLE 2. INTERMOLECULAR CYCLOADDITION OF CYCLIC ALKENES AND TMM

43

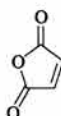
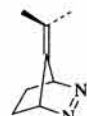
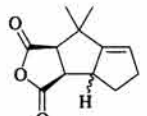
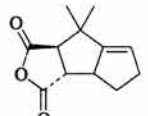
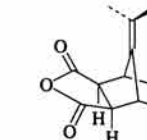
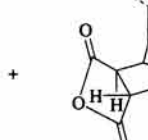
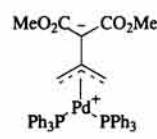
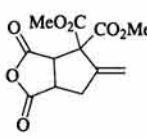


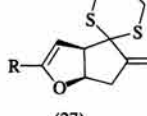
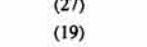


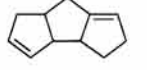
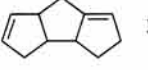

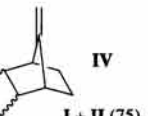


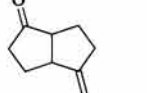
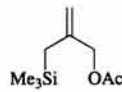
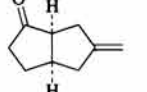

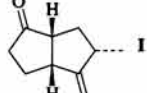
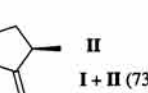
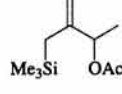
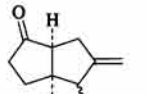

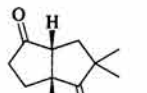
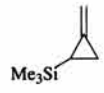
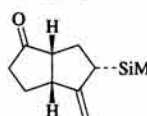
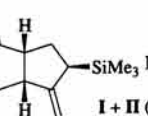
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄ 		MeCN, 60°, 8 h, alkene, 6.6 M	 I +  II +  III +  IV I:II:III:IV = 84:2:23:1	39
		—	 (—)	81
C ₄₋₇  R = H R = SiMe ₃		<i>hν</i> , MeCN, 25° 4 h 48 h	 (27)  (19)	107
C ₅ 		<i>hν</i> (350 nm), 0°	 I +  II +  III +  IV I + II (75), III (23), IV (<2)	44
		Ni(cod) ₂ /Ph ₃ P (1:1), Et ₃ B	 (50)	130
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux	 (56)	69
		Ni(cod) ₂ /Ph ₃ P (1:1), Et ₃ B	 I +  II I + II (73), I:II = 1.7:1	130
		(Ph ₃ P) ₄ Pd/Ph ₃ P, THF, reflux	 (52)	74
		Ni(cod) ₂ /Ph ₃ P (1:1), Et ₃ B	 (37)	130
		Ni(cod) ₂ /Ph ₃ P (1:1), Et ₃ B	 I +  II I + II (50), I:II = 2.1:1	130

TABLE 2. INTERMOLECULAR CYCLOADDITION OF CYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 144°, 5 h	 I + II + III I + II + III (81), I:II:III = 2.4:1:1.3	125
		Cyclopentenone (10 equiv), 70°, 1 h	 I + II + III I + II + III (90-98), I:II:III = 1.3:1:3	80
		[Pd ₂ (dba) ₃ CHCl ₃]/dppf, THF, reflux, 18 h	 (71)	70
		Ni(cod) ₂ /Ph ₃ P (1:1), Et ₃ B	 I + II I + II (68), I:II = 5.6:1	130
		MeCN, 80°, 28 h	 (88)	16
		Ni(cod) ₂ /Ph ₃ P (1:1), Et ₃ B	 (72)	130
		Ni(cod) ₂ /Ph ₃ P (1:1), Et ₃ B	 I + II I + II (75), I:II = 1:1.6	130
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, toluene, reflux	 (75)	75
		(Ph ₃ P) ₄ Pd, toluene, 80°	 I + II I + II (41), I:II = 1:1	155
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, toluene, reflux	 (60)	75

TABLE 2. INTERMOLECULAR CYCLOADDITION OF CYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		—	 (24-30)	84
		[Pd ₂ (dba) ₃ CHCl ₃]/dppe, THF, reflux, 10 h	 (65)	70
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 90°, 3 h	 I (90)	64
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 90°, 3 h	I (97)	64
		MeCN, 1 atm, 80°, 90 h	 I (84)	16
		CH ₂ Cl ₂ , 13 kbar, 70°, 16 h	I (87)	16
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 130°, 6 h	 (61)	64
		Ni(cod) ₂ /(2-PhC ₆ H ₄) ₃ P (1:4.5), THF, 120°, 10 h	 (87)	127
R = Me		Ni(cod) ₂ /(2-PhC ₆ H ₄) ₃ P, (1:1.5), THF, 120°, 5 h	(67)	
R = Ph		Ni(cod) ₂ /(2-PhC ₆ H ₄) ₃ P, (1:1.5), THF, 120°, 5 h	(67)	
R = Ph		Ni(cod) ₂ /(2-PhC ₆ H ₄) ₃ P, (1:4), THF, 120°, 14 h	(84)	
R = Ph		Pd(allyl)Cp, <i>i</i> -Pr ₃ P (1:1), THF, 110°, 22 h	(26)	
		MeCN, 75°, 1.2 h	 I + II (89), I:II = 1.3:1	246
		1. MeCN, reflux 2. DBN, THF, rt	 I + II (67), I:II = 3.6:1	246

TABLE 2. INTERMOLECULAR CYCLOADDITION OF CYCLIC ALKENES AND TMM (Continued)



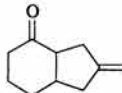
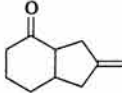
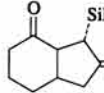
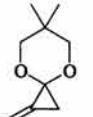
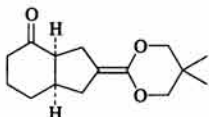

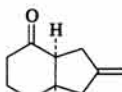
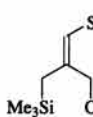
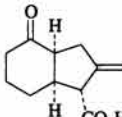
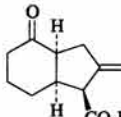

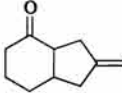
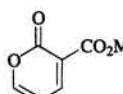

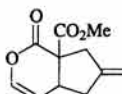
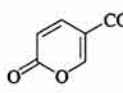

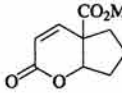
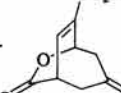






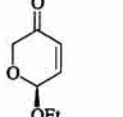

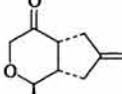



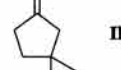
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 110°, 15 h	 I +  II +  III I + II + III (31), (I + II):III = 2.1:1	125
		MeCN, 80°, 28 h	 (85)	16
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux, 20 h	 (17)	25, 154
		(Ph ₃ P) ₄ Pd, toluene, 80°	 I +  II I + II (41), I:II = 1:1	155
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 125°, 3 h	 (76)	64
C ₇ 		Pd(OAc) ₂ / <i>i</i> -PrO ₃ P (1:6), <i>n</i> -BuLi, C ₆ H ₆	 (71)	247
		Pd(OAc) ₂ / <i>i</i> -PrO ₃ P (1:6), <i>n</i> -BuLi, C ₆ H ₆	 I +  II I + II (87), I:II = 1:1-2	247
		Pd(acac) ₂ /Et ₂ Al(OEt)/ <i>i</i> -Pr ₃ P, C ₆ H ₆ , 100°, 2 h reactant:precursor = 2:1 reactant:precursor = 1:2	 I +  II I (80) I (25) + II (39)	124
		Pd(dba) ₂ / <i>i</i> -Pr) ₂ (<i>t</i> -Bu)P, 110°, 0.5 h	 (61)	126
		Pd(OAc) ₂ /Ph ₃ P, <i>n</i> -BuLi, THF, reflux	 (25)	248
		Pd(acac) ₂ /Et ₂ Al(OEt)/ <i>i</i> -Pr ₃ P, C ₆ H ₆ , 100°, 1 h alkene (1 eq) alkene (2 eq)	 I +  II I (78) + II (21) I (96)	124, 22

TABLE 2. INTERMOLECULAR CYCLOADDITION OF CYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(dba) ₂ /(<i>i</i> -Pr) ₂ (<i>t</i> -Bu)P, 110°, 0.5 h	 I + isomer II I + II (66), I:II = 10:1	126
		Ni(cod) ₂ , toluene, 40°, 3 h Pd(0), 80-100°	 (78) (>75)	235
		Pd(dba) ₂ / <i>i</i> -Pr ₃ P (1:1), toluene	 I + II + III (9), I:II:III = 1:1:12 I + II + III (72), I:II:III = 1:1.1:7 I + II + III (72), I:II:III = 1.1:1:3.4	128
		Ni(0), 40-60° Pd(0), 80-100°	 (75) (>75)	235
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 144°, 6 h	 I + II + III (71), (I + II):III = 2.6:1	125
		Pd(allyl)Cp/ <i>i</i> -Pr ₃ P (1:1), 125°, 7 h	 (80)	64
		MeCN, reflux	 I + II (96), I:II = 5:1	246
		Pd(OAc) ₂ , Et ₃ P, THF, reflux	 (6) (46)	147
		Neat, 5-fold excess of diylophile, 75°, 1.2 h	 I + II (94), I:II = 4.5:1	246
		—	 (50)	84

TABLE 2. INTERMOLECULAR CYCLOADDITION OF CYCLIC ALKENES AND TMM (Continued)

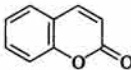
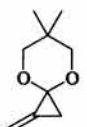
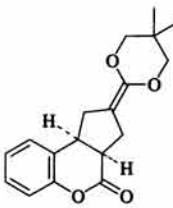
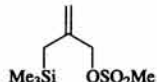
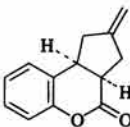
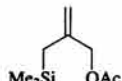
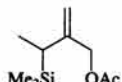
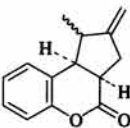
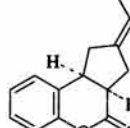
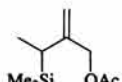
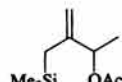
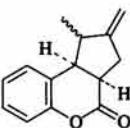
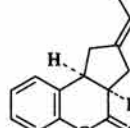
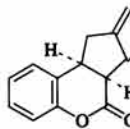
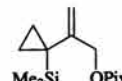
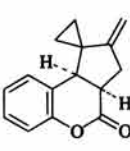
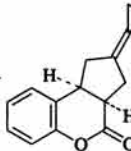
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, 80°, 20 h	 (95)	16
		[(EtO) ₃ P] ₂ Ni, toluene, reflux	 I (77)	88
		(Ph ₃ P) ₄ Pd/dppe, toluene, 115°, 14 h	I (52)	25, 69
		(Ph ₃ P) ₄ Pd/(Ph ₃ P) ₃ , THF, 65°	 I +  II I + II (63), I:II = 10:1	74, 155
		(η ³ -C ₃ H ₅ PdCl) ₂ /(i-PrO) ₃ P, toluene, benzene 15 kbar, 25°	I + II (67), I:II = 14:1	74, 155
		(Ph ₃ P) ₄ Pd/Ph ₃ P, THF, 65°	 I +  II +  III I + II + III (63), I:II:III = 8.9:1:0	74, 153
"		(η ³ -C ₃ H ₅ PdCl) ₂ /Ph ₃ P, toluene, C ₆ H ₆ , 15 kbar, 70°	I + II + III (38), I:II:III = 1:2.2:1	74, 153
"		Pd(OAc) ₂ /(i-PrO) ₃ P, toluene, 9.8 kbar, 25°	I + II + III (12), I:II:III = 1:3.7:0	74, 153
"		Pd(OAc) ₂ /(i-PrO) ₃ P, toluene, 9.8 kbar, 25°	I + II + III (30), I:II:III = 1:1.4:0	74, 153
"		(η ³ -C ₃ H ₅ PdCl) ₂ /(i-PrO) ₃ P, toluene, 9.8 kbar, 25°	I + II + III (71), I:II:III = 1:1.4:0	74, 153
"		(η ³ -C ₃ H ₅ PdCl) ₂ /(i-PrO) ₃ P, toluene, C ₆ H ₆ , 15 kbar, 25°	I + II + III (64), I:II:III = 1.2:1:2.9	74, 153
"		(η ³ -C ₃ H ₅ PdCl) ₂ /tpdp, toluene, C ₆ H ₆ , 15 kbar, 70°	I + II + III (77), I:II:III = 1.1:1:3.1	74, 153
		(i-PrO) ₃ Pd, dioxane, 150°	 I +  II I + II (85), I:II = 8.1:1	242

TABLE 2. INTERMOLECULAR CYCLOADDITION OF CYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, toluene, reflux	 (61)	75
		(Ph ₃ P) ₄ Pd, toluene, 80°	 I + II (62), I:II = 9:1	154, 155
		(Ph ₃ P) ₄ Pd, toluene, 80°	 (81)	154, 155
		(Ph ₃ P) ₄ Pd, toluene, reflux	 (76)	75
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:7), <i>n</i> -BuLi, THF, 60°, 1.5 h	 (69)	249
		Pd(Cp)(allyl)/(<i>i</i> -Pr) ₃ P, toluene, 120°, 5 h	 I + II (77), I:II = 1:7	250
		Pd(OAc) ₂ /Ph ₃ P, solvent, reflux	I + II (81) THF I:II = 1:3 toluene I:II = 1:5.3 DME I:II = 1:4.8 DMF I:II = 1:1.7	250
		MeCN, 80°	 I + II (quant), I:II = 1:2	250
		Pd(Cp)(allyl)/(<i>i</i> -Pr) ₃ P, toluene, 110°, 1 h	 (81) (66)	250
		Pd(Cp)(allyl)/(<i>i</i> -Pr) ₃ P, <i>o</i> -xylene, 120°	 (48)	250

TABLE 2. INTERMOLECULAR CYCLOADDITION OF CYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(Cp)(allyl)/(i-Pr) ₃ P, toluene, 140°, 8 h	(88)	250
C ₉₋₁₀ R = Me R = Et		Pd(OAc) ₂ /(i-PrO) ₃ P, THF, reflux	I + II I + II (85), I:II = 4-5:1 I + II (87), I:II = 4.6:1	149
C ₁₀ 		Ni(cod) ₂ /(2-PhC ₆ H ₄) ₃ P (1:1), THF, 70°, 20 h	(7)	127
		Ni(cod) ₂ /(2-PhC ₆ H ₄) ₃ P (1:1), THF, 110°, 8 h	(44)	127
		Ni(cod) ₂ /(2-PhC ₆ H ₄) ₃ P (1:1), THF, 110°, 8 h	(82)	127
		Ni(cod) ₂ /(2-PhC ₆ H ₄) ₃ P (1:2), toluene, 120°, 2 h	I (83)	127
		Pd(allyl)Cp/i-Pr ₃ P (1:1), THF, 110°, 22 h	I (56)	127
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux	(52)	69
		Pd(OAc) ₂ /(i-PrO) ₃ P (1:10), dioxane, 150°	(50-60)	183
		Pd(OAc) ₂ /(i-PrO) ₃ P, DIBAL-H, dioxane, 100°	(56)	155
		(Ph ₃ P) ₄ Pd, toluene, 80°	I + II I + II (68), I:II = 2.3:1	154, 155

TABLE 2. INTERMOLECULAR CYCLOADDITION OF CYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(acac) ₂ /Et ₂ Al(OEt)/ <i>i</i> -Pr ₃ P, C ₆ H ₆ , 100°, 4 h	 (74)	124
		Pd(OAc) ₂ /Et ₃ P, THF, reflux	 (92)	147
C ₁₀₋₁₂ R = <i>n</i> -C ₅ H ₁₁ R = (CH ₂) ₃ OBU- <i>t</i>		Pd(OAc) ₂ / <i>i</i> -PrO ₃ P, THF, reflux	 (45) (65)	251
C ₁₁ 		(Ph ₃ P) ₄ Pd/dppe, THF, reflux, 40 h	 (58)	25
		Ni(cod) ₂ /Ph ₃ P (1:1), toluene, 80-100°, 5 h	 I (62) + II (0)	66, 69
		Pd(OAc) ₂ / <i>i</i> -PrO ₃ P, THF, reflux	I (63)	149
		(Ph ₃ P) ₄ Pd/dppe, THF, reflux	I + II (72), I:II = 4:1	60
		Pd(OAc) ₂ / <i>i</i> -PrO ₃ P, THF, reflux	 I + II E = CO ₂ Me I + II (71), I:II = 5:1	149
C ₁₁₋₁₄ 		Pd(OAc) ₂ / <i>i</i> -PrO ₃ P, <i>n</i> -BuLi, THF, 60°	 I + II I (48) + II (39) I (38) + II (26) I (33) + II (48)	249
		1.5 h overnight 6 h		
C ₁₂ 		[Pd ₂ (dba) ₃ CHCl ₃]/Ph ₃ P, THF, 70°, 6 h	 I + II I + II (54), I:II = 2:1	154
C ₁₃ 		Pd(OAc) ₂ / <i>i</i> -PrO ₃ P, THF, reflux	 (7)	149

TABLE 2. INTERMOLECULAR CYCLOADDITION OF CYCLIC ALKENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		(Ph ₃ P) ₄ Pd, toluene, 80°		(66) 155
C ₁₄ 		Pd(OAc) ₂ /Ph ₃ P, <i>n</i> -BuLi, THF, reflux, 4 h		(94) 248, 146
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, THF, reflux		(29) 149
		(Ph ₃ P) ₄ Pd, toluene, 80°		(70) 155
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, toluene, 150°		I + II (51), I:II = 2:1 148
C ₁₄₋₁₅ 		Pd(OAc) ₂ /Ph ₃ P, <i>n</i> -BuLi, THF, reflux		(70) 248, 146
			(70)	
			(70)	
C ₁₄₋₂₈ 		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P Pd(PPh ₃) ₄ Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P		I + II (53), I:II = 9:1 I + II (36), I:II = 8.5:1 I + II (35), I:II = 5.5:1 I + II (72), I:II = 6.3:1 I + II (56), I:II = 5.4:1 77
C ₁₅₋₂₉ 		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P Pd(PPh ₃) ₄ Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P		I + II (50), I:II = 4.6:1 I + II (12), I:II = 4:1 I + II (50), I:II = 3:1 I + II (54), I:II = 8:1 77
C ₁₈₋₁₉ 		Pd(OAc) ₂ /P(OEt) ₃ THF, reflux		(5) (71) 180

TABLE 2. INTERMOLECULAR CYCLOADDITION OF CYCLIC ALKENES AND TMM (Continued)

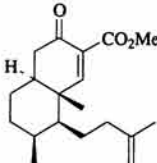
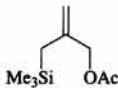
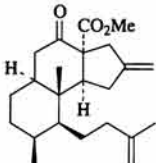

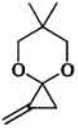
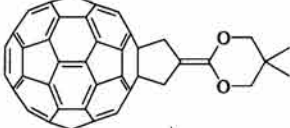
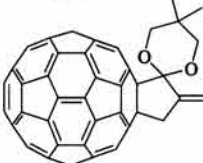
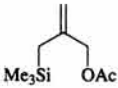
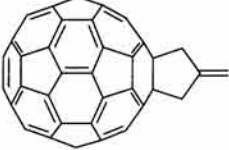
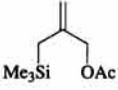

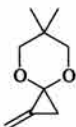
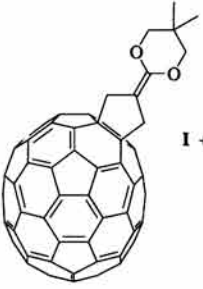
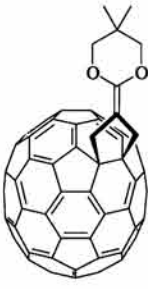

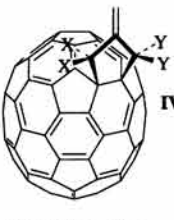
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₉ 		Pd(OAc) ₂ /(EtO) ₃ P, THF, reflux	 (98)	147
C ₆₀ 		1,2-Cl ₂ C ₆ H ₄ , 70°, overnight	 I +  II I + II (61), I:II = 1:1.3	173
		Pd(PPh ₃) ₄ , toluene, reflux, 48 h	 I (33)	252
		Pd(PPh ₃) ₄ , benzene, reflux, 72 h	I (25)	253
C ₇₀ 		1,2-Cl ₂ C ₆ H ₄ , 80-90°, 26 h	 I +  II +  III +  IV	254
X, X = OCH ₂ CMe ₂ CH ₂ O, Y, Y = H or X, X = H, Y, Y = OCH ₂ CMe ₂ CH ₂ O I + II (32), III + IV (25), I:II = 1:1, III:IV = 1:1.5				

TABLE 3. INTERMOLECULAR CYCLOADDITION OF ALKYNES OR ALLENES AND TMM

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃ H ₂ C=CH ₂		Pd(acac) ₂ /Et ₂ Al(OEt)/ <i>i</i> -Pr ₃ P (1:1:2), 100°, 2 h	 I (40) + II (10)	255
		Pd(dba) ₂ / <i>i</i> -Pr ₃ P (1:1), 100°, 2 h	I (14) + II (25)	255
C ₆ MeO ₂ C≡CO ₂ Me		THF, reflux	 (76)	85
		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 I + II +	132
			 III I + II + III (48), I:II:III = 1:5.2:2.1	
Me ₃ Si≡SOMe		MeCN, 80°, 14 h	 (88)	107
C ₇ MeO ₂ C-CH=CH-CO ₂ Me		Solvent, reflux, slow addition of precursor, 4.5 h	 (15)	86
			 (70)	
Me ₃ Si≡CO ₂ Me		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 (72)	132
		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 I + II +	132
			 III I + II + III (64), I:II:III = 2:1:1.8	
		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 I + II +	132
			 III I + II + III (65), I:II:III = 1.1:1:2.4	

TABLE 3. INTERMOLECULAR CYCLOADDITION OF ALKYNES OR ALLENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, 80°, 18 h	 I + II (72), I:II = 13:1	107
		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 I + II + III (63), I:II:III = 1.1:1:1.5	132
		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 (63)	132
<i>n</i> -Bu-C≡C-SOMe		MeCN, 100°, 27 h	 (63)	107
<i>n</i> -Bu-C≡C-SO ₂ Me		MeCN, 100°, 27 h	 (85)	107
Me ₃ Si-C≡C-Et		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 (48)	132
		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 I + II (88), I:II = 5.7:1	132
		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 I + II + III (92), I:II:III = 3.8:1.5:1	132
C ₈ Me ₃ Si-C≡C-SiMe ₃		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 (50)	132

TABLE 3. INTERMOLECULAR CYCLOADDITION OF ALKYNES OR ALLENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h		132
		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 I + II (71), I:II = 1:1.1	132
<i>n</i> -Bu-C≡C-CO ₂ Me		MeCN, 100°, 56 h	 I (49), I:II = 4.6:1	107
C ₉ H ₂ C=C(Ph)CH ₂ Ph	 I + II I:II = 3:1	25°	 (-)	80
Ph-C≡C-SO ₂ Me		MeCN, 80°, 26 h	 I (66), I:II = 4.6:1	107
Me ₃ Si-C≡C-CO ₂ Pr- <i>i</i>		MeCN, 100°, 10 h		107
Me ₃ SiO-C≡C-SiMe ₃		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h		132
		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 I + II + III (64), I:II:III = 1:10:5.7	132
		Ni(cod) ₂ /(2-PhC ₆ H ₄ O) ₃ P (1:1), 80°, 5-8 h	 I + II + III (90), I:II:III = 27:1:13	132

TABLE 3. INTERMOLECULAR CYCLOADDITION OF ALKYNES OR ALLENES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ Ph-C≡C-CO ₂ Me		MeCN, 80°, 29 h	 I (58), I:II = 2.1:1	107
C ₁₂ THPO-CH ₂ -C≡C-CO ₂ Pr- <i>i</i>		MeCN, 80°, 44 h	 I (61), I:II = 4.6:1	107
C ₁₃ 		MeCN, 100°, 36 h	 I (68), I:II = 4.:1	107

TABLE 4. INTRAMOLECULAR CYCLOADDITION OF ALKENES AND TMM

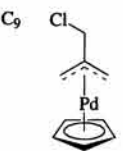
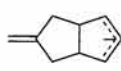
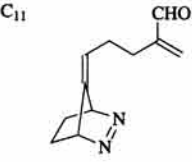
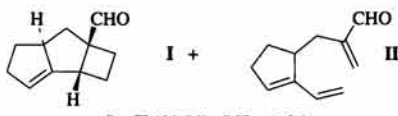
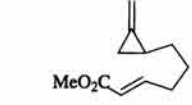
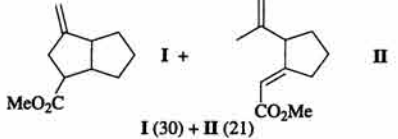
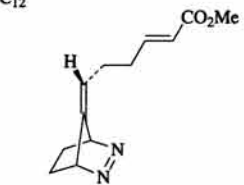
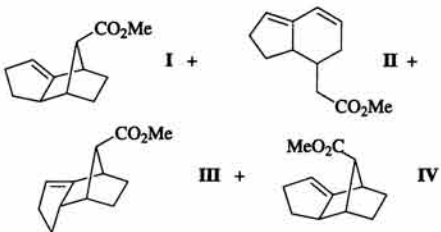
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₉</p> 	CD ₃ NO ₂ , 25°	 -PdCl (66)	256
<p>C₁₁</p> 	THF, 67°, 3 h	 I + II I + II (66-85), I:II = 1.6:1	95
	Pd(allyl)Cp/ <i>i</i> -Pr ₃ P, <i>o</i> -xylene, 137°	 I + II I (30) + II (21)	144
<p>C₁₂</p> 	THF, reflux	 I + II + III + IV I + II + III + IV (83), I:II:III:IV = 16.5:1.5:1	95

TABLE 4. INTRAMOLECULAR CYCLOADDITION OF ALKENES AND TMM (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	PdCl ₂ (PPh ₃) ₂ , DIBAL-H, toluene, 90°	(74)	143
	THF, reflux, 3-4 h	I + II + III + IV I + II + III + IV (91), I:II:III:IV = 13:1:12:15	93
	Pd(allyl)Cp/ <i>i</i> -Pr ₃ P, <i>o</i> -xylene, 120°	(87)	144
C_{12-13} 	Me ₃ NO, benzene, 80°	(40) (42)	169
C_{13} 	Me ₃ NO, benzene, 80°	I (52) + II (5)	169
	THF (0.1 M), reflux	I + II I + II (76), I:II = 5:1	92
	MeCN, 81° MeCN, <i>hν</i> , 6° MeOH, 61° MeOH, <i>hν</i> , 6° MeOH, <i>hν</i> , -60°	I I + sum of minor isomers (Mir) I:Mir (-) 3.8:1 (87-96) 9.1:1 (-) 4.7:1 (-) 9.1:1 (-) 30:1	98, 99
	THF, reflux, 3-4 h	I + II + III + IV I + II + III + IV (98), I:II:III:IV = 32:1:3:2	93

TABLE 4. INTRAMOLECULAR CYCLOADDITION OF ALKENES AND TMM (Continued)

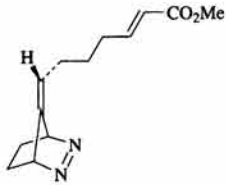
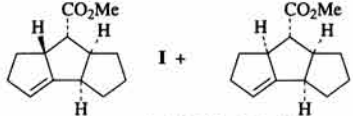
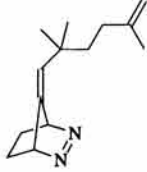
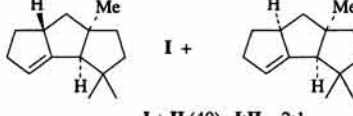
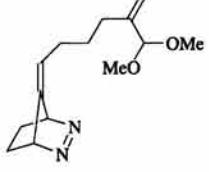
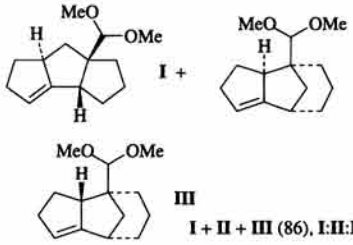
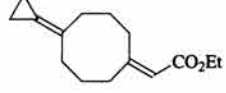
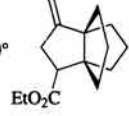
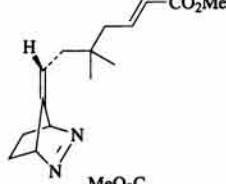
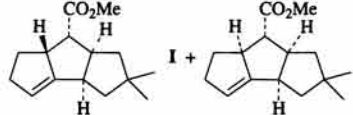
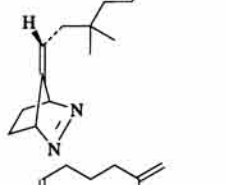
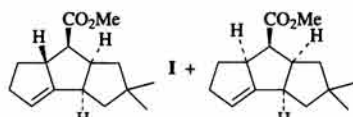
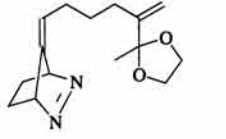
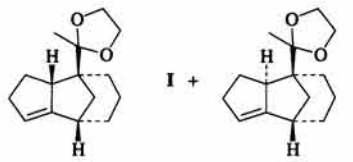
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeCN, reflux	 I + II (87), I:II = 7:1	91
C ₁₄ 	MeCN, reflux, 10 h	 I + II (40), I:II = 2:1	91
	THF, reflux, 3-4 h	 I + II + III (86), I:II:III:IV = 12:1:1.4	93
C ₁₅ 	Ni(cod) ₂ /Ph ₃ P, toluene, 110° Ni(acac) ₂ , DIBAL-H, Ph ₃ P, toluene, 90° PdCl ₂ (PPh ₃) ₂ , DIBAL-H, toluene, 130°	 I (74)	142, 143
	MeCN, reflux, 6 h	 I + II (85), I:II = 9:1	89, 90, 91
	MeCN, reflux, 6 h	 I + II (87), I:II = 3:1	91
	MeCN, reflux, 48 h	 I + II (80), I:II = 1:1	185

TABLE 4. INTRAMOLECULAR CYCLOADDITION OF ALKENES AND TMM (Continued)

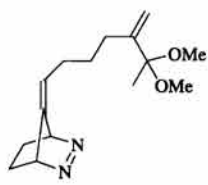
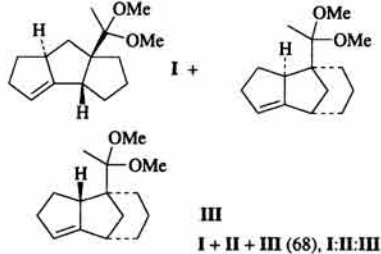
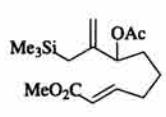
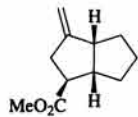
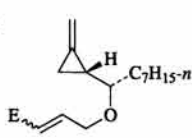
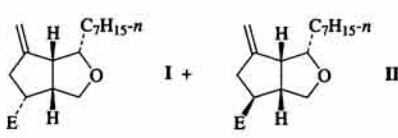
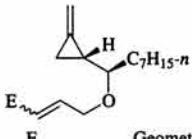
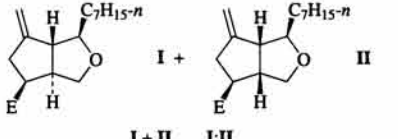
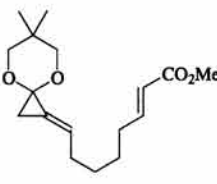
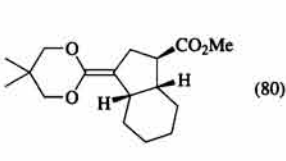
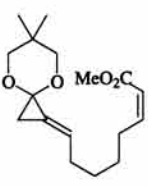
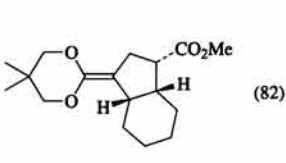
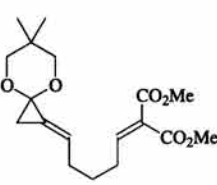
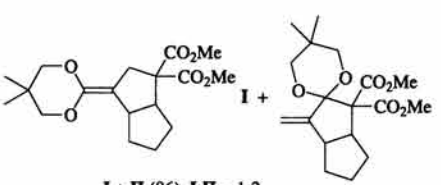
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																								
	THF, reflux, 3-4 h	 I + II + III (68), I:II:III = 1:8.2:7.5	93																								
<p>C₁₆</p> 	(Ph ₃ P) ₄ Pd/dppe, BSA, THF, reflux	 (51)	165																								
<p>C₁₆₋₂₁</p>  <table border="1" data-bbox="295 929 590 1113"> <thead> <tr> <th>E</th> <th>Geometry of Alkene</th> </tr> </thead> <tbody> <tr> <td>CO₂Et</td> <td>E</td> </tr> <tr> <td>CO₂Et</td> <td>Z</td> </tr> <tr> <td>COMe</td> <td>E</td> </tr> <tr> <td>SO₂Ph</td> <td>E</td> </tr> <tr> <td>CN</td> <td>Z:E = 1:2</td> </tr> </tbody> </table>	E	Geometry of Alkene	CO ₂ Et	E	CO ₂ Et	Z	COMe	E	SO ₂ Ph	E	CN	Z:E = 1:2	Pd(PPh ₃) ₄ , toluene, reflux, 2-5 h	 <table border="1" data-bbox="1006 929 1128 1113"> <thead> <tr> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>(78)</td> <td>1:0</td> </tr> <tr> <td>(75)</td> <td>1:0</td> </tr> <tr> <td>(81)</td> <td>1:0</td> </tr> <tr> <td>(60)</td> <td>1:0</td> </tr> <tr> <td>(92)</td> <td>1:1</td> </tr> </tbody> </table>	I + II	I:II	(78)	1:0	(75)	1:0	(81)	1:0	(60)	1:0	(92)	1:1	58
E	Geometry of Alkene																										
CO ₂ Et	E																										
CO ₂ Et	Z																										
COMe	E																										
SO ₂ Ph	E																										
CN	Z:E = 1:2																										
I + II	I:II																										
(78)	1:0																										
(75)	1:0																										
(81)	1:0																										
(60)	1:0																										
(92)	1:1																										
 <table border="1" data-bbox="295 1297 590 1435"> <thead> <tr> <th>E</th> <th>Geometry of Alkene</th> </tr> </thead> <tbody> <tr> <td>CO₂Et</td> <td>E</td> </tr> <tr> <td>CO₂Et</td> <td>Z</td> </tr> <tr> <td>SO₂Ph</td> <td>E</td> </tr> <tr> <td>CN</td> <td>Z:E = 1:4</td> </tr> </tbody> </table>	E	Geometry of Alkene	CO ₂ Et	E	CO ₂ Et	Z	SO ₂ Ph	E	CN	Z:E = 1:4	Pd(PPh ₃) ₄ , toluene, reflux, 2-5 h	 <table border="1" data-bbox="1006 1297 1128 1435"> <thead> <tr> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>(87)</td> <td>1:1</td> </tr> <tr> <td>(83)</td> <td>1:1</td> </tr> <tr> <td>(86)</td> <td>4:1</td> </tr> <tr> <td>(91)</td> <td>1:1.5</td> </tr> </tbody> </table>	I + II	I:II	(87)	1:1	(83)	1:1	(86)	4:1	(91)	1:1.5	58				
E	Geometry of Alkene																										
CO ₂ Et	E																										
CO ₂ Et	Z																										
SO ₂ Ph	E																										
CN	Z:E = 1:4																										
I + II	I:II																										
(87)	1:1																										
(83)	1:1																										
(86)	4:1																										
(91)	1:1.5																										
<p>C₁₇</p> 	MeCN, 80°, 16 h	 (80)	113																								
	MeCN, 80°, 32 h	 (82)	113																								
<p>C₁₈</p> 	MeCN, 80°, 1.5 h	 I + II (86), I:II = 1:2	112, 113																								

TABLE 4. INTRAMOLECULAR CYCLOADDITION OF ALKENES AND TMM (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Pd(PPh ₃) ₄ , toluene, reflux, 4 h	 I + II + III + IV (25); I:II:III:IV = 1:1:1:1	58
	Pd(PPh ₃) ₄ , toluene, reflux, 1 h	 I + II (54), I:II = 1:1	58
	1. Pd ₂ (dba) ₃ /(<i>i</i> -PrO) ₃ P, toluene, 110° 2. DIBAL-H, toluene, -78°	 I + II (36), I:II = 5:1	257, 143
	MeCN, 80°, 5 h	 I + II (81), I:II = 1:1.8	113
	MeCN, reflux	 I + II (80-91), I:II = 11.8:1	97
	MeCN, reflux, 2.5 h	 I + II + III (91), I:II:III = 13.6:1.15:1	97, 258
	<i>hν</i> , MeCN, 7°	 I + II + III (85), I:II:III = 26:1:1.5	97, 258
	Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:6) THF, 60° BSA, dioxane, 100°	 I + II (34), I:II = 1:1.2 I + II (72), I:II = 1:7.2	168

TABLE 4. INTRAMOLECULAR CYCLOADDITION OF ALKENES AND TMM (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Pd(OAc) ₂ /dppe, BSA, <i>m</i> -xylene, reflux, overnight	 I + II + III (70), I:II:III = 10:1:2	184
	Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, 100°	 I + II + III (47), I:II:III = 5.4:2:1	168
	(Ph ₃ P) ₄ Pd/dppe, BSA, THF, reflux	 (45)	165
C ₂₁ 	Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, Me ₃ SnOAc, MS, toluene	 (71)	167
	Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P (1:6), BSA, dioxane, 100-110°	 (75)	168
	Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P (1:6), BSA, THF, rt, 18 h	 (81)	168
	(Ph ₃ P) ₄ Pd/dppe, BSA, THF, reflux	 I + II (73), I:II = 2:1	165
C ₂₂ 	Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, 100°	 I + II (66), I:II = 2.4:1	168
	(Ph ₃ P) ₄ Pd/dppe, BSA, THF, reflux	 (33)	165

TABLE 4. INTRAMOLECULAR CYCLOADDITION OF ALKENES AND TMM (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:6), dioxane, 100°	I + II (51), I:II = 8.2:1	168
	Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:6), dioxane, reflux	I + II (62), I:II = 1.7:1	166
	(Ph ₃ P) ₄ Pd/dppe, BSA, THF, reflux	I + II + III + IV + V (68), I:II:III:IV:V = 8:4:3:1:1	166
C ₂₃ 	Pd(dba) ₂ /(<i>i</i> -PrO) ₃ P (1:1), toluene, 110°, 42 h	(47)	140, 141
	Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:6), dioxane, reflux	I + II + III (63), I:II:III = 25:7:1	166
C ₂₄ 	Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P (1:6), dioxane, reflux	I + II + III (78), I:II:III = 9:8:1	166

TABLE 4. INTRAMOLECULAR CYCLOADDITION OF ALKENES AND TMM (Continued)

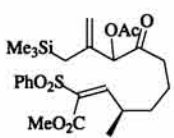
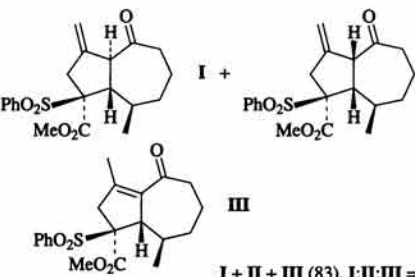
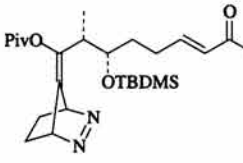
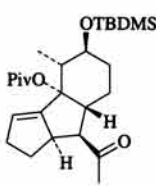
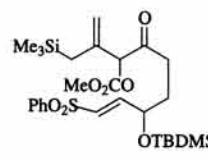
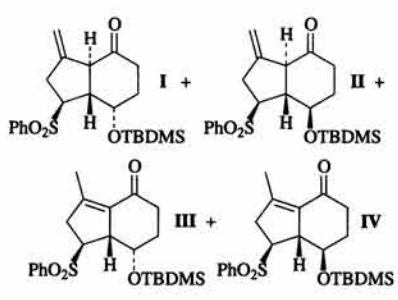
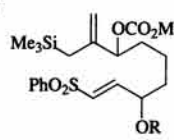
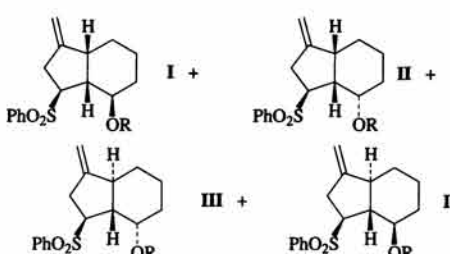
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₅</p> 	<p>Pd(OAc)₂/(<i>i</i>-PrO)₃P, Me₃SnOAc, MS, toluene</p>	 <p>I + II + III (83), I:II:III = 9.5:5:1</p>	167
<p>C₂₆</p> 	<p>MeCN, reflux</p>	 <p>(80-90)</p>	96
<p>C₂₇</p> 	<p>Pd(OAc)₂/(<i>i</i>-PrO)₃P, THF, rt, 9 h</p>	 <p>I + II + III + IV (90), I:II:III:IV = 2:8:2:1</p>	168
<p>C₂₇₋₃₇</p>  <p>R = TBDMS R = TBDPS</p>	<p>Pd(OAc)₂/(<i>i</i>-PrO)₃P, BSA, THF</p>	 <p>I + II + III + IV (76-82), I:II:III:IV = 4:3:2:1, I:II:III:IV = 9:4:2:1</p>	165

TABLE 4. INTRAMOLECULAR CYCLOADDITION OF ALKENES AND TMM (Continued)

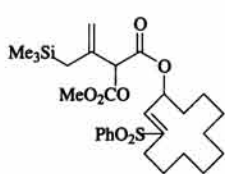
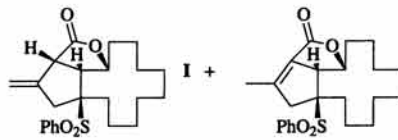
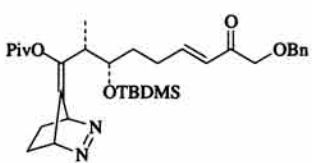
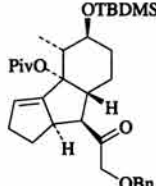
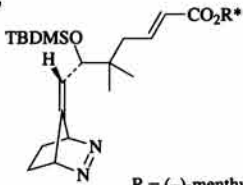
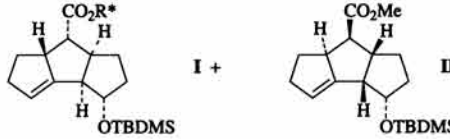
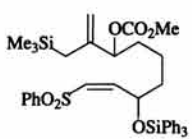
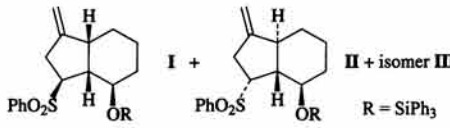
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₈</p> 	<p>Pd(OAc)₂/(<i>i</i>-PrO)₃P (1:6), dioxane, rt</p>	 <p>I + II (64), I:II = 1.6:1</p>	166
<p>C₃₃</p> 	<p>MeCN, reflux</p>	 <p>(85)</p>	96
<p>C₃₀₋₃₆</p>  <p>R = (-)-menthyl R = (-)-8-phenylmenthyl</p>	<p>MeCN, reflux</p>	 <p>I + II (83), I:II = 5.6 (1:1.2 ds):1 I + II (84), I:II = 3.3 (1:1.2 ds):1</p>	100
<p>C₃₉</p> 	<p>Pd(OAc)₂/(<i>i</i>-PrO)₃P</p>	 <p>I + II + III (67), I:II:III = 5.2:4.5:1 R = SiPh₃</p>	165

TABLE 5. INTRAMOLECULAR CYCLOADDITION OF ALKYNES AND TMM

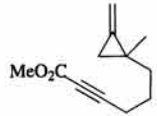
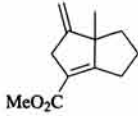
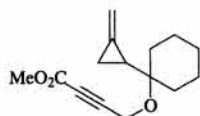
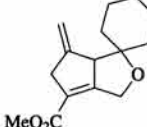
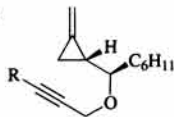
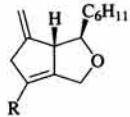
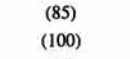
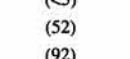
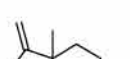
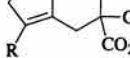
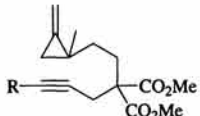
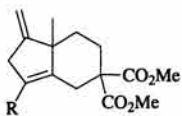
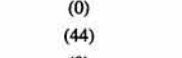
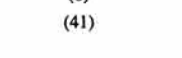

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₂</p> 	<p>Pd₂(dba)₃/(<i>i</i>-PrO)₃P (1:4), toluene, 110°</p>	 (54)	259
<p>C₁₅</p> 	<p>Pd₂(dba)₃/(<i>i</i>-PrO)₃P (1:2), toluene, reflux, 1.5-2 h</p>	 (68)	57
<p>C₁₅₋₂₁</p>  <p>R = CH₂OH R = CH₂OTBDMS R = Me R = COMe R = COMe</p>	<p>Pd₂(dba)₃/(<i>i</i>-PrO)₃P, toluene, reflux, 3 h</p> <p>Pd(PPh₃)₄, toluene, reflux, 2-4 h</p>	 (85)  (100)  (<5)  (52)  (92)	57, 240
 <p>R = H R = CN R = SiMe₃ R = SO₂Ph</p>	<p>Pd₂(dba)₃/(<i>i</i>-PrO)₃P (1:2), toluene, 110°</p>	 (0)  (44)  (0)  (41)	259

TABLE 5. INTRAMOLECULAR CYCLOADDITION OF ALKYNES AND TMM (Continued)

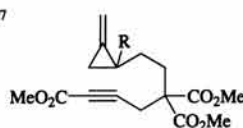
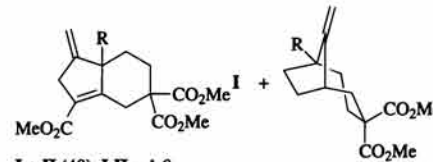
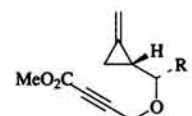
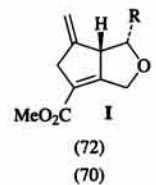
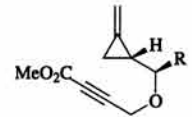
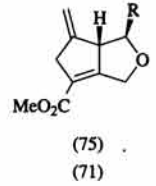
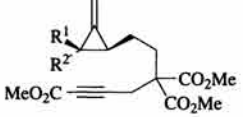
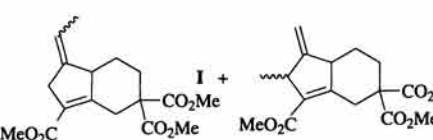
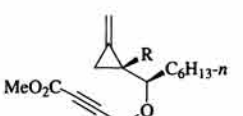
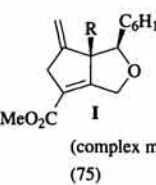
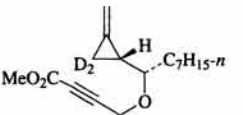
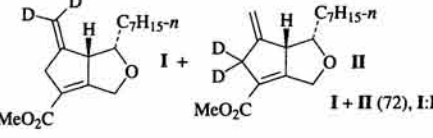
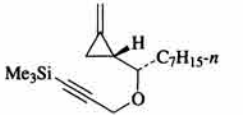
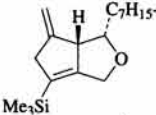
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₆₋₁₇</p>  <p>R = H R = Me</p>	<p>Pd(dba)₂/(<i>i</i>-PrO)₃P, toluene, 110°, 42 h</p>	 <p>I + II (40), I:II = 1:0 I + II (59), I:II = 1:0</p>	139, 259
<p>R = H R = Me</p>	<p>Ni(cod)₂, toluene, 0°</p>	<p>I + II (20), I:II = 0:1 I + II (50), I:II = 0:1</p>	139, 259
 <p>R = <i>c</i>-C₆H₁₁ R = <i>n</i>-C₇H₁₅ R = <i>n</i>-C₇H₁₅</p>	<p>Pd₂(dba)₃/(<i>i</i>-PrO)₃P (1:2), toluene, reflux, 1.5-2 h</p>	 <p>I (72) I (70)</p>	57, 240
<p>R = <i>c</i>-C₆H₁₁ R = <i>n</i>-C₇H₁₅</p>	<p>Pd(PPh₃)₄, toluene, reflux, 2 h</p>	<p>I (83)</p>	57, 240
 <p>R = <i>c</i>-C₆H₁₁ R = <i>n</i>-C₇H₁₅</p>	<p>Pd₂(dba)₃/(<i>i</i>-PrO)₃P (1:2), toluene, reflux, 1.5-2 h</p>	 <p>I (75) I (71)</p>	57, 240
<p>C₁₇</p>  <p>R¹ = Me, R² = H R¹ = H, R² = Me</p>	<p>Pd₂(dba)₃/(<i>i</i>-PrO)₃P, toluene, 110°</p>	 <p>I + II (59), I:II = 5:1 I + II (21), I:II = 5:1</p>	144
 <p>R = Me R = OMe R = Me</p>	<p>Pd₂(dba)₃/(<i>i</i>-PrO)₃P (1:2), toluene, reflux, 1.5-2 h</p>	 <p>I (75) (complex mixture)</p>	57
<p>R = Me</p>	<p>Pd(PPh₃)₄, toluene, reflux, 2 h</p>	<p>I (43)</p>	57
 <p>D₂ C₇H_{15-n}</p>	<p>Pd₂(dba)₃/(<i>i</i>-PrO)₃P (1:4), toluene, reflux, 7 h</p>	 <p>I + II (72), I:II = 1:1</p>	240, 57
<p>C₁₈</p>  <p>Me₃Si C₇H_{15-n}</p>	<p>Pd(PPh₃)₄, toluene, reflux, 12 h</p>	 <p>I (46)</p>	57

TABLE 5. INTRAMOLECULAR CYCLOADDITION OF ALKYNES AND TMM (Continued)

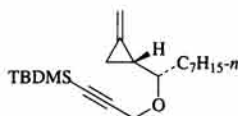
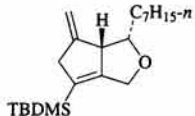
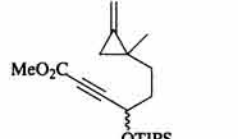
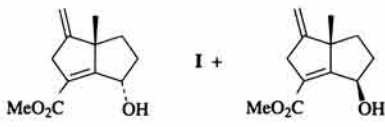
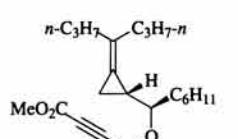
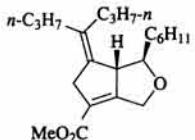
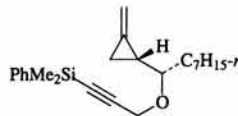
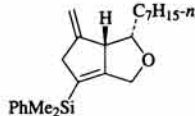
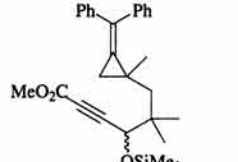
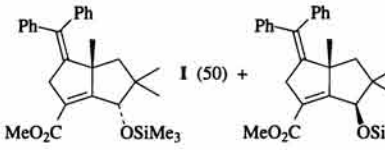
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₁ 	Pd ₂ (dba) ₃ / <i>i</i> -PrO) ₃ P (1:2), MS, toluene, reflux, 12 h	 (40)	57
	1. Pd ₂ (dba) ₃ / <i>i</i> -PrO) ₃ P (1:4), toluene, 110° 2. TBAF, THF	 I + II (61), I:II = 1:1	259
C ₂₂ 	Pd ₂ (dba) ₃ / <i>i</i> -PrO) ₃ P (1:2), toluene, reflux, 1.5-2 h	 (58)	57
C ₂₃ 	Pd(PPh ₃) ₄ , toluene, reflux, 12 h	 (40)	57
C ₂₉ 	Pd(dba) ₂ / <i>i</i> -PrO) ₃ P (1:1), toluene, 110°	 I (50) + II (38)	140, 141

TABLE 6. INTERMOLECULAR CYCLOADDITION OF CARBONYL COMPOUNDS AND TMM


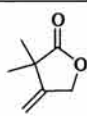
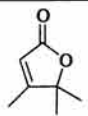

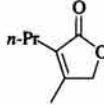
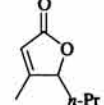

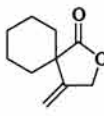
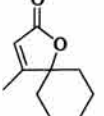


	Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁					
	CO ₂		C ₆ H ₆ , 40 atm CO ₂ , 130°, 20 h Pd(dba) ₂ /Ph ₃ P (1:4) Pd(dppe) ₂ Pd(dba) ₂ /(EtO) ₃ P (1:4) Pd(dba) ₂ / <i>n</i> -Bu ₃ P (1:4) Pd(dba) ₂ /Me ₂ P(CH ₂) ₂ PMe ₂ (1:2)	 I +  II I (69) + II (8) I (trace) + II (48) I (8) + II (trace) I (1) + II (5) I (4) + II (7)	136
			C ₆ H ₆ , 40 atm CO ₂ , 130°, 20 h Pd(Ph ₃ P) ₄ Pd(dppe) ₂	 I +  II I (38) + II (29) I (14) + II (12)	136
			C ₆ H ₆ , 40 atm CO ₂ , 130°, 20 h Pd(dba) ₂ /Ph ₃ P (1:4) Pd(dppe) ₂	 I +  II I (32) + II (trace) I (5) + II (21)	136
	(CH ₂ O) _n		ZnCl ₂ , THF, reflux	 (87)	85

TABLE 6. INTERMOLECULAR CYCLOADDITION OF CARBONYL COMPOUNDS AND TMM (Continued)

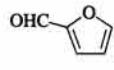
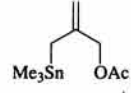
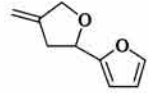
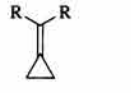
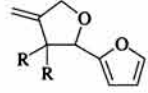
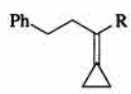
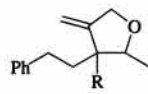
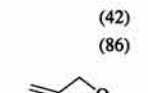
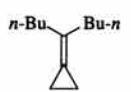
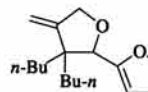
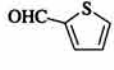
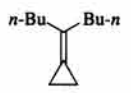
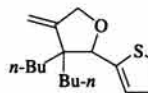
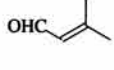
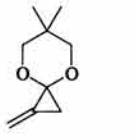
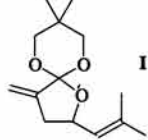
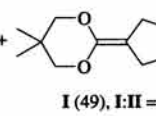
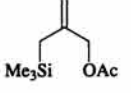
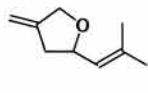
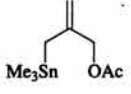
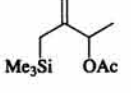
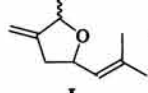
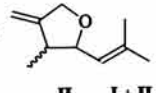
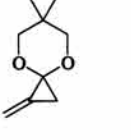
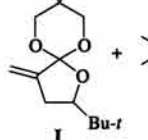
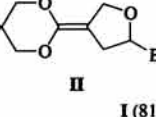
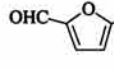
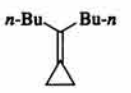
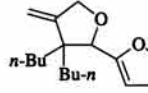

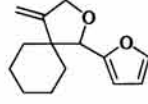
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅ 		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, dioxane, 40°	 (81)	159
		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), neat, 120°	 (75)	135
	R = <i>n</i> -C ₄ H ₉ R = <i>n</i> -C ₆ H ₁₃	5 h 11 h	(71)	
		R = H R = Me	20 h 16 h	 (42)  (86)
		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), neat, 120°, 12 h	 (51)	135
		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), neat, 120°, 19 h	 (64)	135
		Toluene, 80-100°, 19 h	 I +  II I (49), I:II = 2:1	110
		Pd(OAc) ₂ /Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, THF, reflux	 I (80)	260, 146
		Pd(OAc) ₂ /Ph ₃ P, THF, reflux	I (73)	146
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOAc	 I +  II I + II (68), I:II = 2.7:1	161
<i>n</i> -BuCHO		Toluene, 100°, 63 h	 I +  II I (81), I:II = 13:1	110
C ₆ 		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), neat, 120°, 6 h	 (65)	135
		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), neat, 120°, 20 h	 (77)	135

TABLE 6. INTERMOLECULAR CYCLOADDITION OF CARBONYL COMPOUNDS AND TMM (Continued)


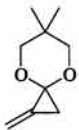
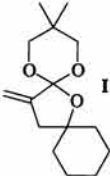
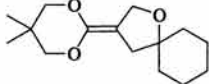

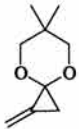
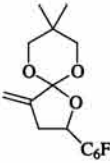
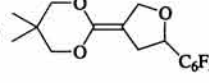
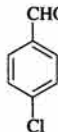
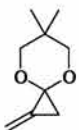
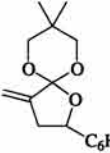
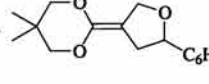
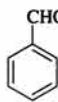

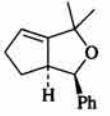
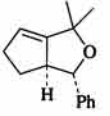
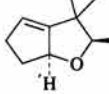
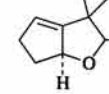
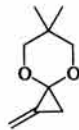
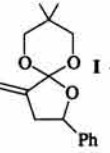
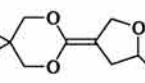
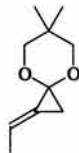
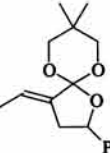
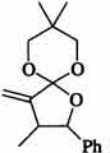
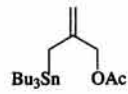
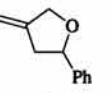
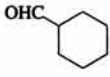
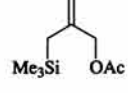

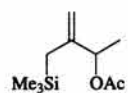
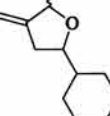
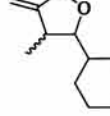
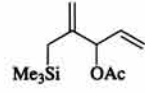
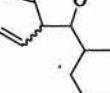
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Toluene, 130°, 18 h	 I +  II I (56), I:II = 24:1	110
C ₇ 		Toluene, 80°, 4 h	 I +  II I (75), I:II = 12:1	110
		Toluene, 80°, 8 h	 I +  II I (81), I:II = 6.7:1	110
		THF, reflux	 I +  II +  III +  IV I + II + III + IV (78), I:II:III:IV = 8.4:1:9.6:1	85
		Toluene, 80°, 11 h	 I +  II I (84), I:II = 8.1:1	110
		C ₆ H ₆ , 80°, 21 h	 I +  II I + II (85), I:II = 2.9:1	110
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P dioxane, reflux	 (100)	159
		Pd(OAc) ₂ /Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, THF, reflux	 (88)	260, 146
		Pd(OAc) ₂ /Ph ₃ P <i>n</i> -Bu ₃ SnOAc Me ₃ SnOAc	 I +  II I + II (46), I:II = 1.1:1 I + II (82), I:II = 3.1:1	161
		Pd(OAc) ₂ / <i>i</i> -Pr ₃ P, Me ₃ SnOAc, C ₆ H ₆	 (82)	161

TABLE 6. INTERMOLECULAR CYCLOADDITION OF CARBONYL COMPOUNDS AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ /tpdp, dioxane, 100°		(57) 162
		Toluene, 80°, 4 h		I + II I (84), I:II = 24:1 110
		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), neat, 120°, 19 h		(43) 135
		Toluene, 80°, 20 h		I + II I (82), I:II = 6.7:1 110
		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), neat, 120°, 32 h		(38) 135
		Toluene, 100°, 30 h		I + II I (81), I:II = 13:1 110
		THF, reflux		(75) 85
		THF, reflux		I + II + III (63), I:II:III = 1.6:1.1:1 85
		(2,4-pentadionato) ₃ In, [Pd ₂ (dba) ₃ CHCl ₃]/Ph ₃ P, dioxane		(81) 160
		Pd(OAc) ₂ /(i-PrO) ₃ P, dioxane, reflux, slow addition of TMM precursor		I (75) 146

TABLE 6. INTERMOLECULAR CYCLOADDITION OF CARBONYL COMPOUNDS AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ /Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, THF, reflux	I (89)	260
		Pd(OAc) ₂ /Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, THF, reflux	I (95)	146
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, reflux	I (65)	159
		Pd(OAc) ₂	 I + II	161
		Ph ₃ P, THF	I + II (30), I:II = 1:1	
		Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, THF	I + II (48), I:II = 1.6:1	
		Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, C ₆ H ₆	I + II (85), I:II = 1.6:1	
		Ph ₃ P, Me ₃ SnOAc, THF	I + II (95), I:II = 3.3:1	
		Ph ₃ P, Me ₃ SnOAc, C ₆ H ₆	I + II (86), I:II = 12:1	
		Ph ₃ P, Me ₃ SnOAc, C ₆ H ₁₂	I + II (55), I:II = 2.6:1	
		TIPP, Me ₃ SnOAc, C ₆ H ₆	I + II (64), I:II = 1.5:1	
		Ph ₃ P, (AcOSnBu ₂) ₂ O, C ₆ H ₆	I + II (80), I:II = 3.4:1	
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOTs, C ₆ H ₆	I + II (82), I:II = 32:1	161
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOAc, C ₆ H ₆	I + II (94), I:II = 1:200	161
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, Me ₃ SnOAc	 I + II (good)	242
		(Ph ₃ P) ₄ Pd, Me ₃ SnOTs, 8 h	 I + II	161
			I + II (50), I:II = 6:1	
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOTs, THF, 24 h	 I + II	161
			I + II (53), I:II = 2:1	
		(Ph ₃ P) ₄ Pd/Ph ₃ P, Me ₃ SnOTs, C ₆ H ₆ , 70°, 2 d	 I + II	161
			I + II (40), I:II = 9:1	
			I + II (49), I:II = 2:1	
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOAc, C ₆ H ₆	 I (72)	161
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOAc, C ₆ H ₆	I (51)	161

TABLE 6. INTERMOLECULAR CYCLOADDITION OF CARBONYL COMPOUNDS AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ /tpdp dioxane, 100°	 (50-56)	162
OHC-CH ₂ -CH ₂ -Ph		Pd(OAc) ₂ /Ph ₃ P, R ₃ SnOAc, THF, reflux	 R = <i>n</i> -Bu (71) R = Me (99)	260, 146
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, Me ₃ SnOAc	 (good)	242
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, reflux	 (81)	159
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, Me ₃ SnOAc	 I + II (good), I:II = 3:1	242
		Pd(OAc) ₂ /Ph ₃ P, dioxane, 100°, 8 h	 (61)	146
		(2,4-pentadionato) ₃ In, Pd(OAc) ₂ , DIBAL-H, ligand	 I + II	160
		ligand	I + II	I:II
		<i>i</i> -Pr) ₃ P toluene, reflux	(63)	3:1
		dppp toluene, reflux	(73)	1:10
		(<i>n</i> -Bu) ₃ P toluene, reflux	(59)	1:21
		Ph ₃ P toluene, reflux	(82)	1:24
		Ph ₃ P dioxane	(—)	1:9
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, reflux, slow addition of TMM precursor	 I (71)	260, 146
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, reflux	I (59)	159
		Toluene, 130°, 18 h	 I + II (81), I:II = 4:1	110
	"	13-14 kbar, CH ₂ Cl ₂ , 100°, 62 h	I + II (74), I:II = 4:1	110
<i>n</i> -C ₉ H ₁₉ CHO		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, reflux	 (68)	159

TABLE 6. INTERMOLECULAR CYCLOADDITION OF CARBONYL COMPOUNDS AND TMM (Continued)

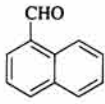
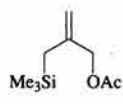
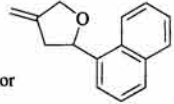
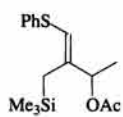
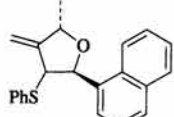
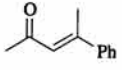
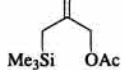
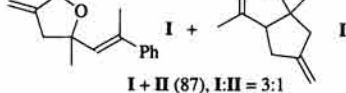
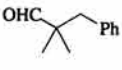
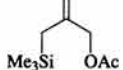
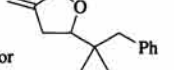
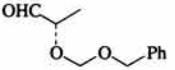
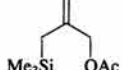
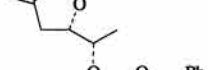
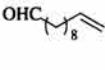
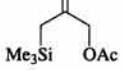
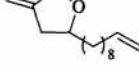
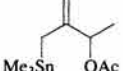
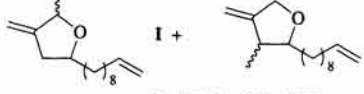
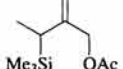
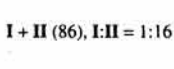
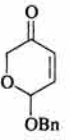
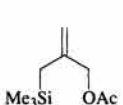
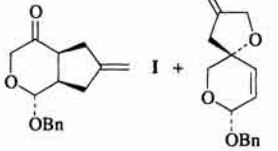
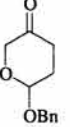
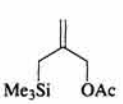
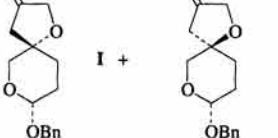
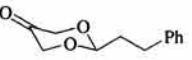
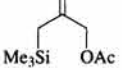
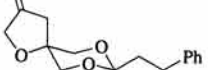
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁ 		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, dioxane, reflux, slow addition of TMM precursor	 (88)	146
		Pd(OAc) ₂ /tpdp, dioxane, 100°	 (50-56)	162
		(2,4-pentadionato) ₃ In, Pd(OAc) ₂ , DIBAL-H, Ph ₃ P	 I + II (87), I:II = 3:1	160
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, dioxane, reflux, slow addition of TMM precursor	 (75)	260, 146
		Pd(OAc) ₂ /Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, THF, reflux	 (74) 4:1 ds	260, 146
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOAc, THF, reflux	 (89)	146
		Pd(OAc) ₂ /Ph ₃ P	 I + II (72), I:II = 2.9:1	161
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOAc	 I + II (86), I:II = 1:16	161
C ₁₂ 		[Pd ₂ (dba) ₃ CHCl ₃]/Ph ₃ P, THF, 70°, 6 h	 I + II (54) I:II = 2:1	146
		(Ph ₃ P) ₄ Pd/Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, THF, 70°, 2 h	 I + II (84) I:II = 2:1	146
		[Pd ₂ (dba) ₃ CHCl ₃]/Ph ₃ P, THF, reflux	 (59)	248

TABLE 6. INTERMOLECULAR CYCLOADDITION OF CARBONYL COMPOUNDS AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOAc, THF, reflux	(84)	146
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOAc	I + II (90), I:II = 11:1	161
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOAc	I + II (81), I:II = 1:95	161
		Pd(OAc) ₂ /Ph ₃ P, Me ₃ SnOAc	(71)	161
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, Me ₃ SnOAc, BSA, toluene, 65-95°	(41)	162
C ₁₃ 		(2,4-pentadionato) ₃ In, Pd(OAc) ₂ , DIBAL-H, Ph ₃ P	(81)	160
		[Pd ₂ (dba) ₃ CHCl ₃]/Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, C ₆ H ₆ , 2 h	(91)	146
		Pd(OAc) ₂ /Ph ₃ P, C ₆ H ₆ , reflux, 1 h	(81)	146
C ₁₄ 		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, reflux	(66)	159

TABLE 6. INTERMOLECULAR CYCLOADDITION OF CARBONYL COMPOUNDS AND TMM (Continued)

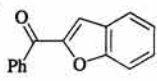
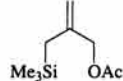
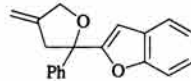
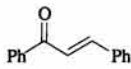
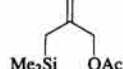
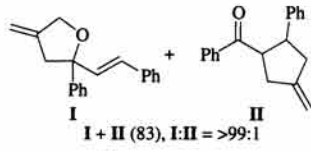
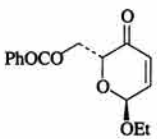
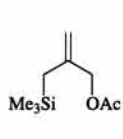
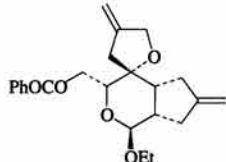
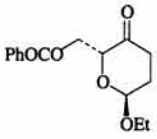
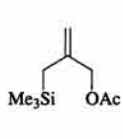
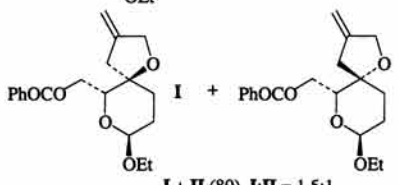
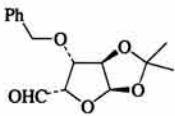
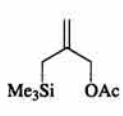
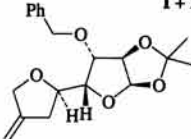
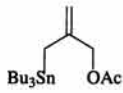

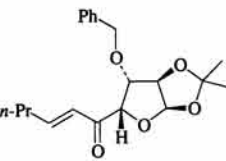
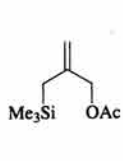
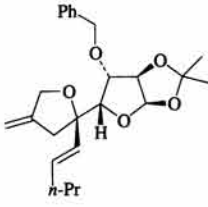
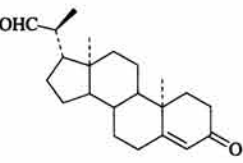
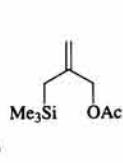
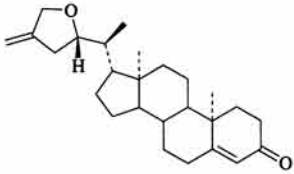
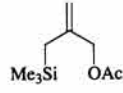
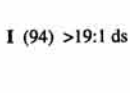
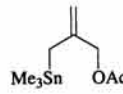

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅ 		Pd(OAc) ₂ /Ph ₃ P, toluene, 100°, 22 h	 (80)	146
		(2,4-pentadionato) ₃ In, Pd(OAc) ₂ , DIBAL-H, Ph ₃ P	 I + II (83), I:II = >99:1	160
		Pd(PPh ₃) ₄ /Ph ₃ P, THF, reflux, 16 h	 (54)	248, 146
		[Pd ₂ (dba) ₃ CHCl ₃]/Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, THF, reflux, 5 h	 I + II (80), I:II = 1.5:1	146
		Pd(OAc) ₂ /Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, THF, reflux	 I (62)	159
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, reflux	 I (74)	146
C ₂₀ 		(2,4-pentadionato) ₃ In, Pd(OAc) ₂ , DIBAL-H, Ph ₃ P	 (74)	160
C ₂₁ 		Pd(OAc) ₂ /Ph ₃ P, <i>n</i> -Bu ₃ SnOAc, THF, reflux	 I (94) 3:1 ds	260, 146
		In(acac) ₃ , Pd(OAc) ₂ , DIBAL-H, Ph ₃ P, toluene	 I (94) >19:1 ds	160
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, 40°	 I (80)	159

TABLE 7. INTRAMOLECULAR CYCLOADDITION OF ALDEHYDES AND TMM

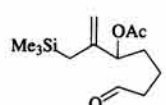
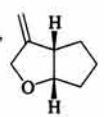
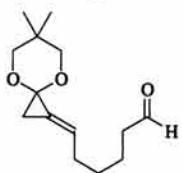
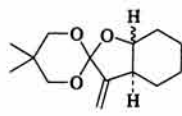
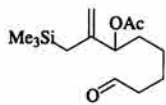
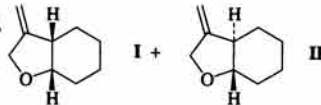
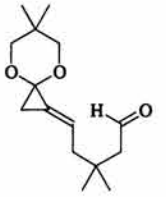
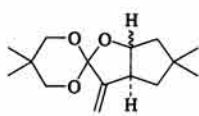
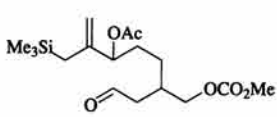
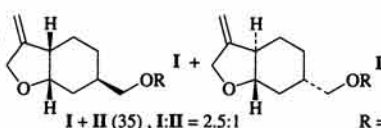
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₃</p> 	<p>[Pd₂(dba)₃CHCl₃]/(<i>i</i>-PrO)₃P, <i>n</i>-Bu₃SnOAc, BSA, THF, reflux</p>	 (31)	261
<p>C₁₄</p> 	<p>MeCN, 100°, 2 h</p>	 (90)	113
<p>C₁₅</p> 	<p>[Pd₂(dba)₃CHCl₃]/(<i>i</i>-PrO)₃P, <i>n</i>-Bu₃SnOAc, BSA, THF, 70°</p>	 <p>I + II (54), I:II = 1.1:1</p>	261
<p>C₁₅</p> 	<p>MeCN, 80°, 1 h</p>	 (55)	113
<p>C₁₇</p> 	<p>[Pd₂(dba)₃CHCl₃]/(<i>i</i>-PrO)₃P, <i>n</i>-Bu₃SnOAc, BSA, THF, 70°</p>	 <p>I + II (35), I:II = 2.5:1 R = CO₂Me</p>	261

TABLE 8. INTERMOLECULAR CYCLOADDITION OF IMINES OR OXIMES AND TMM

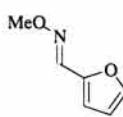

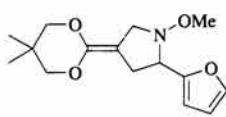
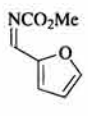
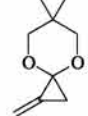
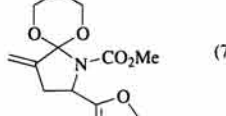
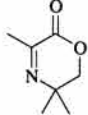
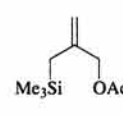
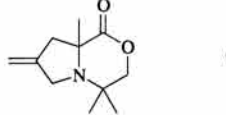
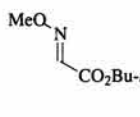
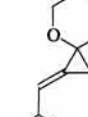
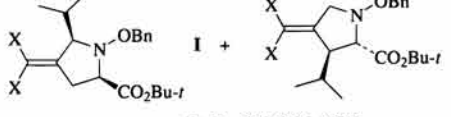
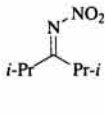
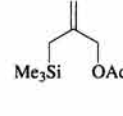
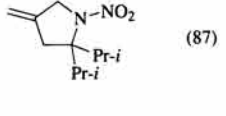
	Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆			MeCN, 100°, 85 h	 (92)	50
C ₇			MeCN, 50°, 12 h	 (78)	111
			Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, dioxane, 140°	 (70)	50
			CD ₃ CN, 80°, 30 h	 I + II X, X = CH ₂ C(Me) ₂ CH ₂ I + II (88), I:II = 8.1:1	50
			Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, THF, 65°	 (87)	163

TABLE 8. INTERMOLECULAR CYCLOADDITION OF IMINES OR OXIMES AND TMM (Continued)

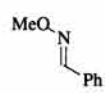
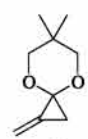
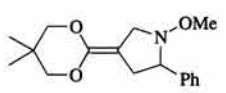
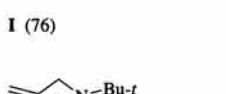

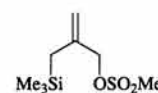
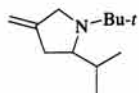

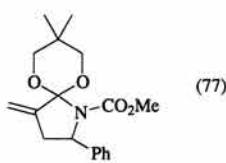
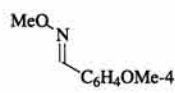
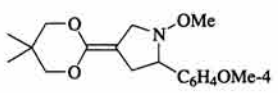

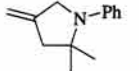

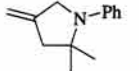
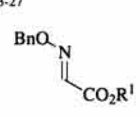
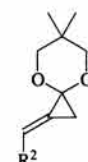
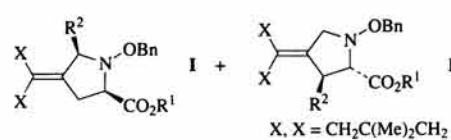

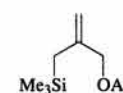
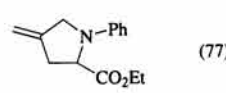
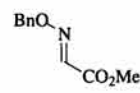

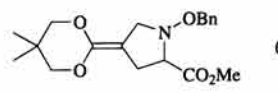
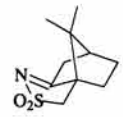
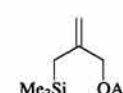
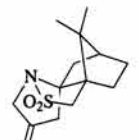
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.	
C_8 		MeCN, 120-130°, 36 h	 I (70)	50	
	"	CH ₂ Cl ₂ , 10 kbar, 80°, 24 h	 I (76)	50	
		[(EtO) ₃ P] ₂ Ni, toluene, reflux	 (50)	88	
C_9		MeCN, 80°, 11 h	 (77)	111	
		CH ₂ Cl ₂ , 10 kbar, 80°, 24 h	 (70)	50	
		[(EtO) ₃ P] ₂ Ni, toluene, reflux	 (40)	88	
		[(EtO) ₃ P] ₂ Ni, toluene, reflux	 (40)	88	
C_{13-27}			 I + II	50	
	R ¹ = Me	R ² = Me	CD ₃ CN, 80°, 4 h	I + II (81), I:II = 2.5:1	
	R ¹ = Me	R ² = <i>i</i> -Pr	CD ₃ CN, 80°, 21 h	I + II (81), I:II = 3.5:1	
	R ¹ = <i>t</i> -Bu	R ² = Me	CD ₃ CN, 80°, 10 h	I + II (99), I:II = 6.8:1	
	R ¹ = <i>t</i> -Bu	R ² = <i>i</i> -Pr	CD ₃ CN, 80°, 17 h	I + II (89), I:II = 9:1	
			DMSO-d ₆ , 80°, 21.5 h	I + II (96), I:II = 10:1	
			toluene-d ₈ , 80°, 36 h	I + II (85), I:II = 6.1:1	
			neat, 80°, 18 h	I + II (83), I:II = 5.3:1	
	R ¹ = Ph	R ² = <i>i</i> -Pr	CD ₃ CN, 80°, 4 h	I + II (41), I:II = 3.3:1	
	R ¹ = CH ₂ Ph	R ² = <i>i</i> -Pr	CD ₃ CN, 80°, 16.5 h	I + II (71), I:II = 4.9:1	
	R ¹ = 2,4,6-Me ₃ C ₆ H ₂	R ² = <i>i</i> -Pr	CD ₃ CN, 80°, 8 h	I + II (83), I:II = 1:1.3	
R ¹ = 2,4,6- <i>t</i> -Bu ₃ C ₆ H ₂	R ² = <i>i</i> -Pr	CD ₃ CN, 80°, 40 h	I + II (41), I:II = 7.3:1		
C_{10}			 (77)	163	
			Neat, 100°, 4 h	 (66)	50
			Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, toluene, 100 °	 (94)	163

TABLE 8. INTERMOLECULAR CYCLOADDITION OF IMINES OR OXIMES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, THF, 65°	 (72)	163
		MeCN, 60°, 3 h	 (89)	111
		Pd(OAc) ₂ , <i>n</i> -BuLi, Ph ₃ P, 64°	 (98)	163
		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), toluene, 120°, 20 h	 (71)	137
		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), toluene, 120°, 13 h	 (91)	137
		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), toluene, 120°	 (89)	137
	R = <i>n</i> -C ₄ H ₉ R = <i>n</i> -C ₆ H ₁₃	16 h 18 h	 (88)	
		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), toluene, 120°, 17 h	 (91)	137
		MeCN, 60°, 4.5 h	 (72) + (14)	111
		MeCN, 80°, 5.5 h	 (86)	111
		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, toluene, 100°	 (90)	163
		Pd(PPh ₃) ₄ /P(O)Bu ₃ (1:2), toluene, 120°, 3 d	 (57)	137
		[(EtO) ₃ P] ₂ Ni, toluene, reflux	 (58)	88

TABLE 8. INTERMOLECULAR CYCLOADDITION OF IMINES OR OXIMES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.	
		THF, reflux	 I + II + III (75), I:II:III = 12:1:12	85	
		X = OMs X = OMs X = OAc X = OAc X = OMs	[(EtO) ₃ P] ₂ Ni [Pd ₂ (dba) ₃ CHCl ₃], P(OEt) ₃ (1:8) " (PPh ₃) ₄ Pd (PPh ₃) ₄ Pd	(77) (52) (73) (27) (19)	88
		MeCN, 100°, 29 h		(66)	50
		Pd(OAc) ₂ , <i>n</i> -BuLi, (<i>i</i> -PrO) ₃ P, 40°		(94)	163
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, THF, 65°		(84)	163
		[Pd ₂ (dba) ₃ CHCl ₃]/ P(OEt) ₃ (1:8), toluene, reflux		(55)	88
		MeCN, 100°, 31 h		(99)	50
		MeCN, 80°, 3 h		(90)	111
		MeCN, 80°, 2 h		(92)	111
		Pd(OAc) ₂ , <i>n</i> -BuLi, Ph ₃ P, 64°		(97)	163
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, THF, reflux		(quant)	163
		MeCN, heat	 I + II (98), I:II = 1.7:1 I + II (47), I:II = 1.6:1	I + II (98), I:II = 1.7:1 I + II (47), I:II = 1.6:1	111
	R, R = Et R, R = CH ₂ C(Me) ₂ CH ₂				

TABLE 8. INTERMOLECULAR CYCLOADDITION OF IMINES OR OXIMES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, heat	(35)	111
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, THF, 40°	I + II I + II (quant), I:II = 4.7:1	163
		Pd(OAc) ₂ , <i>n</i> -BuLi, (<i>i</i> -PrO) ₃ P, 40°	(90)	163
		Pd(OAc) ₂ , <i>n</i> -BuLi, (<i>i</i> -PrO) ₃ P, 64°	(95)	163
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, toluene, 100°	(50)	163
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, toluene, 100°	(50)	163
		[(EtO) ₃ P] ₂ Ni, toluene, reflux	(69)	88
		Pd(PPh ₃) ₄ , 127°, 29 h	(38)	138
		Pd(PPh ₃) ₄ / P(O)Bu ₃ (1:2), toluene, 120°, 24 h	(88)	137
		Pd(PPh ₃) ₄ / P(O)Bu ₃ (1:2), toluene, 120°, 12 h	(91)	137
		Pd(OAc) ₂ , <i>n</i> -BuLi, Ph ₃ P, 64°	(95)	163
		Pd(PPh ₃) ₄ / P(O)Bu ₃ (1:2), toluene, 120°, 9 h	(94)	137
		Pd(OAc) ₂ , <i>n</i> -BuLi, (<i>i</i> -PrO) ₃ P, 40°	(99)	163
		Pd(PPh ₃) ₄ / P(O)Bu ₃ (1:2), toluene, 120°, 16 h	(93)	137
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, toluene, 100°	(72)	163

TABLE 8. INTERMOLECULAR CYCLOADDITION OF IMINES OR OXIMES AND TMM (Continued)

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₆ 		MeCN, 60°, 3.5 h	(81) + (12)	111
		Pd(OAc) ₂ , <i>n</i> -BuLi, (<i>i</i> -PrO) ₃ P, 40°	(99)	163
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, 150°	(quant)	242
		Pd(OAc) ₂ /tpdp, dioxane, 100°	(—)	162
C ₁₇ 		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, toluene, 100°	(80)	163
		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, dioxane, 100°	(22)	163
C ₁₈ 		Pd(OAc) ₂ / <i>i</i> -PrO) ₃ P, toluene, 100°	(80)	163
C ₂₀ 		Pd(PPh ₃) ₄ , 126°, 24 h	(96)	138
		Pd(PPh ₃) ₄ , 123°, 22 h	I (46) + II (31)	138
		Pd(PPh ₃) ₄ , 128°, 30 h	I (44) + II (31)	138
		Pd(PPh ₃) ₄ , 123°, 30 h	I (93)	138
	"	Ni(cod) ₂ / (2-PhC ₆ H ₄ O) ₃ P (1:1), I (93) 70°, 7 h	I (93)	138
		Pd(PPh ₃) ₄ , 123°, 30 h	I (91)	138
	"	Ni(cod) ₂ / (2-PhC ₆ H ₄ O) ₃ P (1:1), I (94) 70°, 7 h	I (94)	138

TABLE 8. INTERMOLECULAR CYCLOADDITION OF IMINES OR OXIMES AND TMM (Continued)



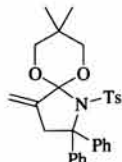
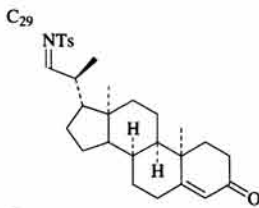
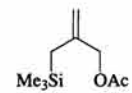
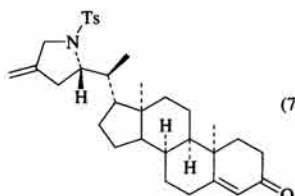
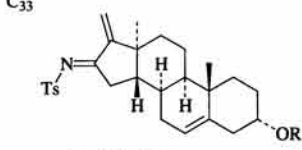
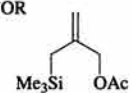
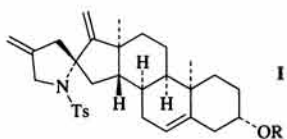
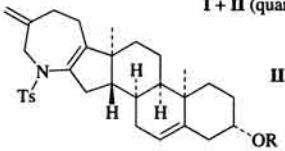
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, 60°, 12 h	 (85)	111
<p>C₂₉</p> 		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, dioxane, 100°	 (76)	163
<p>C₃₃</p>  <p>R = TBDMS</p>		Pd(OAc) ₂ /(<i>i</i> -PrO) ₃ P, dioxane, 100°	 I +  II I + II (quant), I:II = 1:1	163

TABLE 9. INTERMOLECULAR CYCLOADDITION OF OXYGEN AND TMM

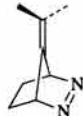
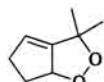
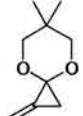
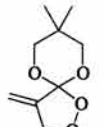

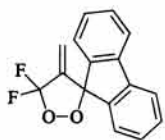

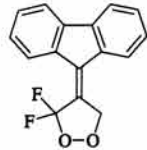
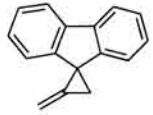
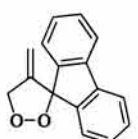
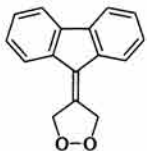
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
O_2		$h\nu, O_2$ (80 psi), $CCl_4, 40^\circ, 36$ h	 (40)	262
		Toluene, $80^\circ, 24$ h	 (40)	48
		$CHCl_3, 28^\circ, 32$ h	 I +  II +  III I + II + III (67), I:II:III = 12:7.2:1	51
		$CHCl_3, 28^\circ, 32$ h	 I +  II I + II (75), I:II = 12:1	51

TABLE 9. INTERMOLECULAR CYCLOADDITION OF OXYGEN AND TMM (Continued)




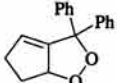
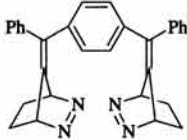
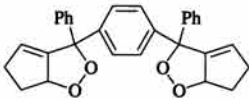
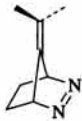
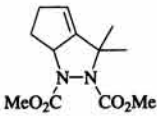

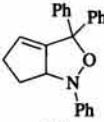

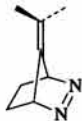
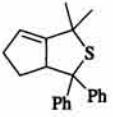
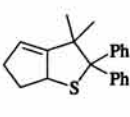
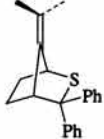
Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
		<i>hν</i>	 (100)	263
		DCA, MeCN, 15 min	(100)	
		DCA-BP, MeCN, 15 min	(100)	
		TCNB, MeCN, 20 min	(100)	
		TCNB, CH ₂ Cl ₂ , 30 min	(4)	
		TCNB-BP, CH ₂ Cl ₂ , 15 min	(96)	
		NMQ ⁺ BF ₄ ⁻ , toluene, MeCN, 5 min	(100)	
		<i>hν</i> , O ₂ (150 psi), CFCl ₃ , 40 °, 51 h	 (37)	262
		<i>hν</i> , O ₂ (5 bar), MeCN, -10 °, 2 h	 (70)	264

TABLE 10. MISCELLANEOUS

Reactant	TMM Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄ MeO ₂ CN=NC ₂ OMe		Acceptor (xs), 40-60°	 (-)	8
C ₆ Ph-N=O		MeCN 60°, 3 h <i>hν</i> (λ>300 nm), 4 h	 (77) (25)	87
C ₁₃ 		THF, reflux	 I +  II +  III I + II + III (91), I:II:III = 2.6:1.1:1	85

References

1. Dowd, P. J. *Am. Chem. Soc.* 1966, **88**, 2587.
2. Dowd, P. *Acc. Chem. Res.* 1972, **5**, 242.
3. Cramer, C. J. *J. Chem. Soc., Perkin Trans. 2* 1998, 1007.
4. Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. *J. Am. Chem. Soc.* 1976, **98**, 5725.
5. Baseman, R. J.; Pratt, D. W.; Chow, M.; Dowd, P. J. *Am. Chem. Soc.* 1976, **98**, 5726.
6. Dowd, P.; Chow, M. *Tetrahedron* 1982, **38**, 799.
7. Dowd, P.; Sengupta, G.; Sachdev, K. J. *Am. Chem. Soc.* 1970, **92**, 5726.
8. Berson, J. A.; McDaniel, D.
9. Berson, J. A. *Acc. Chem. Res.* 1978, **11**, 446.
10. Little, R. D. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I.; Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. **5**, pp. 239–270.
11. Little, R. D. *Chem. Rev.* 1986, **86**, 875.
12. Little, R. D. *Chem. Rev.* 1996, **96**, 93.
13. Allan, A. K.; Carroll, G. L.; Little, R. D. *Eur. J. Org. Chem.* 1998, 1.
14. Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; pp. 311–390.
15. Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press New York 1981;
16. Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* 1989, **111**, 7285.
17. Nakamura, E. In *Organic Synthesis in Japan. Past, Present, and Future*; Noyori, R., Ed.; Tokyo Kagaku Dojin, 1992; p 275.
18. Emerson, G. F.; Ehrlich, K.; Giering, W. P.; Lauterbur, P. C. *J. Am. Chem. Soc.* 1966, **88**, 3172.
19. Ehrlich, K.; Emerson, G. F. *J. Am. Chem. Soc.* 1972, **94**, 2464.
20. Jones, M. D.; Kemmitt, R. D. W. *Adv. Organomet. Chem.* 1987, **27**, 279.
21. Noyori, R.; Nishimura, T.; Takaya, H. *J. Chem. Soc., Chem. Commun.* 1969, 89.
22. Binger, P.; Schuchardt, U. *Angew. Chem. Int. Ed. Engl.* 1977, **16**, 249.
23. Binger, P.; Büch, H. M. *Top. Curr. Chem.* 1987, **135**, 77.
24. Ohta, T.; Takaya, H. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I.; Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. **5**, pp. 1185–1205.
25. Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* 1979, **101**, 6429.
26. Trost, B. M. *Angew. Chem., Int. Ed. Engl.* 1986, **25**, 1.

27. Trost, B. M. *Pure Appl. Chem.* 1988, **60**, 1615.
28. Chan, D. M. T. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I.; Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. **5**, pp. 271–314.
29. Akiba, K. J. *Syn. Org. Chem. Japan* 1973, **31**, 635; *Chem. Abstr.* 1973, **80**, 59028.
30. Welzel, P. *Nachr. Chem., Tech. Lab.* 1983, **31**, 638; *Chem. Abstr.* 1983, **99**, 212170.
31. Binger, P.; Fox, D. In *Methoden der Organischen Chemie (Houben-Weyl)*; Helmchen, G.; Hoffmann, R. W.; Mulzer, J.; Schaumann, E., Eds.; Georg Thieme Verlag: Stuttgart, 1995; Vol. **E 21c**, pp. 2997–3059.
32. Binger, P.; Schmidt, T. *Methoden der Organischen Chemie (Houben-Weyl)*; de Meijere, A., Ed.; Georg Thieme Verlag: Stuttgart, 1996, Vol. **E 17c**, pp. 2217–2294.
33. Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* 1996, **96**, 49.
34. Nakamura, E.; Yamago, S. *Acc. Chem. Res.* 2002, **35**, in press.
35. Berson, J. A.; Duncan, C. D.; Corwin, L. R. *J. Am. Chem. Soc.* 1974, **96**, 6175.
36. Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* 1980, **102**, 2358.
37. Berson, J. A.; Corwin, L. R.; Davis, J. H. *J. Am. Chem. Soc.* 1974, **96**, 6177.
38. Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* 1977, **99**, 5178.
39. Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* 1980, **102**, 276.
40. Berson, J. A.; Duncan, C. D.; O'Connell, G. C.; Platz, M. S. *J. Am. Chem. Soc.* 1976, **98**, 2358.
41. Berson, J. A.; McDaniel, D. M.; Corwin, L. R. *J. Am. Chem. Soc.* 1972, **94**, 5510.
42. Siemionko, R. K.; Berson, J. A. *J. Am. Chem. Soc.* 1980, **102**, 3870.
43. Carpenter, B. K.; Little, R. D.; Berson, J. A. *J. Am. Chem. Soc.* 1976, **98**, 5723.
44. Siemionko, R.; Shaw, A.; O'Connell, G.; Little, R. D.; Carpenter, B. K.; Shen, L.; Berson, J. A. *Tetrahedron Lett.* 1980, **38**, 3529.
45. Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* 1982, **104**, 967.
46. Buchwalter, S. L. *Tetrahedron* 1982, **38**, 799.
47. Creary, X.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* 1989, **54**, 2904.
48. Nakamura, E.; Yamago, S.; Ejiri, S.; Dorigo, A. E.; Morokuma, K. *J. Am.*

- Chem. Soc. 1991, **113**, 3183.
49. LeFevre, G. N.; Crawford, R. J. J. *J. Org. Chem.* 1986, **51**, 747.
 50. Yamago, S.; Nakamura, M.; Wang, X.-Q.; Yanagawa, M.; Tokumitsu, S.; Nakamura, E. *J. Org. Chem.* 1998, **63**, 1694.
 51. Dolbier, Jr. W. R.; Burkholder, C. R. *Tetrahedron* 1985, **41**, 297.
 52. Noyori, R.; Hayashi, N.; Kato, M. *J. Am. Chem. Soc.* 1971, **93**, 4948.
 53. Noyori, R.; Hayashi, N.; Kato, M. *Tetrahedron Lett.* 1973, 2983.
 54. Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* 1970, **92**, 2168.
 55. Yamago, S.; Ejiri, S.; Nakamura, M.; Nakamura, E. *J. Am. Chem. Soc.* 1993, **115**, 5344.
 56. Ejiri, S.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* 1992, **114**, 8707.
 57. Lautens, M.; Ren, Y. *J. Am. Chem. Soc.* 1996, **118**, 9597.
 58. Lautens, M.; Ren, Y. *J. Am. Chem. Soc.* 1996, **118**, 10668.
 59. Oishi, Y.; Sakamoto, E.; Fujimoto, H. *Inorg. Chem.* 1996, **35**, 231.
 60. Binger, P.; Wedemann, P. *Tetrahedron Lett.* 1985, **26**, 1045.
 61. Binger, P.; Schuchardt, U. *Chem. Ber.* 1981, **114**, 3313.
 62. Noyori, R.; Kumagai, Y.; Umeda, I.; Takaya, H. *J. Am. Chem. Soc.* 1972, **94**, 4018.
 63. Noyori, R.; Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* 1970, **92**, 5780.
 64. Binger, P.; Bentz, P. *Angew. Chem., Int. Ed. Engl.* 1982, **21**, 622.
 65. Binger, P.; Wedemann, P. *Tetrahedron Lett.* 1983, **24**, 5847.
 66. Trost, B. M.; Chan, D. M. *J. Am. Chem. Soc.* 1980, **102**, 6359.
 67. Trost, B. M.; Chan, D. M. *J. Am. Chem. Soc.* 1983, **105**, 2326.
 68. Gordon, D. J.; Fenske, R. F.; Nanninga, T. N.; Trost, B. M. *J. Am. Chem. Soc.* 1981, **103**, 5974.
 69. Trost, B. M.; Chan, D. M. *J. Am. Chem. Soc.* 1983, **105**, 2315.
 70. Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* 1984, **25**, 5183.
 71. Trost, B. M.; Miller, M. *J. Am. Chem. Soc.* 1988, **110**, 3687.
 72. Singleton, D. A.; Schulmeier, B. E. *J. Am. Chem. Soc.* 1999, **121**, 9313.
 73. Trost, B. M.; Nanninga, T. N. *J. Am. Chem. Soc.* 1985, **107**, 1075.
 74. Trost, B. M.; Chan, D. M. *J. Am. Chem. Soc.* 1981, **103**, 5972.
 75. Trost, B. M.; Nanninga, T. N.; Satho, T. *J. Am. Chem. Soc.* 1985, **107**, 721.
 76. Trost, B. M.; Lynch, J.; Renaut, P. *Tetrahedron Lett.* 1985, **26**, 6313.
 77. Trost, B. M.; Mignani, S. M. *Tetrahedron Lett.* 1986, **27**, 4137.
 78. Ward, J. S.; Pettit, R. *J. Chem. Soc., Chem. Commun.* 1970, 1419.
 79. Mondo, J. A.; Berson, J. A. *J. Am. Chem. Soc.* 1983, **105**, 3340.
 80. Aumann, R.; Uphoff, J. *Angew. Chem., Int. Ed. Engl.* 1987, **26**, 357.

81. Su, C.-C.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* 1994, **116**, 4999.
82. Little, R. D.; Carroll, G. L. *J. Org. Chem.* 1979, **44**, 4720.
83. Stone, K. J.; Little, R. D. *J. Org. Chem.* 1984, **49**, 1849.
84. Little, R. D.; Bukhari, A.; Venegas, M. *Tetrahedron Lett.* 1979, **20**, 305.
85. Little, R. D.; Bode, H.; Stone, K. J.; Wallquist, O.; Dannecker, R. *J. Org. Chem.* 1985, **50**, 2401.
86. Lin, X.; Little, R. D. *Tetrahedron Lett.* 1997, **38**, 15.
87. Adam, W.; Bottle, S. E.; Peters, K. *Tetrahedron Lett.* 1991, **32**, 4283.
88. Jones, M. D.; Kemmitt, R. D. *W. J. Chem. Soc., Chem. Commun.* 1986, 1201.
89. Little, R. D.; Muller, G. W. *J. Am. Chem. Soc.* 1979, **101**, 7129.
90. Little, R. D.; Muller, G. W. *J. Am. Chem. Soc.* 1981, **103**, 2744.
91. Little, R. D.; Muller, G. W.; Venegas, M.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stone, K. *Tetrahedron* 1981, **37**, 4371.
92. Little, R. D.; Higby, R. G.; Moeller, K. D. *J. Org. Chem.* 1983, **48**, 3139.
93. Masjedizadeh, M. R.; Dannecker-Doerig, I.; Little, R. D. *J. Org. Chem.* 1990, **55**, 2742.
94. Campopiano, O.; Little, R. D.; Petersen, J. L. *J. Am. Chem. Soc.* 1985, **107**, 3721.
95. Billera, C. F.; Philipp, C.; Little, R. D. *J. Org. Chem.* 1994, **59**, 2270.
96. McLoughlin, J. I.; Brahma, R.; Campopiano, O.; Little, R. D. *Tetrahedron Lett.* 1990, **31**, 1377.
97. Little, R. D.; Stone, K. J. *J. Am. Chem. Soc.* 1983, **105**, 6976.
98. Hijfte, L. V.; Little, R. D. *J. Org. Chem.* 1985, **50**, 3940.
99. Hijfte, L. V.; Little, R. D.; Petersen, J. L.; Moeller, K. D. *J. Org. Chem.* 1987, **52**, 4647.
100. Little, R. D.; Moeller, K. D. *J. Org. Chem.* 1983, **48**, 4487.
101. Moeller, K. D.; Little, R. D. *Tetrahedron Lett.* 1985, **26**, 3417.
102. Griller, D.; Ingold, K. U. *Acc. Chem. Res.* 1980, **13**, 317.
103. Newcomb, M. *Tetrahedron* 1993, **49**, 1151.
104. Nonhebel, D. C. *Chem. Soc. Rev.* 1993, 347.
105. Carroll, G. L.; Little, R. D. *Tetrahedron Lett.* 1998, **39**, 1893.
106. Isaka, M.; Ejiri, S.; Nakamura, E. *Tetrahedron* 1992, **48**, 2045.
107. Nakamura, M.; Tohanoh, H.; Ohara, H.; Nakamura, E. *Org. Lett.* 1999, **1**, 7.
108. *Organic High Pressure Chemistry*; Le Noble, W. J., Ed.; Elsevier: Amsterdam, 1988.
109. Yamago, S.; Ejiri, S.; Nakamura, E. *Angew. Chem., Int. Ed. Engl.* 1995,

34, 2154.

110. Yamago, S.; Nakamura, E. *J. Org. Chem.* 1990, **55**, 5553.
111. Yamago, S.; Yanagawa, M.; Nakamura, E. *Chem. Lett.* 1999, 879.
112. Yamada, T.; Uekusa, H.; Ohashi, Y.; Yamago, S.; Wang, X.-Q.; Nakamura, E. *Acta Cryst.* 1995, **C51**, 1137.
113. Nakamura, M.; Togano, M.; Wang, X. Q.; Yamago, S.; Nakamura, E. *Chem. Lett.* 2000, 664.
114. Salaun, J. R.; Champion, J.; Conia, J. M. *Org. Synth. Coll. Vol.6* 1988, 320.
115. Arora, S.; Binger, P. *Synthesis* 1974, 801.
116. Lautens, M.; Delanghe, P. H. M. *J. Org. Chem.* 1993, **58**, 5037.
117. Lautens, M.; Delanghe, P. H. M. *J. Am. Chem. Soc.* 1994, **116**, 8526.
118. Lautens, M.; Ren, Y. *J. Org. Chem.* 1996, **61**, 2210.
119. Utimoto, K.; Tamura, M.; Sisido, K. *Tetrahedron* 1973, **29**, 1169.
120. Halazy, S.; Dumont, W.; Krief, A. *Tetrahedron Lett.* 1981, **22**, 4737.
121. Hiyama, T.; Kanakura, A.; Morizawa, Y.; Nozaki, H. *Tetrahedron Lett.* 1982, **23**, 1279.
122. Sternberg, E.; Binger, P. *Tetrahedron Lett.* 1985, **26**, 301.
123. Brandi, A.; Goti, A. *Chem. Rev.* 1998, **98**, 589.
124. Binger, P.; Schuchardt, U. *Chem. Ber.* 1980, **113**, 3334.
125. Binger, P.; Sternberg, E.; Wittig, U. *Chem. Ber.* 1987, **120**, 1933.
126. Binger, P.; Wedemann, P.; Kozhushkov, S. I.; de Meijere, A. *Eur. J. Org. Chem.* 1998, 113.
127. Binger, P.; Freund, A.; Wedemann, P. *Tetrahedron* 1989, **45**, 2887.
128. Binger, P.; Germer, A. *Chem. Ber.* 1981, **114**, 3325.
129. Binger, P.; Brinkmann, A.; Wedemann, P. *Chem. Ber.* 1983, **116**, 2920.
130. Binger, P.; Schäfer, B. *Tetrahedron Lett.* 1988, **29**, 4539.
131. Buch, H. M.; Schroth, G.; Mynott, R.; Binger, P. *J. Organomet. Chem.* 1983, **247**, C63.
132. Binger, P.; Lü, Q.-H.; Wedemann, P. *Angew. Chem., Int. Ed. Engl.* 1985, **24**, 316.
133. Binger, P.; Schäfer, B. *Tetrahedron Lett.* 1988, **29**, 529.
134. Binger, P.; Brinkmann, A.; Roefke, P.; Schäfer, B. *Liebigs Ann. Chem.* 1989, 739.
135. Nakamura, I.; Oh, B. H.; Saito, S.; Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* 2001, **40**, 1298.
136. Inoue, Y.; Hibi, T.; Satake, M.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* 1979, 982.
137. Oh, B. H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *Tetrahedron Lett.* 2001,

- 42**, 6203.
138. Weintz, H.-J.; Binger, P. *Tetrahedron Lett.* 1985, **26**, 4075.
 139. Bapuji, S. A.; Motherwell, W. B.; Shipman, M. *Tetrahedron Lett.* 1989, **30**, 7107.
 140. Lewis, R. T.; Motherwell, W. B.; Shipman, M. J. *Chem. Soc., Chem. Commun.* 1988, 948.
 141. Corlay, H.; Lewis, R. T.; Motherwell, W. B.; Shipman, M. *Tetrahedron* 1995, **51**, 3303.
 142. Yamago, S.; Nakamura, E. J. *Chem. Soc., Chem. Commun.* 1988, 1112.
 143. Yamago, S.; Nakamura, E. *Tetrahedron* 1989, **45**, 3081.
 144. Corlay, H.; Motherwell, W. B.; Pennell, A. M. K.; Shipman, M.; Slawin, A. M. Z.; Williams, D. J. *Tetrahedron* 1996, **52**, 4883.
 145. Trost, B. M.; Chan, D. M. T.; Nanninga, T. N. *Org. Synth. Coll. Vol.7* 1990, 266.
 146. Trost, B. M.; King, S. A.; Schmidt, T. J. *Am. Chem. Soc.* 1989, **111**, 5902.
 147. Cleary, D. G.; Paquette, L. A. *Synth. Commun.* 1987, **17**, 497.
 148. Trost, B. M.; Seoane, P.; Mignani, S.; Acemoglu, M. J. *Am. Chem. Soc.* 1989, **111**, 7487.
 149. Trost, B. M.; Balkovec, J. M.; Angle, S. R. *Tetrahedron Lett.* 1986, **27**, 1445.
 150. Trost, B. M.; Nanninga, T. N.; Chan, D. M. *Organometallics* 1982, **1**, 1543.
 151. Trost, B. M.; Seoane, P. J. *Am. Chem. Soc.* 1987, **109**, 3483.
 152. Trost, B. M.; Seoane, P. J. *Am. Chem. Soc.* 1987, **109**, 615.
 153. Trost, B. M.; Parquette, J. R.; Marquart, A. L. *J. Am. Chem. Soc.* 1995, **117**, 3284.
 154. Trost, B. M.; Mignani, S. M.; Nanninga, T. N. *J. Am. Chem. Soc.* 1986, **108**, 6051.
 155. Trost, B. M.; Mignani, S. M.; Nanninga, T. N. *J. Am. Chem. Soc.* 1988, **110**, 1602.
 156. Chaigne, F.; Gotteland, J.-P.; Malacria, M. *Tetrahedron Lett.* 1989, **30**, 1803.
 157. Trost, B. M.; Yang, B.; Miller, M. J. *Am. Chem. Soc.* 1989, **111**, 6482.
 158. Yamamoto, A.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* 1989, **30**, 375.
 159. Trost, B. M.; Bonk, P. J. *J. Am. Chem. Soc.* 1985, **107**, 8277.
 160. Trost, B. M.; Sharma, S.; Schmidt, T. J. *Am. Chem. Soc.* 1992, **114**, 7903.
 161. Trost, B. M.; King, S. A. *J. Am. Chem. Soc.* 1990, **112**, 408.
 162. Trost, B. M.; Matelich, M. C. *J. Am. Chem. Soc.* 1991, **113**, 9007.

163. Trost, B. M.; Marrs, C. M. J. Am. Chem. Soc. 1993, **115**, 6636.
164. Trost, B. M.; Chan, D. M. T. J. Am. Chem. Soc. 1982, **104**, 3733.
165. Trost, B. M.; Grese, T. A.; Chan, D. M. T. J. Am. Chem. Soc. 1991, **113**, 7350.
166. Trost, B. M.; Grese, T. A. J. Am. Chem. Soc. 1991, **113**, 7363.
167. Trost, B. M.; Higuchi, R. I. J. Am. Chem. Soc. 1996, **118**, 10094.
168. Trost, B. M.; Grese, T. A. J. Org. Chem. 1992, **57**, 686.
169. Franck-Neumann, M.; Kastler, A. Synlett 1995, 61.
170. Trost, B. M.; Lynch, J.; Renaut, P.; Steinman, D. H. J. Am. Chem. Soc. 1986, **108**, 284.
171. Trost, B. M.; Renaut, P. J. Am. Chem. Soc. 1982, **104**, 6668.
172. Trost, B. M.; Nanninga, T. N. J. Am. Chem. Soc. 1985, **107**, 1293.
173. Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T.; Rickborn, B.; Yamago, S.; Nakamura, E. J. Am. Chem. Soc. 1993, **115**, 1594.
174. Tokuyama, H.; Yamago, S.; Nakamura, E.; Shiraki, T.; Sugiura, Y. J. Am. Chem. Soc. 1993, **115**, 7918.
175. Nakamura, E.; Tokuyama, H.; Yamago, S.; Shiraki, T.; Sugiura, Y. Bull. Chem. Soc. Jpn. 1996, **69**, 2149.
176. Botorine, A. S.; Tokuyama, H.; Takasugi, M.; Isobe, H.; Nakamura, E.; Hélène, C. Angew. Chem., Int. Ed. Engl. 1994, **33**, 2462.
177. Irie, K.; Nakamura, Y.; Ohigashi, H.; Tokuyama, H.; Yamago, S.; Nakamura, E. Biosci. Biotech. Biochem. 1996, **60**, 1359; Chem. Abstr. 1996, **125**, 215866.
178. Yamago, S.; Tokuyama, H.; Nakamura, E.; Kikuchi, K.; Kananishi, S.; Sueki, K.; Nakahara, H.; Enomoto, S.; Ambe, F. Chem. Biology 1995, **2**, 385.
179. Cossy, J.; Belotti, D.; Pete, J. P. Tetrahedron Lett. 1987, **28**, 4547.
180. Paquette, L. A.; Sauer, D. R.; Cleary, D. G.; Kinsella, M. A.; Blackwell, C. M.; Anderson, L. G. J. Am. Chem. Soc. 1992, **114**, 7375.
181. Cotteland, J.-P.; Malacria, M. Tetrahedron Lett. 1989, **30**, 2541.
182. Trost, B. M.; Greenspan, P. D.; Yang, B. V.; Saulnier, M. G. J. Am. Chem. Soc. 1990, **112**, 9022.
183. Trost, B. M.; Parquette, J. R. J. Org. Chem. 1994, **59**, 7568.
184. Hashimoto, K.; Ohfuné, Y.; Shirahama, H. Tetrahedron Lett. 1995, **36**, 6235.
185. Ott, M. M.; Little, R. D. J. Org. Chem. 1997, **62**, 1610.
186. Padwa, A. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I.; Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. **4**, pp. 1069–1109.

187. Wade, P. A. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I.; Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. **4**, pp. 1111–1168.
188. Trost, B. M. *Chem. Soc. Rev.* 1982, **11**, 141.
189. Paquette, L. A. *Top. Curr. Chem.* 1984, **119**, 1.
190. Boger, D. L.; Brotherton-Pleiss, C. E. *Advances in Cycloaddition*; JAI Press Inc.: London, 1990; Vol. **2**, pp. 147–219.
191. Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* 1986, **108**, 6695.
192. Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* 1986, **108**, 6713.
193. Tokuyama, H.; Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* 1992, **114**, 5523.
194. Tokuyama, H.; Yamada, T.; Nakamura, E. *Synlett* 1993, 589.
195. Tokuyama, H.; Isobe, H.; Nakamura, E. *Bull. Chem. Soc. Jpn.* 1995, **68**, 935.
196. Isobe, H.; Tokuyama, H.; Sawamura, M.; Nakamura, E. *J. Org. Chem.* 1997, **62**, 5034.
197. Nakamura, E.; Isobe, H.; Tomita, N.; Sawamura, M.; Jinno, S.; Okayama, H. *Angew. Chem., Int. Ed. Engl.* 2000, **39**, 4254.
198. Eidenschink, R.; Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* 1972, **11**, 292.
199. Boche, G.; Martens, D. *Angew. Chem., Int. Ed. Engl.* 1972, **11**, 724.
200. Ford, W. T.; Luteri, G. F. *J. Am. Chem. Soc.* 1977, **11**, 5330.
201. Beak, P.; Burg, D. A. *J. Org. Chem.* 1989, **54**, 1647.
202. Panek, J. S. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. **1**, pp. 596–607.
203. Danheiser, R. L.; Carini, D. J.; Basak, A. J. *J. Am. Chem. Soc.* 1981, **103**, 1604.
204. Danheiser, R. L.; Dixon, B. R.; Gleason, R. W. *J. Org. Chem.* 1992, **57**, 6094.
205. Masse, C. E.; Panek, J. S. *Chem. Rev.* 1995, **95**, 1293.
206. Knölker, H.-J. *J. Prakt. Chem.* 1997, **339**, 304.
207. Akiyama, T. *J. Synth. Org. Chem. Jpn.* 2000, **58**, 285; *Chem. Abstr.* 2000, **132**, 293512n.
208. Herndon, J. W.; Wu, C.; Harp, J. J.; Kreutzer, K. A. *Synlett* 1991, 1.
209. Panek, J. S.; Jain, N. F. *J. Org. Chem.* 1993, **23**, 2345.
210. Welker, M. E. *Chem. Rev.* 1992, **92**, 97.
211. Giering, W. P.; Rosenblum, M. J. *J. Am. Chem. Soc.* 1971, **93**, 5299.
212. Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. J. *J. Am. Chem. Soc.* 1976, **98**,

- 3495.
213. Rosenblum, M.; Watkins, J. C. J. Am. Chem. Soc. 1990, **112**, 6316.
214. Hayamawa, Y.; Yokoyama, K.; Noyori, R. J. Am. Chem. Soc. 1978, **100**, 1791.
215. Hayakawa, Y.; Yokoyama, K.; Noyori, R. J. Am. Chem. Soc. 1978, **100**, 1799.
216. Hayakawa, Y.; Noyori, R. Org. React. 1983, **29**, 168.
217. Masuya, K.; Domon, K.; Tanino, K.; Kuwajima, I. J. Am. Chem. Soc. 1998, **120**, 1724.
218. Mizuno, H.; Komon, K.; Masuya, K.; Tanino, K.; Kuwajima, I. J. Org. Chem. 1999, **64**, 2648.
219. Cekovic, Z.; Saicic, R. Tetrahedron Lett. 1986, **27**, 5893.
220. Curran, D. P.; Chen, M.-H. J. Am. Chem. Soc. 1987, **109**, 6558.
221. Beal, R. B.; Dombroski, M. A.; Snider, B. B. J. Am. Chem. Soc. 1986, **51**, 4391.
222. Wiering, P. G.; Verhoeven, J. W.; Steinberg, H. J. Am. Chem. Soc. 1981, **103**, 7675.
223. Shimizu, I.; Ohashi, Y.; Tsuji, J. Tetrahedron Lett. 1985, **26**, 3825.
224. Miura, K.; Fugami, K.; Oshima, K.; Utimoto, K. Tetrahedron Lett. 1988, **29**, 5135
225. Feldman, K. S.; Romanelli, A. L.; Ruckle Jr., R. E.; Miller, R. F. J. Am. Chem. Soc. 1988, **110**, 3300.
226. Mariano, J. P.; Laborde, E. J. Am. Chem. Soc. 1985, **107**, 734.
227. Saigo, K.; Shimada, S.; Shibasaki, T.; Hasegawa, M. Chem. Lett. 1990, 1093.
228. Crimmins, M. T.; Nantermet, P. G. J. Org. Chem. 1990, **55**, 4235.
229. Kuwajima, I.; Nakamura, E. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. **2**, pp. 441–473.
230. Zhang, C.; Lu, X. J. Org. Chem. 1995, **60**, 2906.
231. Zhu, G.; Chen, Z.; Jiang, Q.; Xiao, D.; Cao, P.; Zhang, X. J. Am. Chem. Soc. 1997, **119**, 3836.
232. Takeda, K.; Fujisawa, M.; Makino, T.; Yoshii, E. J. Am. Chem. Soc. 1993, **115**, 9351.
233. Molander, G.; Shubert, D. C. J. Am. Chem. Soc. 1986, **108**, 4683.
234. Li, Y.-Q.; Li, C.-J. Tetrahedron Lett. 1996, **37**, 471.
235. Binger, P.; Bentz, P. J. Organomet. Chem. 1981, **221**, C33.
236. Painter, S. L.; Blackstock, S. C. J. Am. Chem. Soc. 1995, **117**, 1441.
237. Noyori, R.; Hayashi, N.; Kato, M. J. Am. Chem. Soc. 1971, **93**, 4948.

238. Noyori, R.; Yamakawa, M.; Takaya, H. *Tetrahedron Lett.* 1978, **48**, 4823.
239. Little, R. D.; Brown, L. *Tetrahedron Lett.* 1979, **21**, 2203.
240. Lautens, M.; Ren, Y.; Delanghe, P. H. M. *J. Am. Chem. Soc.* 1994, **116**, 8821.
241. Trost, B. M.; Matelich, M. C. *Synthesis* 1992, 151.
242. Trost, B. M.; Parquette, J. R.; Nübling, C. *Tetrahedron Lett.* 1995, **36**, 2917.
243. Raghavan, S.; Ishida, M.; Shinozaki, H.; Nakanishi, K.; Ohfuné, Y. *Tetrahedron Lett.* 1993, **34**, 5765.
244. Trost, B. M.; Acemoglu, M. *Tetrahedron Lett.* 1989, **30**, 1495.
245. Binger, P.; Brinkmann, A.; Richter, W. J. *Tetrahedron Lett.* 1983, **24**, 3599.
246. Leonetti, J. A.; Gross, T.; Little, R. D. *J. Org. Chem.* 1996, **61**, 1787.
247. Trost, B. M.; Schneider, S. *Angew. Chem., Int. Ed. Engl.* 1989, **28**, 213.
248. Trost, B. M.; King, S. A.; Nanninga, T. N. *Chem. Lett.* 1987, 15.
249. Trost, B. M.; Yamazaki, S. *Chem. Lett.* 1994, 2245.
250. Rosenstock, B.; Gais, H.-J.; Herrmann, E.; Raabe, G.; Binger, P.; Freund, A.; Wedemann, P.; Krüger, C.; Lindner, H. J. *Eur. J. Org. Chem.* 1998, 257.
251. Baker, R.; Keen, R. B. *J. Organomet. Chem.* 1985, **285**, 419.
252. Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* 1994, **116**, 1359.
253. Shiu, L.-L.; Lin, T.-I.; Peng, S.-M.; Her, G.-R.; Ju, D. D.; Lin, S.-K.; Hwang, J.-H.; Mou, C. Y.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* 1994, 647.
254. Yamago, S.; Nakamura, E. *Chem. Lett.* 1996, 395.
255. Binger, P.; Schuchardt, U. *Chem. Ber.* 1980, **113**, 1063.
256. Watanabe, S.; Kurosawa, H. *Organometallics* 1997, **16**, 3601.
257. Motherwell, W. B.; Shipman, M. *Tetrahedron Lett.* 1991, **32**, 1103.
258. Stone, K. J.; Little, R. D. *J. Am. Chem. Soc.* 1985, **107**, 2495.
259. Lewis, R. T.; Motherwell, W. B.; Shipman, M.; Slawin, A. M. Z. *Tetrahedron* 1995, **51**, 3289.
260. Trost, B. M.; King, S. A. *Tetrahedron Lett.* 1986, **27**, 5971.
261. Trost, B. M.; Moeller, K. D. *Heterocycles* 1989, **28**, 321.
262. Wilson, R. M.; Geiser, F. J. *J. Am. Chem. Soc.* 1978, **100**, 2225.
263. Ikeda, H.; Nakamura, T.; Miyashi, T.; Goodman, J. L.; Akiyama, K.; Tero-Kubota, S.; Houmam, A.; Wayner, D. D. M. *J. Am. Chem. Soc.* 1998, **120**, 5832.
264. Adam, W.; Bottle, S. E.; Finzel, R.; Kammel, T.; Peters, E.-M.; Peters, K.;

von Schnering, H. G.; Walz, L. J. Org. Chem. 1992, **57**, 982.