

CHAPTER 1

DIOXIRANE OXIDATIONS OF COMPOUNDS OTHER THAN ALKENES

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DIOXIRANE OXIDATIONS OF COMPOUNDS OTHER THAN ALKENES

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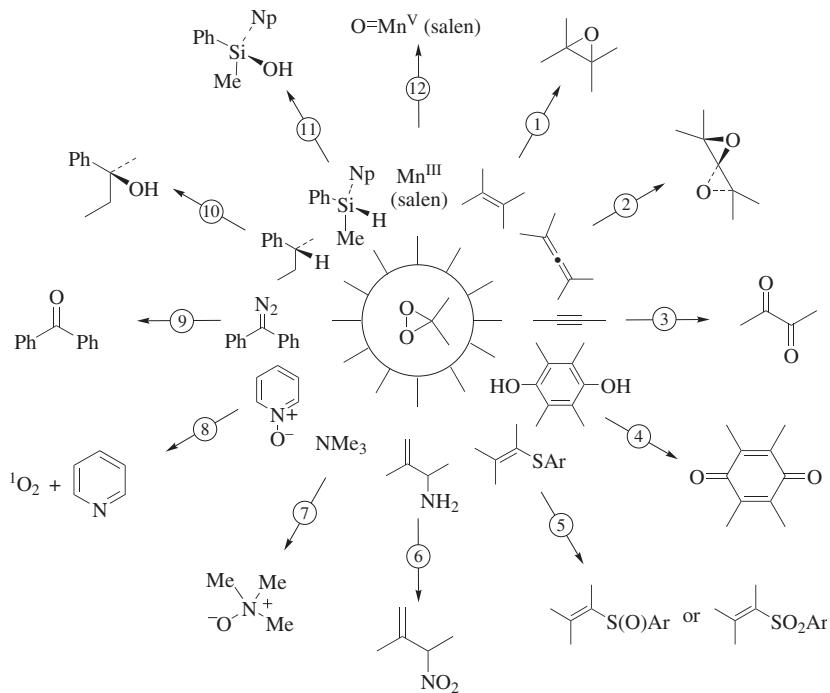
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INTRODUCTION

Epoxidations, heteroatom oxidations, and Y–H insertions constitute the best 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.^{1–14} In a previous chapter,¹⁵ we presented the epoxidation of double bonds [π bonds in simple alkenes and those functionalized with electron donors (ED), electron acceptors (EA), and with both ED and EA substituents; case 1 in the rosette] with either isolated or in situ generated dioxiranes. The recent developments in the dioxirane-mediated asymmetric epoxidation have also been extensively covered there.¹⁵ The present chapter concerns the remaining oxidations in the rosette of Scheme 1, that is, epoxidation of the double bonds in the cumulenes, such as allenes (transformation 2), acetylenes (transformation 3), and arenes (transformation 4); the oxidation of heteroatom functionalities, mainly lone pairs on sulfur (transformation 5), on nitrogen (transformations 6 and 7), and on oxygen as the deoxygenation of *N*-oxides (transformation 8); the oxidation of C=Y functionalities (e.g., transformation 9), Y–H insertions (σ bonds) such as C–H in alkanes (transformation 10) and Si–H in silanes (transformation 11); and the oxidation of organometallic substrates including metal (transformation 12) and ligand-sphere oxidation.

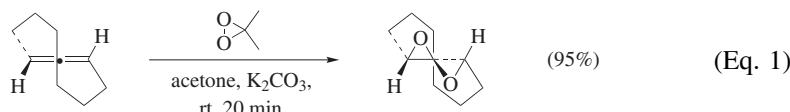


Scheme 1. An overview of dioxirane oxidations (Np = 1-naphthyl).

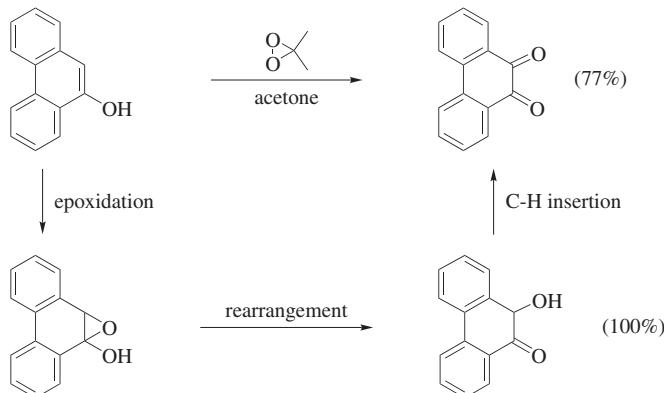
MECHANISM

Allenes, Alkynes, and Arenes

Although the products of the dioxirane oxidation of allenes, alkynes, and arenes are usually more complex than those of the epoxidation of simple C=C double bonds, the initial step of the oxidation is usually epoxidation. Therefore, the same mechanism that has been extensively discussed in the previous chapter¹⁵ also applies in these reactions. The oxygen transfer proceeds with complete retention of the initial olefin configuration through the concerted spiro transition state.¹⁵ An example is shown in Eq. 1, in which the oxidation of the chiral allene proceeds in nearly quantitative yield (95%) with preservation of the starting allene configuration in the spiro-bisepoxide.¹⁶



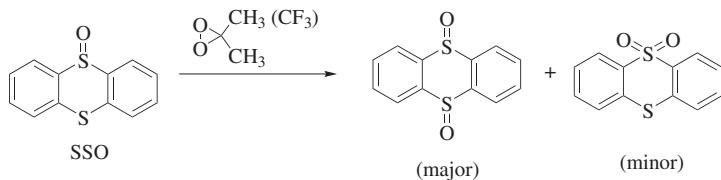
Since the initial epoxidation products of the allenes, alkynes, and arenes are usually labile substances, they may undergo subsequent reactions, which include further oxidation by dioxirane other than epoxidation. For example, in the dimethyldioxirane (DMD) oxidation of the phenanthrene derivative in Scheme 2,¹⁷ the second oxidation by DMD involves C–H insertion instead of epoxidation.



Scheme 2. DMD oxidation of 9-hydroxyphenanthrene.

Heteroatom Substrates

Through a detailed study of the competitive oxidation of the sulfide versus sulfoxide functionalities in thianthrene 5-oxide (SSO),¹⁸ a pronounced electrophilic character has been demonstrated for DMD and methyl(trifluoromethyl)dioxirane (TFD).^{19,20} Thus, dioxiranes prefer to oxidize the sulfide over the sulfoxide functionality, a typical behavior of an electrophilic oxidant (Scheme 3). Also, the

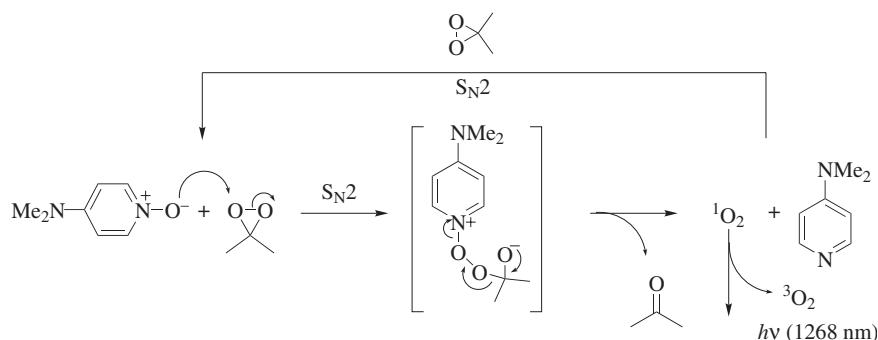


Scheme 3. Competitive oxidation of the sulfide vs. sulfoxide functionalities in thianthrene-5-oxide (SSO) by the dioxiranes DMD and TFD.

kinetic data⁶ for the oxidation of sulfides and sulfoxides have revealed the electrophilic character of dioxiranes. Thus, the heteroatom oxidations by dioxirane are generally explained in terms of a S_N2 -type attack of the heteroatom lone pair on the dioxirane peroxide σ^* -orbital.^{21,22}

A possible single-electron-transfer (SET) mechanism in N-oxidations^{23,24} has been discounted²¹ on the basis of kinetic experiments by comparing the relative rates of oxygen transfer by DMD with those of alkylation by methyl iodide. For the latter, an S_N2 mechanism unequivocally applies. Similar reactivities (linear correlation of rates) for N-oxidation also establish the S_N2 pathway for dioxirane oxidations. This conclusion is supported by a kinetic study of the DMD oxidation of substituted *N,N*-dimethylanilines.²⁵

The heterolytic mechanism is presumably also valid for a variety of oxygen-type nucleophiles, e.g., amine *N*-oxides, ClO^- , HO^- , HOO^- , RO^- , ROO^- , RC(O)OO^- , and $\text{OS(O)}_2\text{OO}^-$, which all catalyze the decomposition of dioxiranes with the evolution of molecular oxygen.^{26,27} A typical case is illustrated with 4-dimethylaminopyridine *N*-oxide in Scheme 4.²⁶ The chemiluminescence emitted by the generated singlet oxygen confirms the heterolytic nature of the dioxirane decomposition.²⁶ Further support for this mechanism has been provided by theoretical work, from which it was concluded that the oxidation of primary amines by DMD does not proceed by a radical process.²⁸



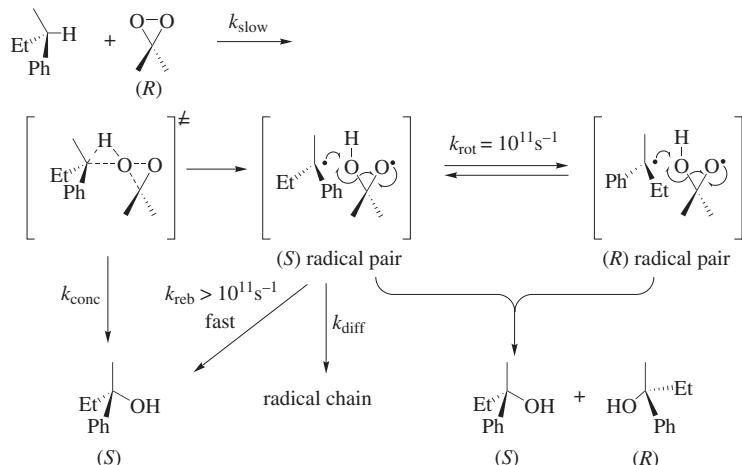
Scheme 4. S_N2 Mechanism for the N-oxide-induced decomposition of DMD.

Alkanes and Silanes

Two mechanisms have been suggested for the insertion of an oxygen atom into the Y–H bond of alkanes and silanes. Abundant evidence, which includes kinetics,²⁹ kinetic isotope effects,³⁰ and stereoselectivity,³¹ all unequivocally support a concerted oxenoid-type mechanism (Figure 1).

Nonetheless, radical reactivity has been observed recently and interpreted in terms of the dioxirane diradical as the active oxidant, in particular, the so-called “molecule-induced homolysis.”^{32–35} It has also been proposed³⁶ that alkane hydroxylation may proceed by a rate-determining oxygen insertion into the alkane C–H bond to generate a caged radical pair, followed by very fast collapse (oxygen rebound) to hydroxylated products (Scheme 5).

That hydroxylation of (*R*)-2-phenylbutane proceeds with 100% retention to furnish (*S*)-2-phenylbutan-2-ol for both DMD³⁷ and TFD³¹ sheds serious doubt on the involvement of out-of-cage radical intermediates in such C–H oxidations (Eq. 2).



Scheme 5. Concerted oxenoid-type (k_{conc}) vs. oxygen-rebound (k_{reb}) mechanisms for C–H insertion by DMD.

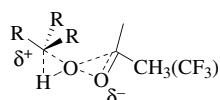
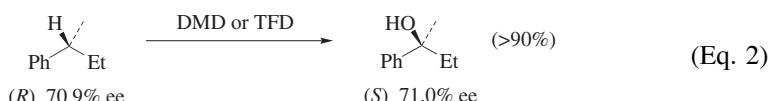
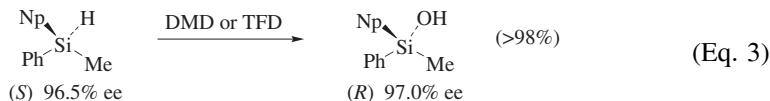


Figure 1. Concerted oxenoid-type transition state for C–H insertion.

The tertiary benzyl radical derived from this optically active substrate is one of the fastest radical clocks (the configurational persistence of this radical is estimated to be about 10^{-11} seconds)³⁸ and serves as a definitive probe for the intervention of radical intermediates. Thus, as shown in Scheme 5,³⁷ if a caged radical pair is formed, collapse with configurational conservation by oxygen rebound (k_{reb}) must be faster than diffusion out of the cage (k_{diff}), as well as in-cage isomerization (k_{rot}), since such competitive processes would lead to racemization.

As in the C–H oxidation of (*R*)-2-phenylbutane (Eq. 2), the hydroxylation of the (+)-(S)-(α-Np)PhMeSiH silane enantiomer by both dioxiranes DMD and TFD proceeds with complete retention of configuration to afford (+)-(R)-(α-Np)PhMeSiOH (Eq. 3).^{39,40} Therefore, a similar mechanism would appear to apply for the oxidation of C–H and Si–H bonds.



Most recent theoretical work on oxygen transfer for C–H insertion supports the concerted spiro oxenoid-type mechanism, in which the transition structure has considerable dipolar and also some diradical character.^{41–43} Under typical preparative conditions, for example, in the presence of molecular oxygen, it was concluded that a concerted mechanism applies for the C–H insertion.

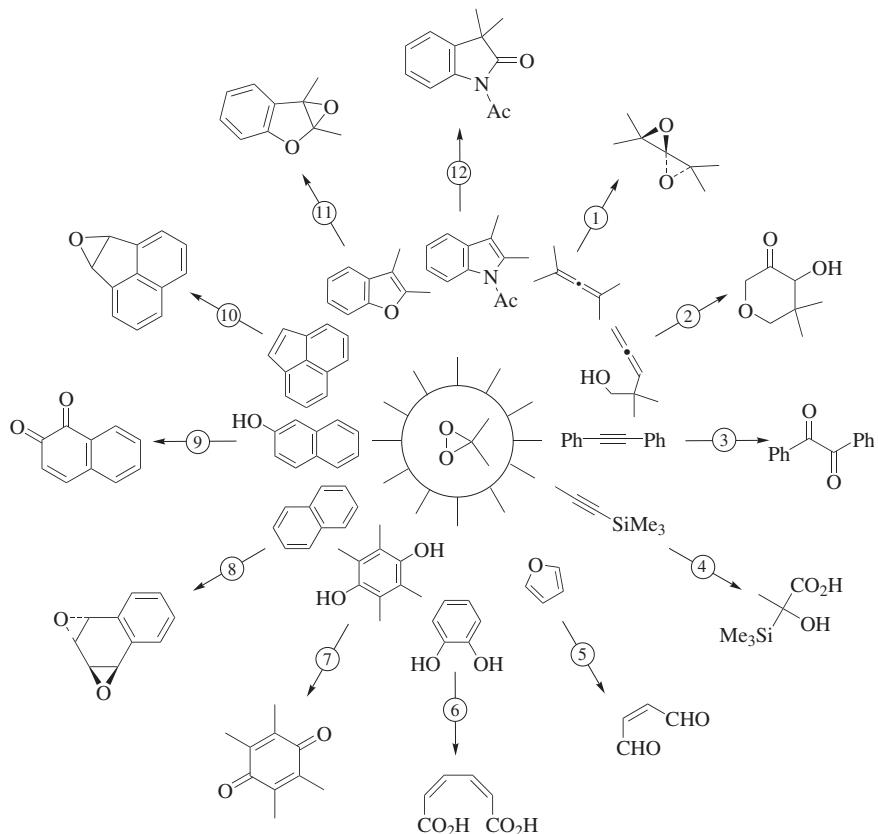
SCOPE AND LIMITATIONS

The oxidation of double bonds (π bonds) in cumulenes (allenies, acetylenes) and arenes, of heteroatom functionalities (lone-pair electrons), of transition-metal complexes, and Y–H insertions (σ bonds) has been successfully performed, either with isolated or with *in situ* generated dioxiranes. Thus, a broad spectrum of substrates has been oxidized by dioxiranes. The pertinent examples are listed in Tables 1–7 (see Tabular Survey). An isolated (distilled) acetone solution [DMD (isol.)] is the most often used dioxirane owing to its convenient preparation and relatively low cost. Although methyl(trifluoromethyl)dioxirane (TFD) is considerably more reactive than DMD, its application is limited because of its high cost and the high volatility of trifluoroacetone. With DMD (isol.), the scale of the reaction is usually limited to 100 mmol because DMD (isol.) is quite dilute (ca. 0.08 M). In the case of TFD (ca. 0.6 M), the prohibitive cost of trifluoroacetone obliges small-scale (ca. 10 mmol) applications. When a large-scale preparation is desired, the *in situ* mode [DMD (*in situ*)] is recommended, for which both biphasic^{44–47} and homogeneous^{48,49} media are available. It should be kept in mind that when one operates in aqueous solution, both the substrate and the oxidized products should resist hydrolysis and persist at temperatures above 0°. An advantage of the *in situ* mode is that it may be carried out with less than stoichiometric amounts (<0.5 equiv.) of ketone, which is important for enantioselective oxidations.^{50–54}

Allenes, Alkynes, and Arenes

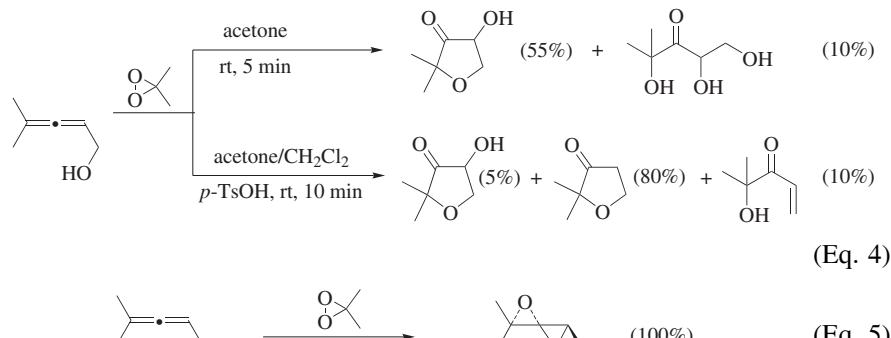
Representative examples of oxidations of allenes, alkynes, and arenes are collected in the rosette of Scheme 6.

The products of dioxirane oxidation of allenes depend on the reaction conditions and the substrate structure. Unfunctionalized allenes give the corresponding spiro-bisepoxides usually in good yields^{16,54} at subambient temperatures when dry dioxirane solution is employed (Eq. 1).¹⁶ If the allene is unsymmetrically substituted, a mixture of regioisomers is obtained, and the selectivity is highly dependent on the allene structure.^{16,55} Since these spiro-bisepoxides are labile toward hydrolysis, the *in situ* oxidation mode is not recommended. If the allene substrate contains a hydroxy functionality, the latter will react with the spiro-bisepoxide intermediate to form ring-opened and/or rearranged products.^{56–58} The final products may be cyclic or acyclic, depending on the reaction conditions, the chain-length of the substituent that contains the hydroxy functionality, and the other substituents on the allene. For example, when the hydroxyallene



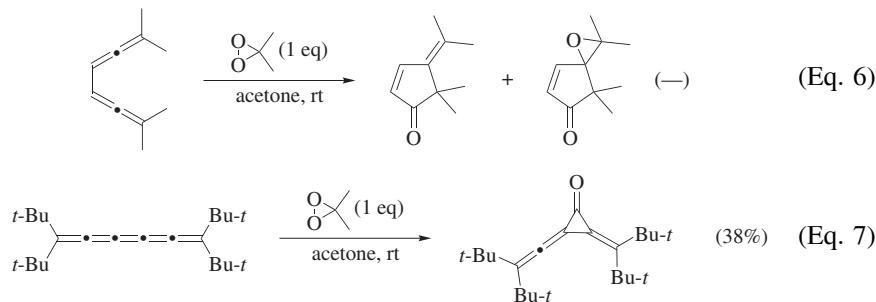
Scheme 6. An overview of dioxirane oxidations of allenes, alkynes, and arenes.

in Eq. 4 is oxidized with an acetone solution of DMD,⁵⁷ the hydroxyfuranone is obtained as the major product (upper route), together with minor amounts of open-chain material. In the presence of catalytic amounts of *p*-TsOH (lower route), however, the above hydroxy-substituted heterocycle is a minor product. On protection of the hydroxy functionality as a silyl ether, these complications are avoided, and the spiro-bisepoxide is obtained (Eq. 5).⁵⁷



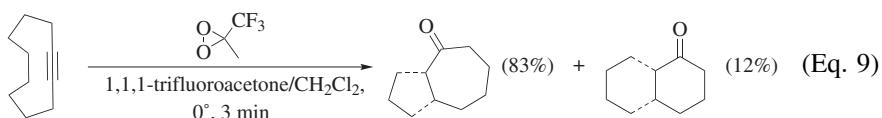
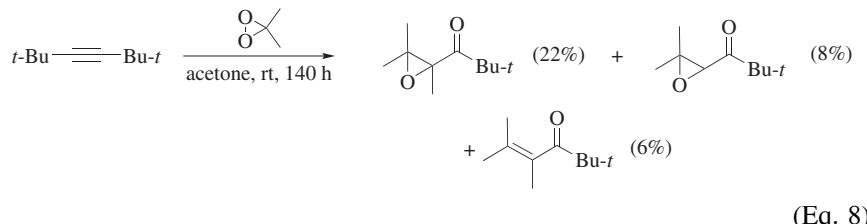
Other reactive functionalities in the allene, such as amine,⁵⁸ amide,⁵⁸ aldehyde,⁵⁹ carboxylic acid,⁶⁰ oxime,⁵⁸ and even ketone⁵⁹ groups, will open the spiro-bisepoxide intermediate and lead to substrate-specific products. These multifunctionalized heterocyclic and acyclic products should be of potential use in organic synthesis.

The oxidation of (bis)allenes and higher cumulenes has been much less studied. Nevertheless, one example of the DMD oxidation of a bisallene yields a cyclopentenone and an exocyclic epoxide (Eq. 6).⁶¹ The epoxide presumably arises from further oxidation of the exomethyleneic double bond. A higher-order cumulene has also been oxidized with DMD to give an unusual cyclopropanone in 38% yield (Eq. 7).⁶²

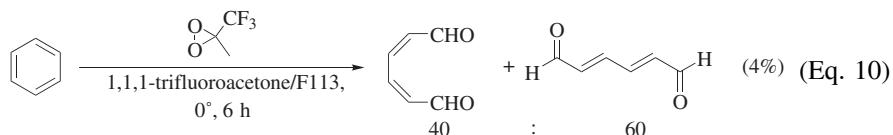


The oxidation of alkynes appears to be little studied, most likely because of the complexity of the product composition obtained in this oxidation. The oxyfunctionalized intermediates, presumably oxirenes, are much more labile than allene oxides and have so far not been detected. This oxidation is usually not

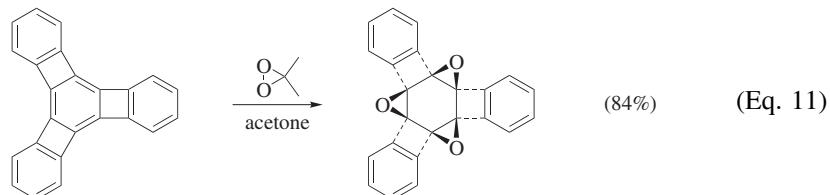
useful for synthetic purposes since extensively rearranged products are obtained in poor yields, especially with open-chain alkynes (Eq. 8).⁶³ The cyclic alkyne in Eq. 9, however, gives well-defined bicyclic rearrangement products in good yields when oxidized with TFD at 0° (Eq. 9).⁶⁴



In contrast, dioxirane oxidation of arenes is a useful reaction and has been thoroughly studied. Among the arenes and heteroarenes, benzene is the most difficult to oxidize. It is inert toward DMD oxidation and, thus, it has been employed as solvent in the biphasic oxidation mode with *in situ* generated DMD.⁴⁷ Nonetheless, benzene has been oxidized with the more reactive TFD in a fluorinated solvent, affording two isomeric dialdehydes in low yield (Eq. 10).⁶⁵

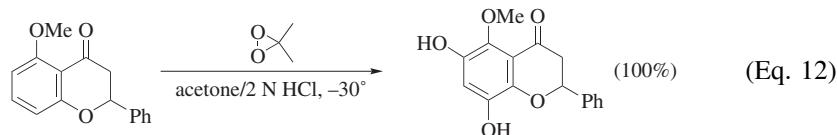


Electron-rich substituted benzenes are more reactive. For example, phenols and naphthols have been oxidized by DMD to the corresponding quinones.^{17,66} Oxidation of the arene substrate in Eq. 11 leads to the tris(epoxide) in high yield.⁶⁷ This transformation demonstrates the usefulness of dioxiranes in the oxidation of arenes, since such a tris(epoxide) would be difficult to make by any other route.

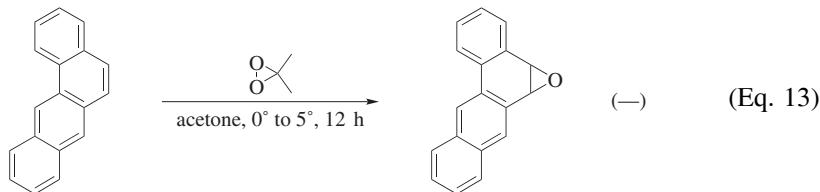


Recently, methoxy-substituted benzenes have been hydroxylated to phenols with isolated DMD under acidic conditions at subambient temperatures (Eq. 12).⁶⁸

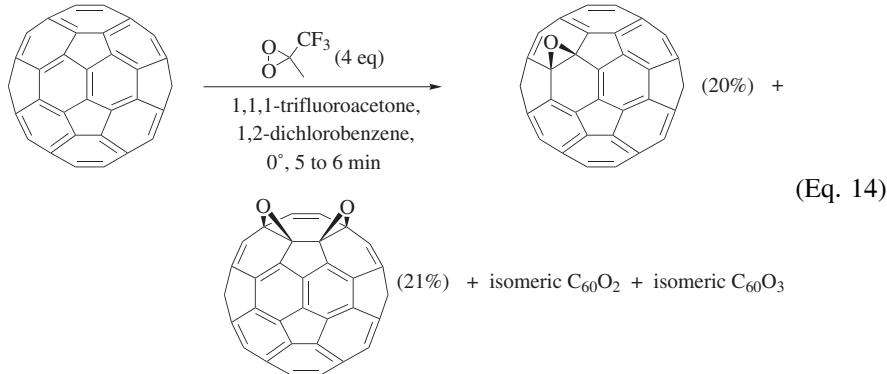
The overall reaction at first appears to be a direct CH insertion, but actually epoxidation takes place followed by an acid-catalyzed rearrangement of the intermediary epoxide.



Indene, naphthalene, and polycyclic arenes are more reactive and thus susceptible to both DMD and TFD oxidation. For example, the tetracyclic arene in Eq. 13 is oxidized by DMD to furnish the corresponding epoxide.⁶⁹ Such arene epoxides are of special interest since they are biologically active metabolites of carcinogenic polycyclic aromatic hydrocarbons.^{69,70}

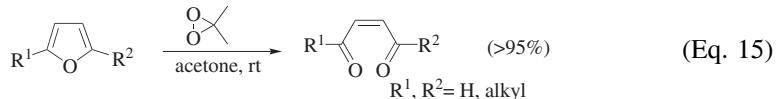


A highlight of arene oxidation by dioxirane reagents is that of the fullerene C₆₀. DMD leads mainly to the monoxide,⁷¹ but the more reactive TFD yields dioxides and even some trioxides of C₆₀ (Eq. 14).⁷²

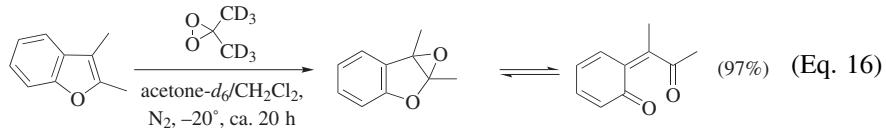


Furan-type heteroarenes are usually more reactive towards dioxirane oxidation than arenes. When subjected to oxidation by DMD (isol.), furan and its 2,5-disubstituted derivatives^{73,74} lead to the ring-opened enediones shown in Eq. 15,⁷³ which are useful building blocks in synthesis.^{73,75} The intermediary mono-epoxide of 2,3-dimethylfuran is presumably involved in the epoxidation with *d*₆-DMD (prepared in *d*₆-acetone), but could not be detected by NMR

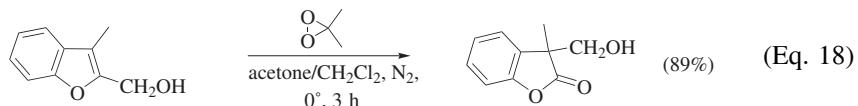
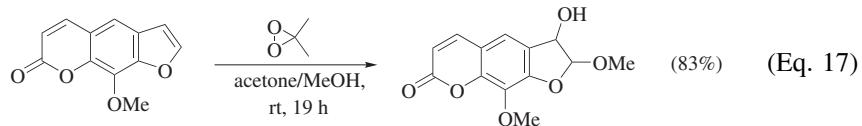
spectroscopy even at -100° ; only the rearrangement product hex-3-ene-2,5-dione was observed.⁷⁶



Related benzofurans also form labile epoxides when epoxidized by dry dioxirane solutions at low temperature under an inert atmosphere; they are sufficiently persistent to be detected at low temperatures.⁷⁷⁻⁸⁶ Depending on the substituents of the heterocycle, the epoxide may undergo opening to dicarbonyl products. Thus, the labile epoxide derived from 2,3-dimethylbenzofuran (Eq. 16) rearranges at -20° to the *o*-quinomethide.^{79,87,88} To characterize this epoxide by NMR spectroscopy, fully deuterated DMD was employed for the oxidation; the epoxide was directly detected *in situ* at -78° without work-up.⁷⁹ This example further emphasizes the importance and convenience of isolated dioxiranes for the synthesis of exceedingly labile oxy-functionalized substances.

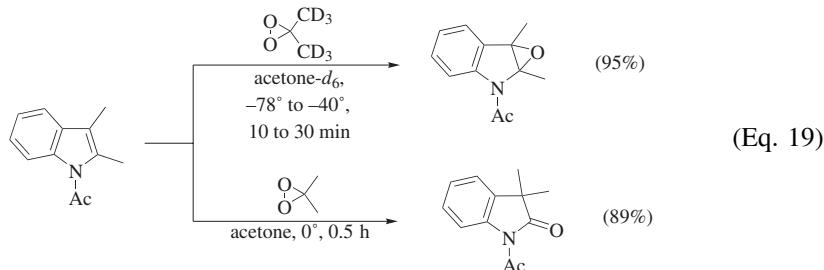


In view of the high reactivity of the benzofuran oxides, ring-opened products are formed in the presence of nucleophiles. For example, when the epoxidation of the structurally related 8-methoxypsoralen was carried out in the presence of MeOH, the hydroxy ether was obtained in good yield as ring-opened product (Eq. 17).⁸⁵ Elevated temperatures lead to rearrangement products as in the oxidation of benzofuran. Thus, when the reaction is carried out at 0° , the rearranged product in Eq. 18 is obtained from the intermediary epoxide by migration of the hydroxymethyl group.⁸⁹

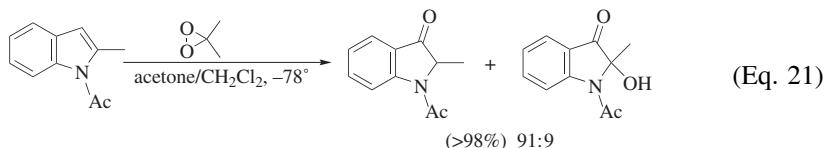
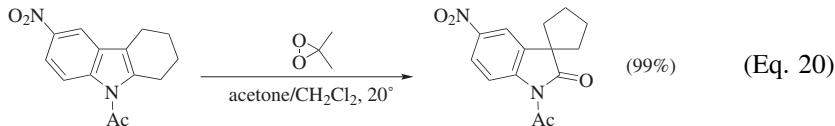


Dioxirane oxidation of the aromatic ring in nitrogen-containing heteroarenes may be even more complex. Since amine nitrogen atoms are more nucleophilic than an arene C=C double bond, N-oxidation usually precedes epoxidation. For example, the oxidation of pyridines takes place at the nitrogen atom to give the corresponding *N*-oxides as the sole products (see the section on Heteroatom

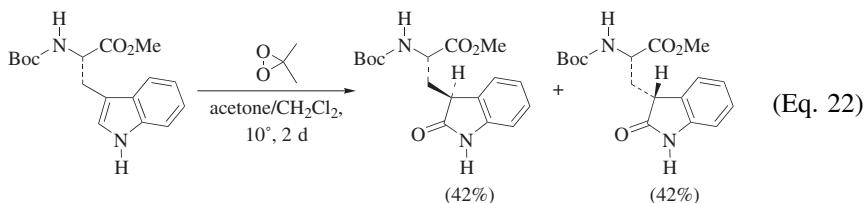
Substrates). Nonetheless, acetylation of the nitrogen functionality may sufficiently suppress N-oxidation, as illustrated for the *N*-acetylated indole in Eq. 19.^{90,91}

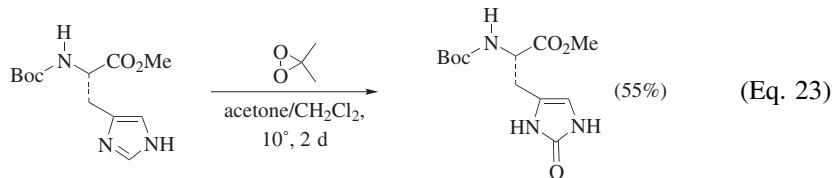


Analogous to the benzofuran example above, the corresponding labile epoxide is produced (upper pathway), when the indole is oxidized with DMD at low temperature (-78°).⁹⁰ In contrast, the rearranged product⁹¹ is obtained when the oxidation is run at subambient temperature (lower pathway). The latter rearrangement has been used for the synthesis of spiro lactams (Eq. 20).⁹² Variation of the substitution pattern of indoles may permit other rearrangements to take place. For example, the oxidation of the indole shown in Eq. 21 yields the respective benzopyrroldihydroindole instead of a lactam.⁹² The minor product presumably results from overoxidation of the pyrrolidone enol tautomer.



Currently little is known about dioxirane oxidations of unprotected indoles. One example is given in Eq. 22, for which the diastereomeric lactams are obtained.⁹³ Examples of dioxirane oxidations of heteroarenes with more than one nitrogen atom are also scarce. An example is the DMD oxidation of a substituted imidazole (Eq. 23), which furnishes an imidazolone in moderate yield.⁹³ In contrast, the DMD oxidation of 1,2,4-triazole results in a complex mixture of unidentified products.⁹⁴

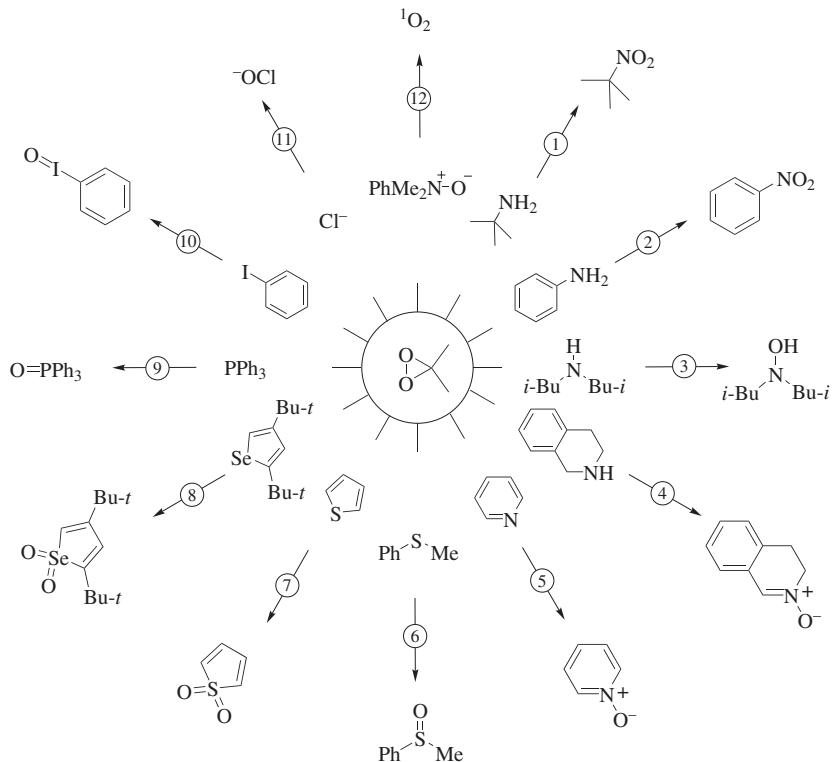




The oxidation of sulfur-containing heteroarenes such as thiophenes takes place only on sulfur, as will be discussed in the next section.

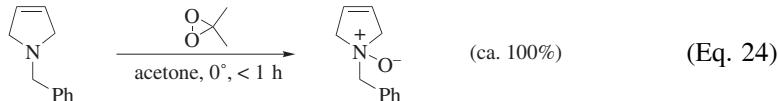
Heteroatom Substrates

Electrophilic dioxiranes are particularly reactive towards heteroatom substrates, for which the electron lone-pair serves as the nucleophile in the oxygen transfer. Because of the importance of their oxidation products, substrates that contain nitrogen, sulfur, and C=Y functionalities are among the best studied. Some typical examples are collected in the rosette of Scheme 7. These oxidations will be discussed separately according to the type of heteroatom that is oxidized, mainly nitrogen and sulfur.

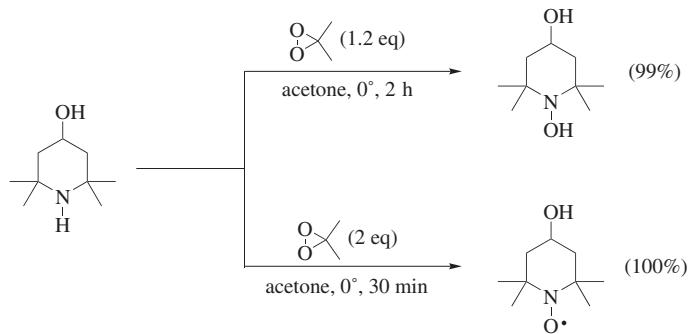


Scheme 7. An overview of dioxirane oxidations of heteroatom substrates.

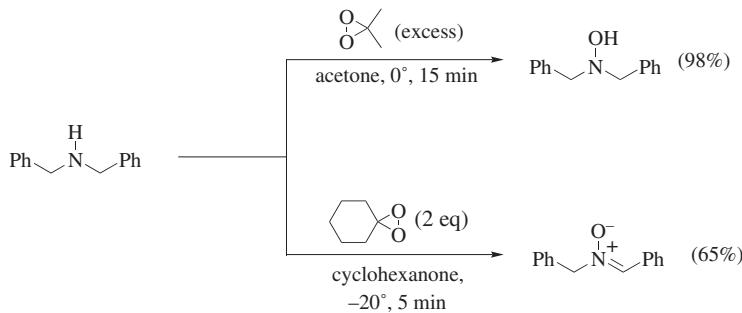
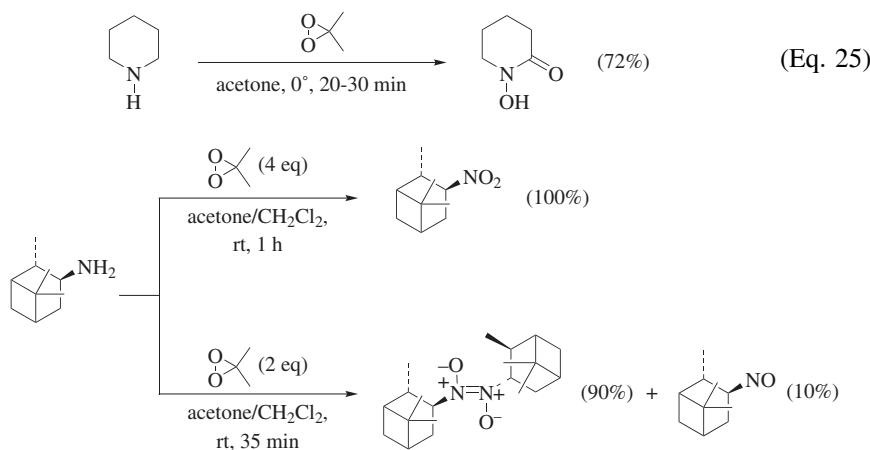
Nitrogen. Irrespective of whether the nitrogen atom in the substrate is sp^3 or sp^2 hybridized, it is readily oxidized by either isolated or in situ generated dioxiranes. The outcome of the dioxirane oxidation of an sp^3 -hybridized nitrogen depends on the structure of the amine. Tertiary amines give cleanly the *N*-oxides, as illustrated in Eq. 24. Particularly noteworthy is the selective oxidation of the nitrogen atom, without epoxidation of the double bond.⁹⁵ Oxidation of secondary amines is more complex. If the secondary amine does not bear α -hydrogen atoms, the product is usually the expected hydroxylamine; however, the latter may be further oxidized by excess DMD to the corresponding nitroxyl radical. An illustrative example is shown in Scheme 8,^{96,97} it should be noted that the alcohol functionality survives, which demonstrates the greater reactivity of the amino group towards DMD oxidation.



If the secondary amine bears α -hydrogen atoms, the product can be either a nitrone or a hydroxylamine, depending on the reaction conditions. For example, *N,N*-dibenzylamine is oxidized to the hydroxylamine with DMD at 0° (upper pathway),⁹⁶ whereas the nitrone is obtained upon treatment with two equivalents of cyclohexanone dioxirane at -20° (lower pathway) (Scheme 9).⁹⁸ Other products may also be obtained, as illustrated in the DMD oxidation of piperidine; here the hydroxamic acid is obtained in good yield (Eq. 25).⁹⁹ Primary amines usually give a complex mixture of products, which may contain hydroxylamine, oxime, nitroso, nitro, and sometimes even azoxy compounds. However, reaction conditions may be chosen to favor one of these products. Thus, a preparatively valuable method is the DMD oxidation of aliphatic and aromatic amines to the corresponding nitro compounds. For example, the optically active amine in Scheme 10 is oxidized with excess DMD to the respective nitroalkane in quantitative yield



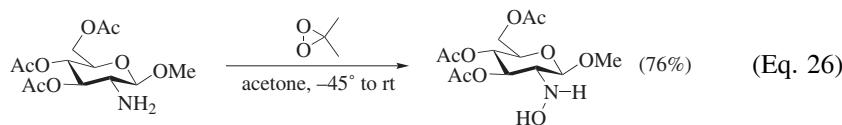
Scheme 8. DMD oxidation of a secondary amine.

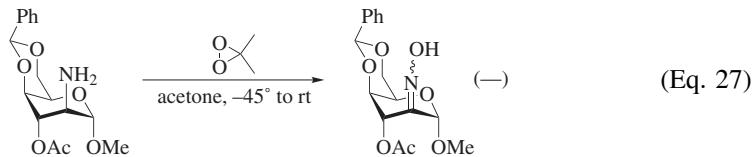
Scheme 9. DMD oxidation of *N,N*-dibenzylamine.

Scheme 10. DMD oxidation of a primary amine.

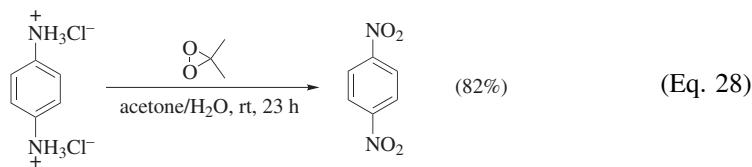
(upper pathway).²² If an insufficient amount (2 equiv.) of DMD is used, the nitroso and the azoxy products are obtained instead (lower pathway).²²

At subambient temperature, primary amines are converted either into hydroxylamines or into oximes by DMD. This transformation can be synthetically useful, as, for example, in the oxidation of the amino sugar derivative in Eq. 26 to the corresponding hydroxylamine in good yield. However, the related amino sugar in Eq. 27 is oxidized to the oxime under identical reaction conditions.¹⁰⁰ Clearly, structural features of the amino sugar strongly influence the course of the oxidation.

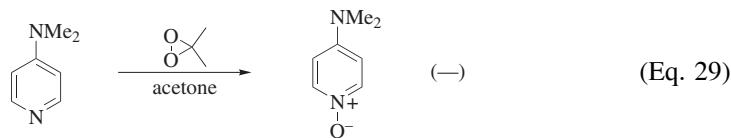




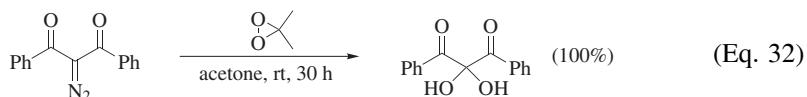
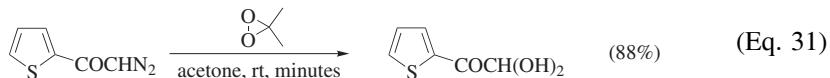
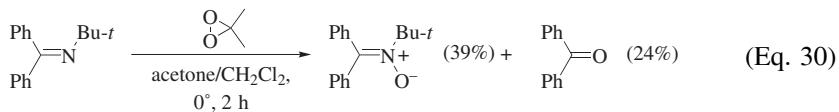
Although amines are readily oxidized by dioxiranes, the corresponding amides persist and are, therefore, often used to protect amines. Protection of the amine by protonation may also be employed, but since ammonium salts dissociate into the free amine, it is essential to conduct the oxidation under strongly acidic conditions; otherwise the oxidation will still take place slowly (Eq. 28).¹⁰¹



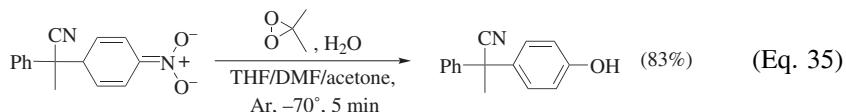
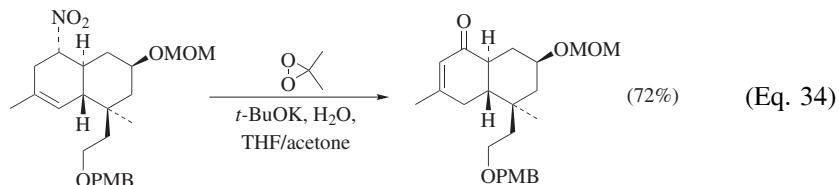
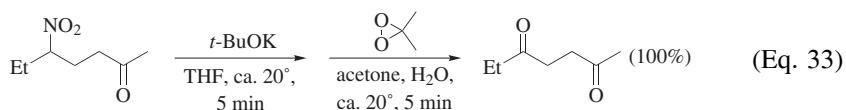
The oxidation of *sp*²-hybridized nitrogen generally falls into two categories: namely, heteroarenes and isolated C=N bonds. The nitrogen-containing arenes usually afford *N*-oxides. Thus, pyridines are generally oxidized to pyridine *N*-oxides. An interesting example is given in Eq. 29 in which the pyridine nitrogen atom is selectively oxidized rather than the dimethylamino group.²¹ Since the resulting *N*-oxide may further react with DMD to give *N,N*-dimethylaminopyridine and singlet oxygen, as illustrated in Scheme 4, it is not possible to achieve full conversion of the substrate in such situations.²¹



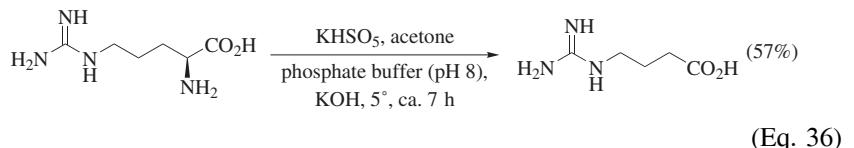
Oxidation of the nitrogen atom in isolated C=N bonds is complicated by the fact that the initial oxidation product may be further oxidized by dioxirane with cleavage of the C=N bond. For example, N-alkylated imines are oxidized by DMD to a mixture of nitrones and ketones (Eq. 30).¹⁰² When imines without substituents on the nitrogen atom are treated with DMD, the main products are oximes,¹⁰² which in turn may be further oxidized by excess dioxirane to the corresponding ketones or aldehydes. The method thus serves as a useful deprotection method for oximes. Similarly, diazoalkanes yield cleavage products (ketones, aldehydes, or their hydrates),^{103–106} when oxidized by DMD (Eq. 31).¹⁰³ This oxidation has been employed to prepare tricarbonyl compounds (Eq. 32),¹⁰⁵ and as such comprises a convenient method for the preparation of these reactive substances.



The DMD oxidation of nitronate anions, generated *in situ* from nitroalkanes, also affords carbonyl compounds through cleavage of the carbon-nitrogen bond (Eq. 33),¹⁰⁷ and in effect constitutes an oxidative Nef reaction.¹⁰⁸ This efficient new method has been successfully employed in the synthesis of the AB ring system of norzoanthamine (Eq. 34).¹⁰⁹ In a similar manner, the σ^H adducts generated *in situ* from nitroarenes by the addition of a carbanion are efficiently oxidized by DMD to the corresponding phenols (Eq. 35).^{110,111} This transformation comprises the first method for the direct oxidation of nitroarenes to phenols.

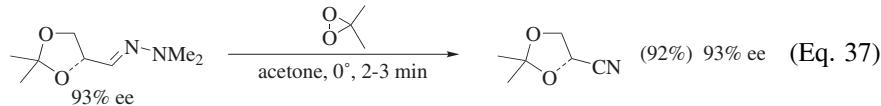


Similar oxidative cleavage reactions have been reported for several α -amino acids. Thus, when arginine is oxidized by DMD under *in situ* conditions, 4-guanidinobutanoic acid is obtained in moderate yield (Eq. 36).¹¹²

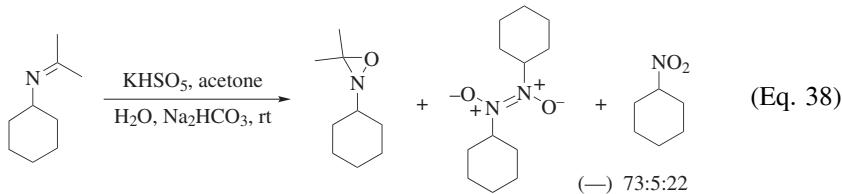


The oxidation of *N,N*-dimethylhydrazone by DMD at 0° produces the corresponding nitriles (Eq. 37)¹¹³. What is remarkable about this useful oxidation is

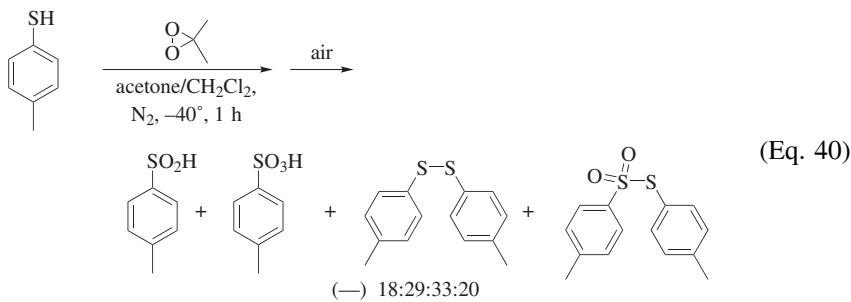
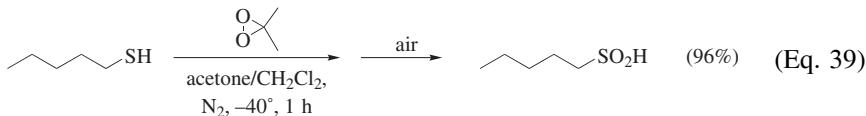
that no racemization takes place at the stereogenic center, which again emphasizes the mild reaction conditions.

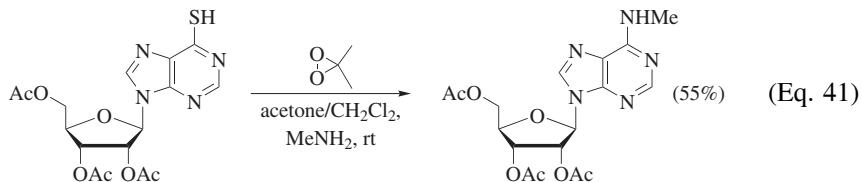


Dioxirane-mediated epoxidation of the C=N bond of imines to oxaziridines is rare, but examples are known for the *in situ* method (Eq. 38).¹¹⁴

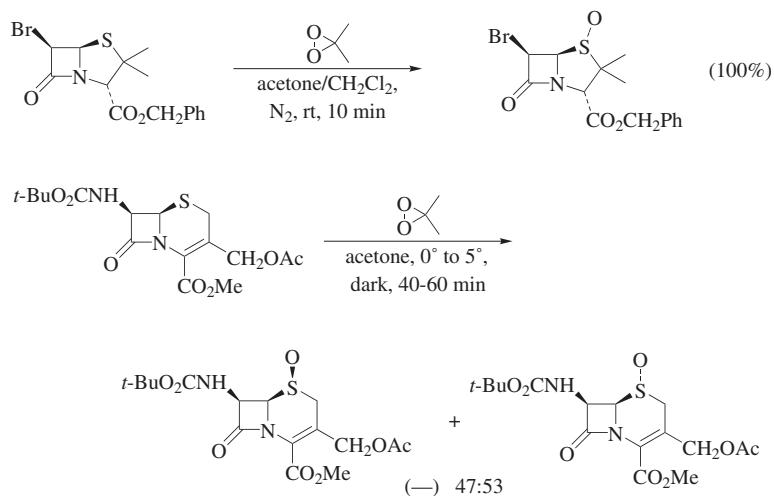
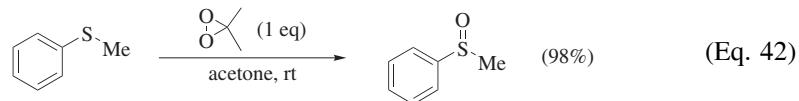


Sulfur and Selenium. In general, sulfur-containing substrates are more reactive toward dioxirane than nitrogen compounds. Thus, the oxidation of aliphatic thiols by DMD (isol.) at low temperature leads to sulfenic acids in good yield (Eq. 39).¹¹⁵ However, under the same reaction conditions, benzyl mercaptan affords a complex mixture of benzylsulfinic acid, benzylsulfonic acid, dibenzyl disulfide, dibenzyl thiosulfonate, and benzaldehyde.¹¹⁵ Similarly, DMD (isol.) oxidation of *p*-methylthiophenol displays this complexity (Eq. 40).¹¹⁵ The latter oxidations are, thus, not synthetically useful, given the multiple products formed; however, the oxidation of 9*H*-purine-6-thiols in the presence of an amine nucleophile produces ribonucleoside analogs in useful yields.^{116–120} An example of such a mercaptan oxidation with DMD (isol.) in the presence of methylamine is illustrated in Eq. 41. This reaction confirms that thiols are more reactive toward DMD oxidation than primary amines, as would be expected from the nucleophilicity of mercaptans compared with amines.¹⁵

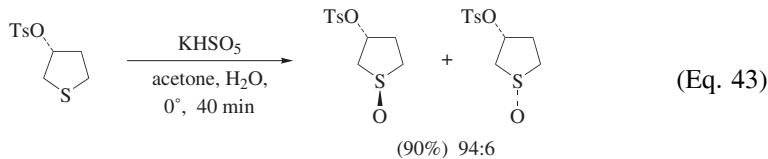




A sulfide may be oxidized by dioxirane to either the sulfoxide or sulfone, depending on the number of equivalents of the oxidant employed (Scheme 3). As pointed out already, sulfides are more readily oxidized than sulfoxides and, therefore, the sulfoxide product may be selectively obtained by employing only one equivalent of DMD (Eq. 42).¹²¹ Since methyl phenyl sulfide is prochiral, DMD oxidation affords the racemic sulfoxide. Similarly, if a chiral sulfide is employed, diastereomeric sulfoxides are expected. For example, DMD (*in situ*) oxidation of the tetrahydrothiophene derivative shown in Eq. 43 furnishes mainly one diastereomeric *S*-oxide with excellent stereocontrol (94:6).¹²² Such high diastereoselective oxidations are not general, as illustrated for the two similar substrates shown in Scheme 11.^{123,124} For the five-membered-ring sulfide (upper equation), the *cis* diastereomer is formed exclusively, whereas for the six-membered cyclic sulfide (lower equation) both diastereomeric sulfoxides are obtained in about equal amounts.

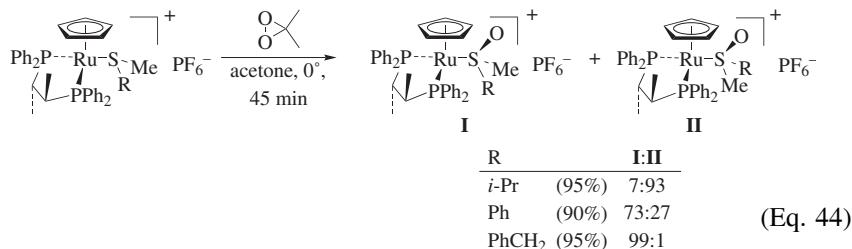


Scheme 11. Sulfoxidation of cyclic sulfides by DMD (isol.).

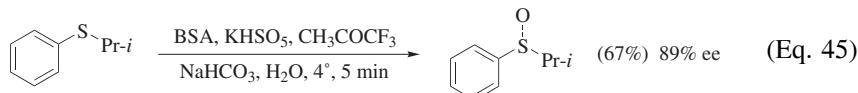


There is only one report on the diastereoselective oxidation of a chiral acyclic sulfide by DMD. In this case, the exocyclic sulfide is oxidized with low diastereoselectivity to the corresponding sulfoxide.¹²⁵

To achieve better diastereomeric control, prochiral sulfides have been coordinated to chiral organometallic complexes and then oxidized with DMD (isol.).^{126–129} As is evident from Eq. 44,¹²⁶ the diastereoselectivity depends highly on the structure of the sulfide, and as such, the outcome is difficult to predict. After decomplexation, enantiomerically enriched sulfoxides are obtained. The overall process qualifies, therefore, as an indirect enantioselective oxidation.



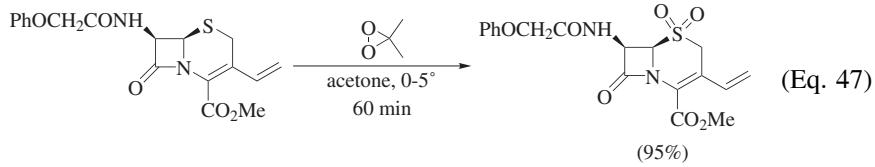
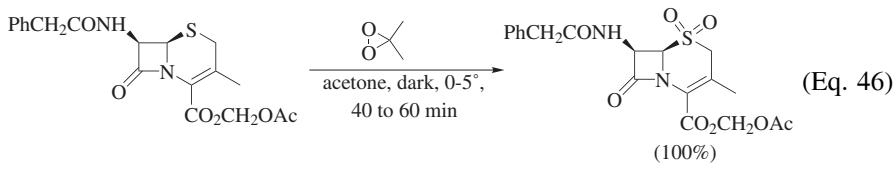
Enantioselective oxidation of sulfides by achiral dioxirane may be performed with bovine serum albumin (BSA). In the presence of this protein, prochiral sulfides have been oxidized by TFD (in situ) to enantioenriched sulfoxides in moderate to good enantioselectivities (up to 89% ee).^{130,131} A typical example is shown in Eq. 45.^{130,131}



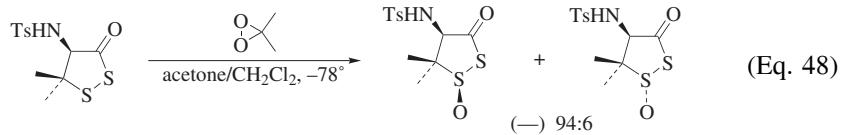
Enantioselective oxidation of a prochiral sulfide with an optically active dioxirane has not yet been accomplished. An attempt with methyl phenyl sulfide as substrate and in situ generated fructose-derived dioxirane, which has been successfully employed in asymmetric epoxidation,^{15,132} resulted in an enantiomeric excess of less than 5%.⁹⁴

If two or more equivalents of dioxirane are used, the sulfone is the main product. An illustrative example with DMD (isol.) is shown in Eq. 46.¹²⁴ It is noteworthy that both alkenyl¹²⁴ and alkynyl¹³³ sulfides are oxidized by dioxirane to the corresponding sulfones without epoxidation of the C–C multiple

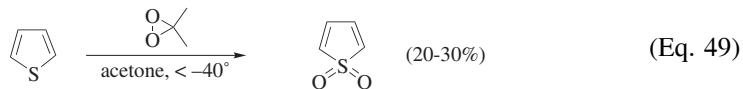
bonds (Eq. 47).¹²⁴ As expected, the dioxirane oxidation of a sulfoxide affords the corresponding sulfone.¹³⁴



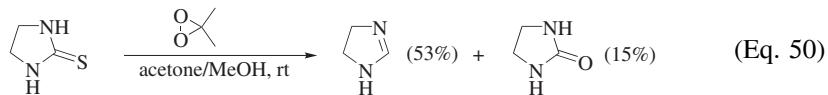
Oxidation of disulfides, trisulfides, and polysulfides by DMD usually leads to a mixture of multiple products,^{135,136} and is not of synthetic importance. Useful selectivities have been observed with DMD (isol.) only when one of the sulfur atoms in the disulfide is substituted by an electron-withdrawing group (Eq. 48).¹³⁷

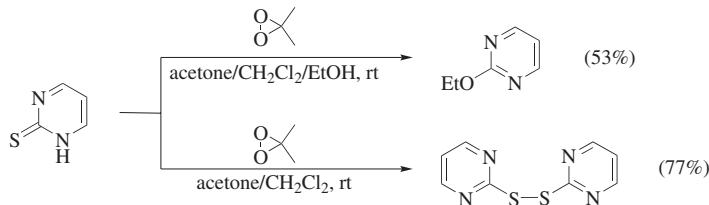


Dioxirane oxidation of sulfur-containing heteroarenes, such as substituted thiophenes, takes place exclusively on the sulfur atom.¹³⁸⁻¹⁴¹ At subambient temperature, the oxidation products are usually the corresponding thiophene 1,1-dioxides. Recently, the oxidation of thiophene with DMD (isol.) below -40° afforded the elusive parent thiophene 1,1-dioxide, which was isolated (Eq. 49).¹⁴⁰ When the oxidation was carried out at higher temperature, the thiophene 1,1-dioxide decomposed to other products.^{140,141}



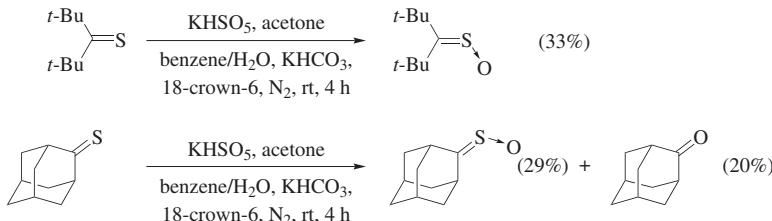
Dioxirane oxidation of the C=S bond in the thiourea functionality of some heterocycles leads to desulfurization products. A typical example is shown for a cyclic thiourea with DMD (isol.) in Eq. 50.¹⁴² This oxidation is, however, complex since disulfides and other products may be formed (Scheme 12).¹⁴²⁻¹⁴⁴



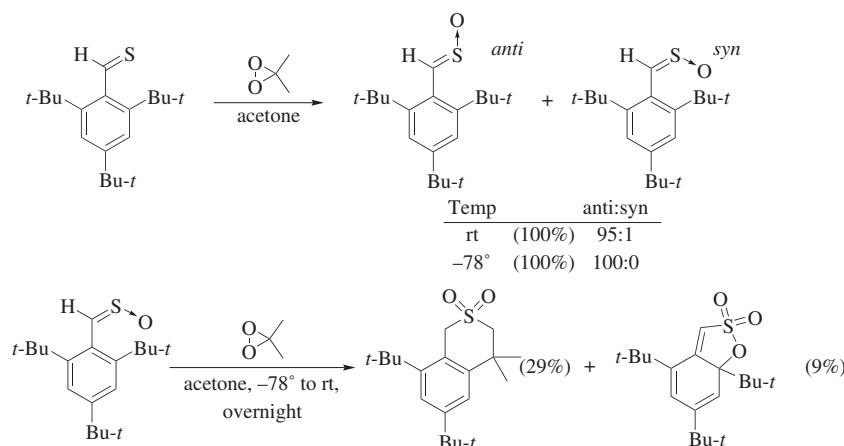


Scheme 12. Oxidation of 1*H*-pyrimidine-2-thione by DMD (isol.).

The dioxirane oxidation of the C=S functionality in thioketones to thioketone *S*-oxides is quite rare. Examples are collected in Scheme 13.^{145,146} The yields of the *S*-oxides from bis(*tert*-butyl)thione and adamantane-2-thione by DMD (*in situ*) are quite low because of further oxidation. Thiobenzaldehyde derivatives with bulky substituents, however, are oxidized by DMD (isol.) to the corresponding *S*-oxides both in good yield and with high diastereoselectivity;¹⁴⁷ further oxidation of the syn diastereomer by DMD (isol.) gives two unusual products in low yields (Scheme 14).¹⁴⁷

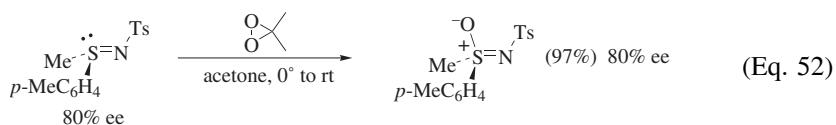
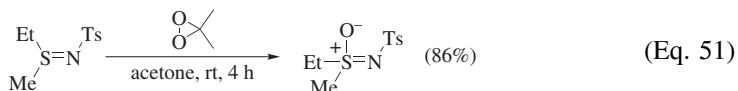


Scheme 13. Oxidation of thioketones by DMD (in situ).

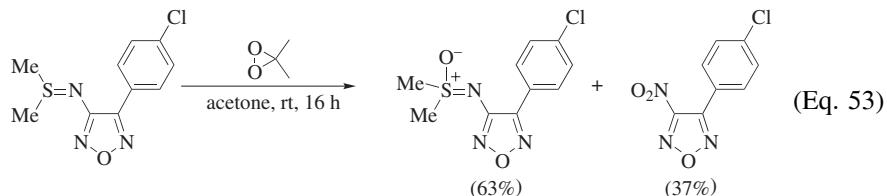


Scheme 14. DMD (isol.) oxidation of a thioaldehyde and its *syn*-*S*-oxide.

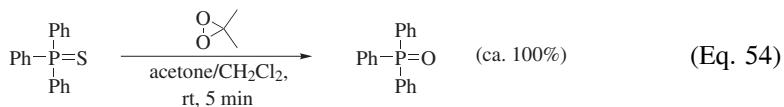
Oxidation of N-tosylated or N-acylated sulfilimines with DMD (isol.) takes place selectively on sulfur to give sulfoximines in good yields (Eq. 51).¹⁴⁸ The oxidation by DMD (isol.) is stereoselective so that a chiral sulfoximine may be obtained from an optically active sulfilimine with complete preservation of the initial enantiomeric purity (Eq. 52).¹⁴⁸



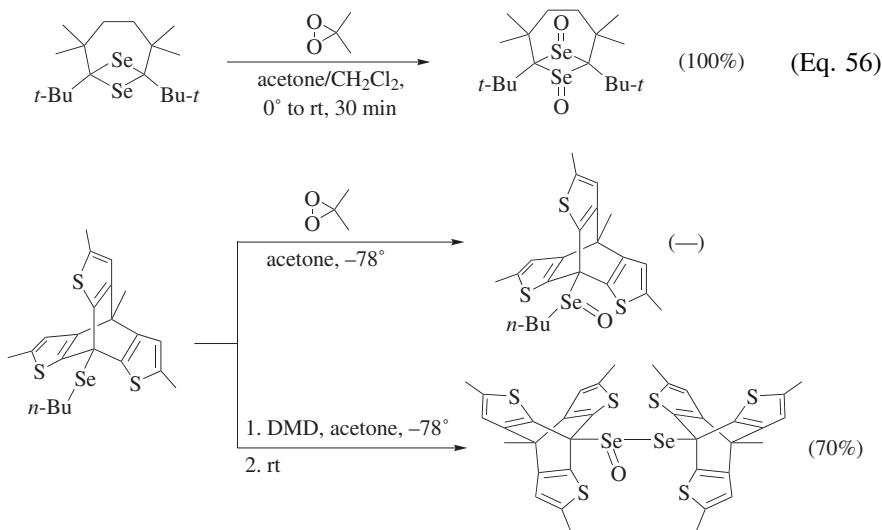
With the more reactive TFD (isol.), some sulfoxides and sulfones are also formed via cleavage of the S=N bond.¹⁴⁸ When the N atom of the sulfilimine bears a heterocyclic ring instead of an acyl or tosyl group, DMD (isol.) oxidation leads to a mixture of S- and N-oxidations, as evidenced by the presence of the nitro product (Eq. 53).¹⁴⁹ With wet DMD (isol.), N-oxidation represents the major process (63% vs. 37%).¹⁴⁹ These results suggest that the chemoselectivity of S versus N oxidation by DMD (isol.) of sulfilimine depends on the electron density of the heteroatoms.



In the oxidation of phosphine sulfides by DMD (isol.), desulfurization affords the corresponding phosphine oxides in nearly quantitative yields (Eq. 54).¹⁵⁰ Similarly, a thiophosphonate is converted into the phosphonate by oxidation with DMD (isol.), as shown in Eq. 55.¹⁵¹



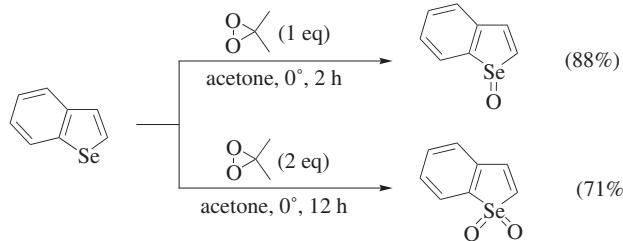
Selenides react with dioxirane like their sulfur analogs to give selenoxides, but the selenium atom is more reactive than the sulfur atom. Since selenoxides are much more labile than sulfoxides, good yields are usually only obtained



Scheme 15. Oxidation of a selenide by DMD (isol.).

for selenoxides with bulky substituents (Eq. 56).¹³⁴ In some cases more complex products may be obtained because of the labile nature of the selenoxides (Scheme 15).¹⁵²

Oxidation of selenophenes by DMD (isol.)^{153–155} at subambient temperatures gives selenophene 1-oxides or 1,1-dioxides in good yields. The amount of DMD used determines which product predominates (Scheme 16).¹⁵³ These results are comparable to those obtained with their sulfur counterparts.^{138–141}



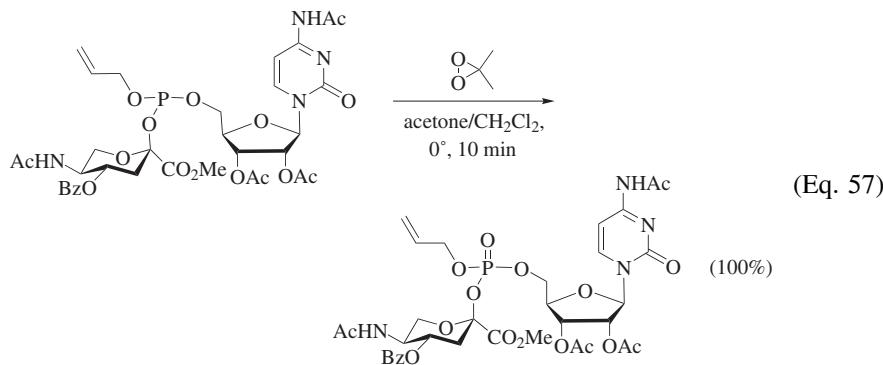
Scheme 16. Oxidation of benzoselenophene by DMD (isol.).

Phosphorus. Trivalent phosphorus compounds are readily oxidized by various oxidants; however, the oxidation of such substrates by dioxiranes has been sparsely studied. Since only a handful of examples are available in the literature, little may be said about general trends in reactivity and/or selectivity. Clearly, more detailed studies are needed to define the scope and limitations

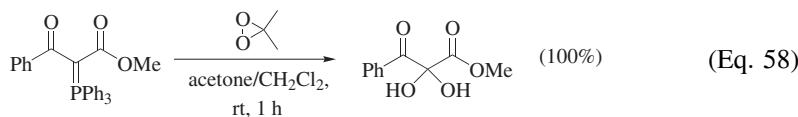
of this oxidation. Nonetheless, the phosphorus atom is readily oxidized by other reagents, such that it is questionable whether dioxiranes need to be used.

Triphenylphosphine is a favorite substrate for testing the oxidation of trivalent phosphorus. DMD (isol.) leads to triphosphine oxide quantitatively under a variety of conditions.^{121,156} DMD (*in situ*) has also been used, although the product yield was not specified.^{121,157}

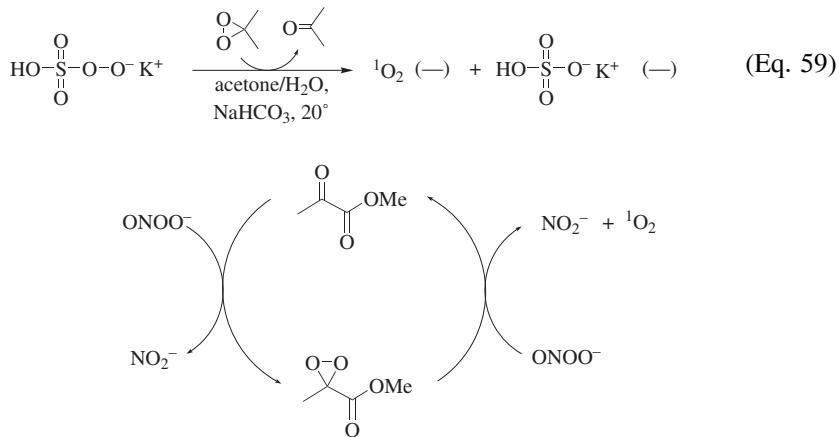
The selective oxidation of the phosphite functionality in nucleoside derivatives bearing a modified sugar on the trivalent phosphorus atom produces the corresponding nucleotides in nearly quantitative yields (Eq. 57).¹⁵⁸ In this reaction, the phosphorus atom is, as expected, selectively oxidized by the dioxirane, without epoxidation of the allylic double bond. Furthermore, this phosphorus oxidation may offer an expedient way of synthesizing unusual nucleotides.



A case of pentavalent phosphorus atom oxidation is documented for α,α -dicarbonylphosphoranes. When oxidized by DMD (isol.), the corresponding tricarbonyl compounds (as their hydrates) are obtained in excellent yields (Eq. 58).¹⁵⁹ These results are comparable with the DMD oxidation of similar diazo compounds¹⁰⁴ discussed above (cf. Eq. 32).



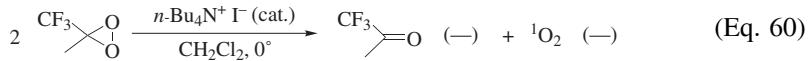
Oxygen. Dioxiranes also oxidize several types of oxygen functionalities, which include peroxides, N-oxides, and N-oxyl radicals. In most of these oxidations, molecular oxygen is produced. Thus, KHSO₅, which is used as reagent for the generation of dioxiranes, reacts with DMD (isol.) to generate oxygen gas, KHSO₄, and acetone as products (Eq. 59).¹⁶⁰ This reaction also takes place under *in situ* conditions and is responsible for the acetone-catalyzed decomposition of KHSO₅, the process that actually led to the discovery of dimethyldioxirane.¹⁶¹ The molecular oxygen that is released in this oxidation is the electronically excited singlet oxygen, as confirmed by the characteristic chemiluminescence emission.¹⁶² Similarly, the catalytic decomposition of peroxy nitrite by ketones,



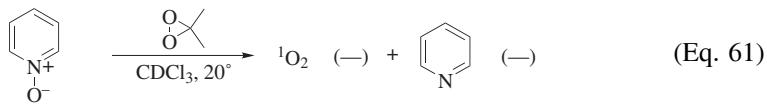
Scheme 17. Catalytic decomposition of peroxynitrite by methyl pyruvate.

such as methyl pyruvate, is rationalized in terms of peroxy nitrite oxidation by the in situ generated dioxirane (Scheme 17).¹⁶³

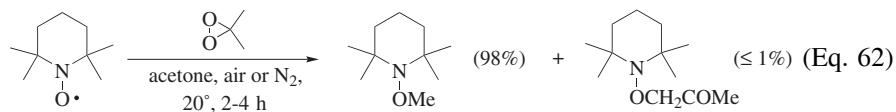
Potassium superoxide (KO_2) decomposes DMD in acetone solution, releasing singlet oxygen as detected by chemiluminescence.⁹⁴ Furthermore, a catalytic amount of $n\text{-Bu}_4\text{NI}$ efficiently converts two molecules of TFD into singlet oxygen and trifluoroacetone (Eq. 60).¹⁶⁴



Aliphatic and aromatic tertiary amine oxides also react with dioxiranes to generate free amines and singlet oxygen (Eq. 61).^{26,165} Since the N -oxide is prepared by DMD oxidation of the tertiary amine, treatment of the latter with excess DMD causes decomposition of the DMD by the in situ formed N -oxide, with concomitant release of O_2 .²⁶ The mechanism of this oxidation is presented in Scheme 4.

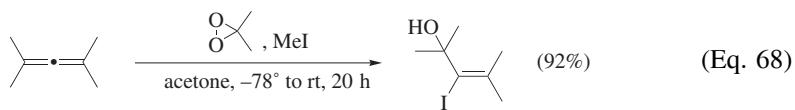
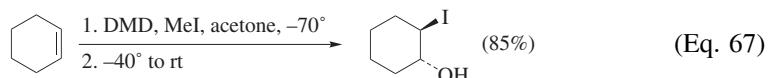
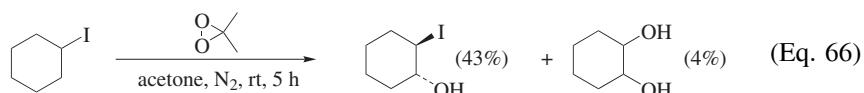
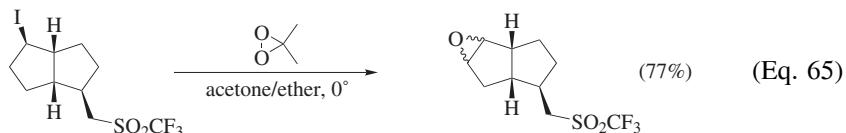
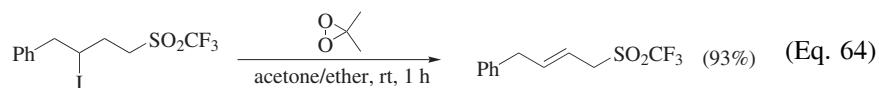
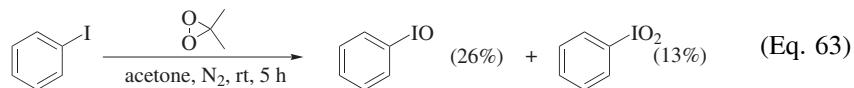


The dioxirane oxidation of an N -oxyl radical is illustrated in Eq. 62.^{23,166} The reaction follows a complex radical mechanism to give two O-alkylated products.



Halogens. There are only a few reports on the dioxirane oxidation of halogen-containing compounds. The oxidation of the chloride ion to the hypochlorite ion by DMD (*in situ*) has been known since the very beginning of dioxirane chemistry. In fact, this reaction constitutes the first example of a dioxirane oxidation.¹⁶¹ Iodometry,^{121,167} which utilizes the oxidation of iodide anion under acidic conditions, serves as the method for quantitative determination of dioxirane concentration.

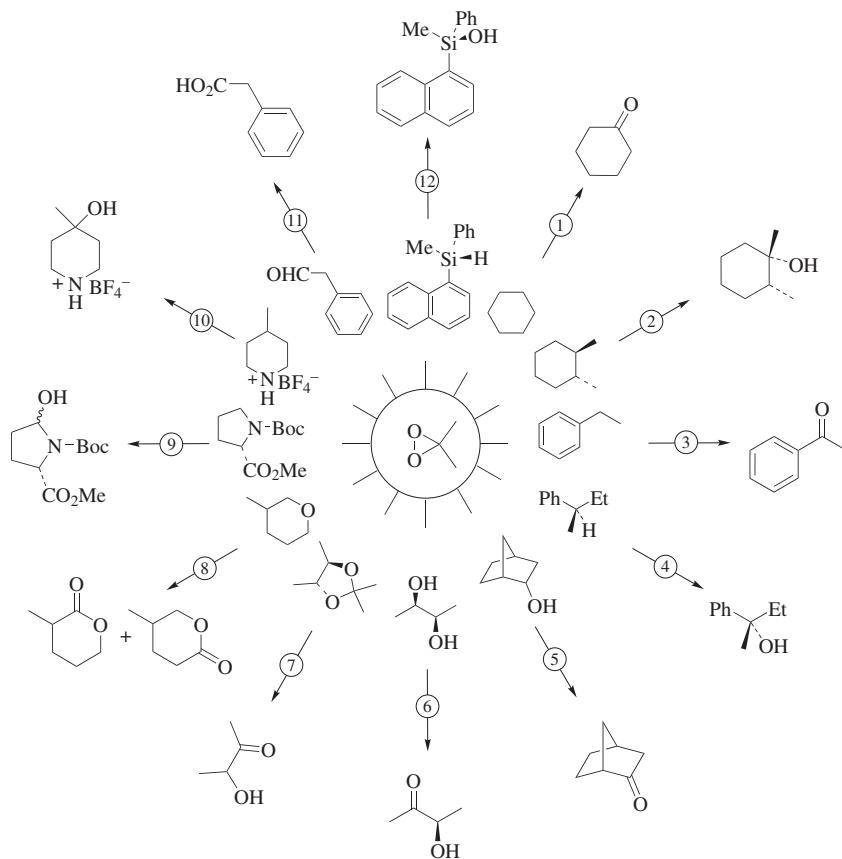
Organoiiodides are also prone to dioxirane oxidation, as illustrated by the DMD oxidation of iodobenzene to a mixture of iodosobenzene and iodylbenzene (Eq. 63).¹⁶⁸ In contrast, alkyl iodides afford labile primary oxidation products, which eliminate the oxidized iodine functionality resulting in alkenes (Eq. 64).¹⁶⁹ In such oxidations, the alkene product may be converted to an epoxide, as illustrated when the cyclic iodide in Eq. 65 is oxidized by DMD (*isol.*).¹⁶⁹ The oxidation of iodocyclohexane by DMD (*isol.*) under nitrogen leads to the iodohydrin and diol as unexpected products (Eq. 66).¹⁶⁸ The formation of iodohydrin, the major product, clearly reveals that hypoiodous acid (HOI) is generated *in situ*, which in turn adds to the liberated cyclohexene. Indeed, when methyl iodide is oxidized by moist DMD (*isol.*) at subambient temperature in the presence of cyclohexene, the corresponding iodohydrin is obtained (Eq. 67).¹⁷⁰ When an allene is used as substrate for this reaction, an allylic alcohol with a vinyl iodo functional group is obtained in high yield (Eq. 68).¹⁷¹



Alkanes and Silanes

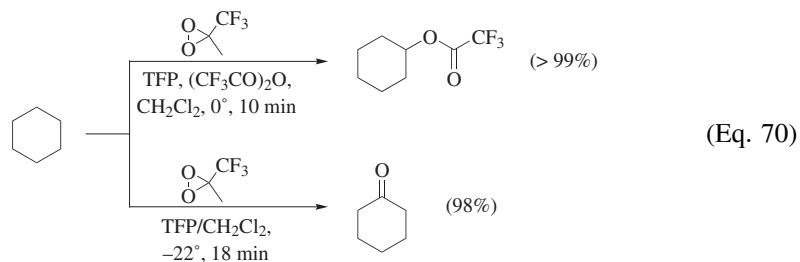
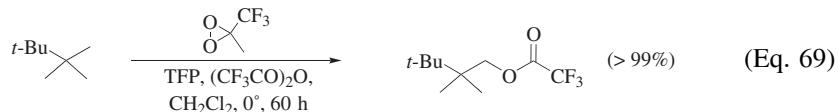
One of the highlights of dioxirane chemistry is the facile oxidation of C–H and Si–H σ bonds. Some typical examples of these oxidations are collected in the rosette of Scheme 18. Both DMD (isol.) and TFD (isol.) are employed for the oxidation of alkanes; TFD is more effective than DMD. In a few cases in situ generated dioxiranes have also been employed for this purpose.

Alkanes. Usually, alkanes are difficult to functionalize, but dioxiranes, especially TFD (isol.), effect hydroxylation under mild conditions. Their reactivity order follows the sequence primary < secondary < tertiary < benzylic < allylic C–H bonds. Only one example of hydroxylation by TFD (isol.) at a primary position of an unfunctionalized alkane (without secondary and tertiary C–H bonds) appears to have been reported (Eq. 69);¹⁷² in contrast, papers on hydroxylation at a secondary position are relatively abundant. For example, cyclohexane gives cyclohexanone as the only product in high yield (98%) under exceedingly

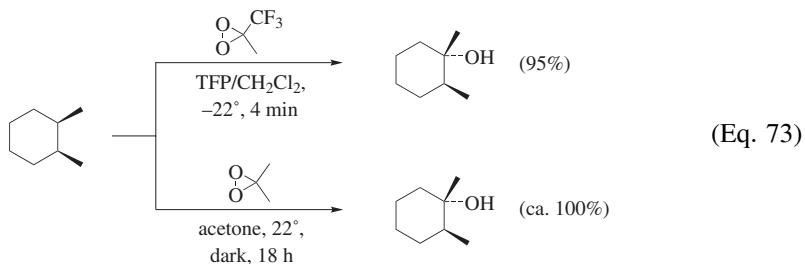
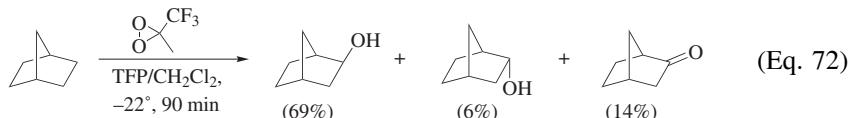
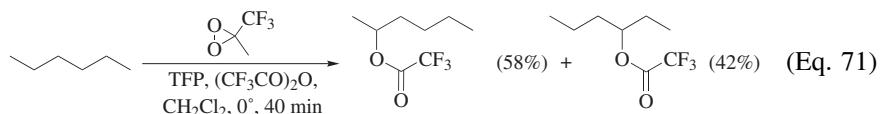


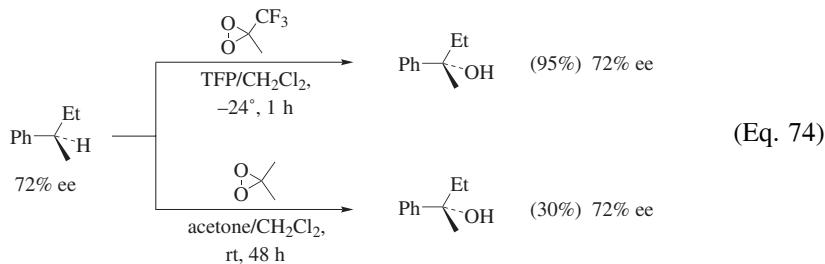
Scheme 18. An overview of dioxirane oxidations of alkanes and silanes.

mild conditions (Eq. 70). The primary oxidation product, namely cyclohexanol, is more reactive toward dioxirane oxidation than cyclohexane. Oxidation of the secondary alcohol may be circumvented by *in situ* acylation with trifluoroacetic anhydride (Eq. 70). Related cycloalkanes follow this reactivity pattern.^{30,172,173}

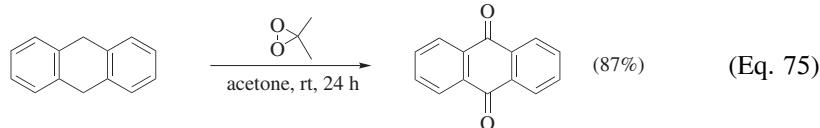


When *n*-alkanes are used, a mixture of regioisomeric ketones is usually obtained,¹⁷² unless the intermediary secondary alcohols are again protected *in situ* through acylation (Eq. 71).¹⁷³ Oxidation of bicyclic substrates usually affords a mixture of diastereomers (Eq. 72).³⁰ That the hydroxylation of a tertiary C–H bond is preferred over primary and secondary C–H bonds is exemplified in the oxidation of *cis*-1,2-dimethylcyclohexane by either DMD (isol.)¹⁷⁴ or TFD (isol.) (Eq. 73).³⁰ The resulting tertiary alcohol of this C–H insertion also demonstrates that oxygen transfer takes place stereoselectively, i.e., with complete retention at the stereogenic center. Absolute stereoretention has been rigorously confirmed by employing optically active 2-phenylbutane as substrate (Eq. 74).³¹

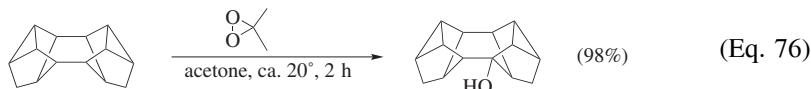




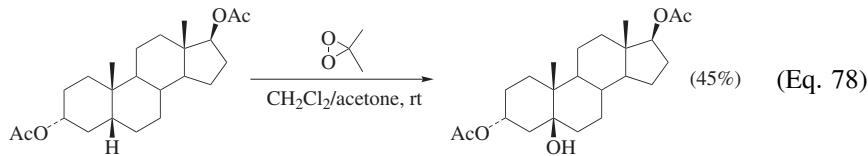
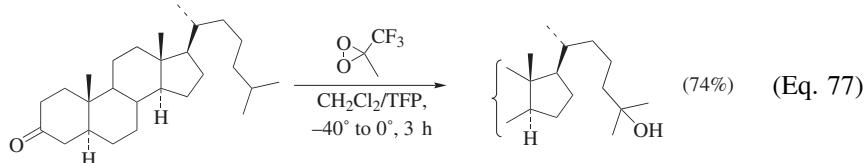
Benzyl C–H bonds are particularly reactive toward dioxirane oxidation, with numerous examples documented in the literature.¹⁷⁵ A preparatively useful approach is shown in Eq. 75, in which a benzhydrol C–H bond is oxyfunctionalized.¹⁷⁶



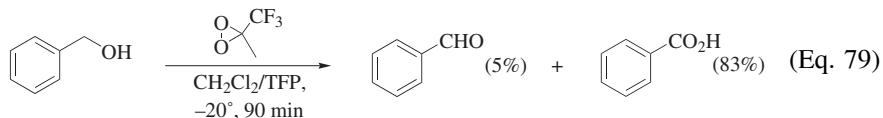
The oxidation of alkanes by dioxiranes is a convenient and useful method in organic synthesis. For example, the polycyclic substrate in Eq. 76¹⁷⁷ is hydroxylated in near quantitative yield by DMD (isol.). Such a transformation would be difficult to realize with conventional oxidants. Similarly, all four bridgehead positions in adamantane may be hydroxylated by TFD (isol.) on repetitive oxidation, affording the tetrahydroxy derivative.¹⁷⁸



Tertiary C–H bonds in the side chains of several steroids have also been selectively hydroxylated (Eq. 77).¹⁷⁹ In the absence of such C–H bonds, the tertiary C–H bond at the junction of the A and B rings is hydroxylated (Eq. 78).¹⁸⁰ This chemoselectivity derives presumably from steric factors, since the tertiary C–H bond in the side chain is sterically more exposed.

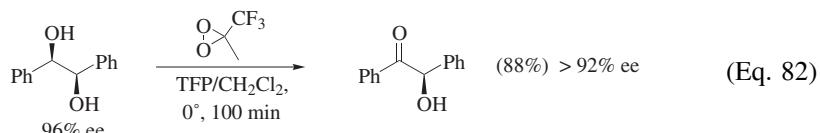
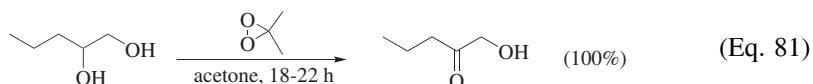
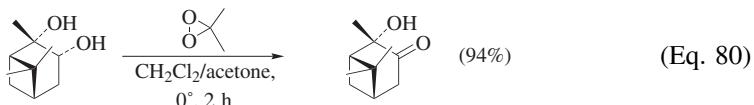


Carbon-hydrogen bonds adjacent to functional groups on the carbon atom are usually more reactive toward dioxirane oxidation, as has already been illustrated for alcohols. Primary alcohols, although much less reactive compared to secondary alcohols, are oxidized to aldehydes and/or carboxylic acids (Eq. 79).²⁹

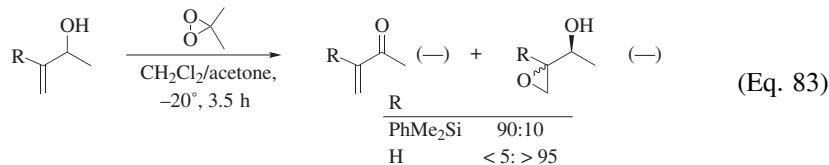


The same reaction may be responsible for the slow decomposition of DMD (isol.) in methanol.¹⁸¹ Consequently, primary and secondary alcohols are not recommended as solvents for conducting oxidations with DMD (isol.) and especially TFD (isol.).

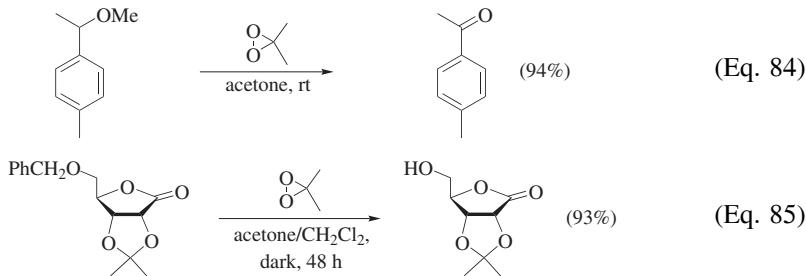
The oxidation of secondary alcohols, which is actually a very facile reaction, leads to the corresponding ketone as the product; expectedly, the tertiary hydroxy functionality is not oxidized (Eq. 80).¹⁸² The reactivity difference between primary and secondary alcohols may be exploited for chemoselective oxidation, as shown in Eq. 81.¹⁸³ Such oxidative transformations of vicinal diols to the corresponding α -hydroxy carbonyl products are particularly useful in organic synthesis, since the latter comprise valuable building blocks. In view of the mild oxidation conditions, this transformation has been employed for the preparation of optically active α -hydroxy ketones from the corresponding diols, as exemplified in Eq. 82.¹⁸⁴ Since the requisite enantioenriched diols may be readily obtained by a Sharpless dihydroxylation, this oxidation constitutes a convenient and effective entry into non-racemic α -hydroxy ketones.



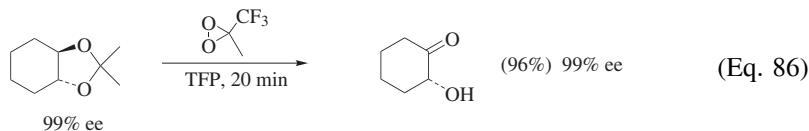
Oxidation of C–H bonds is usually more difficult than epoxidation; however, steric effects can cause allylic C–H oxidation to compete efficiently with epoxidation.¹⁸⁵ In the reaction shown in Eq. 83 the large silyl group directs the DMD oxidation preferably toward C–H insertion (for a detailed discussion see ref. 15).



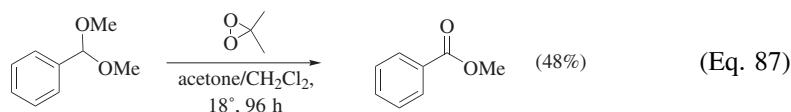
Conversion of the alcohol into the corresponding ether derivative reduces reactivity; however, DMD (isol.), and even more so TFD (isol.), oxidize such substrates to their respective carbonyl products (Eq. 84).¹⁸⁶ Since even ethers, such as diethyl ether and tetrahydrofuran, may be cleaved by dioxiranes, they are not recommended as solvents for dioxirane oxidations. Indeed, for the successful preparation of TFD (isol.), use of ether-free 1,1,1-trifluoropropan-2-one (TFP) is essential.¹⁸⁷ Nevertheless, when properly controlled, oxidation of ethers provides a useful method for the deprotection of the benzyl group in carbohydrates (Eq. 85).^{188,189}

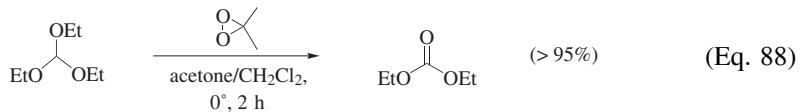


Acetals of vicinal diols are also subject to α -oxidation by dioxirane, especially with the more reactive TFP (isol.). For example, oxidative cleavage of an acetal functionality to the corresponding α -hydroxy ketone (Eq. 86)¹⁹⁰ constitutes a convenient deprotection protocol, coupled with an alcohol oxidation. Like the oxidation of vicinal diols, the second stereogenic center is preserved. Although further oxidation of α -hydroxy ketones to 1,2-diketones is possible, such reactions are sluggish because of electronic reasons, in that the α -carbonyl group deactivates the C–H bond. Thus, 1,2-diketones are not usually formed in appreciable amounts in the dioxirane oxidation of vicinal diols or their acetals.^{184,190}

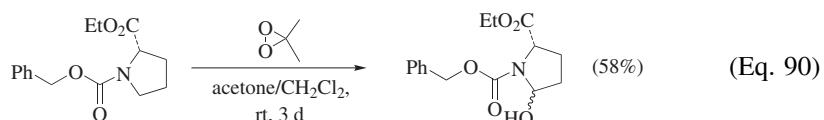
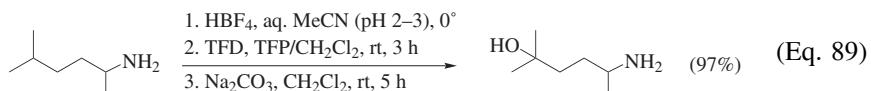


Dioxirane oxidation of the acetals of aldehydes leads to esters (Eq. 87);^{189,191} similarly, oxidation of orthoformates furnishes carbonates (Eq. 88).¹⁹¹

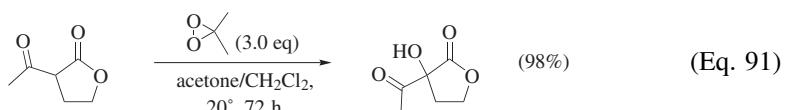




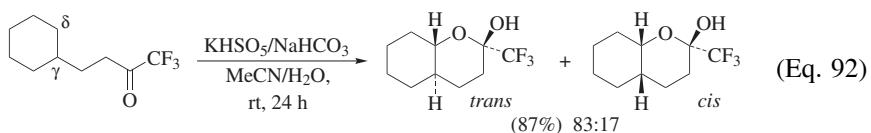
Direct oxidation of the C–H bond in an amine is not feasible given the much higher reactivity of the nitrogen atom; however, protection of the amino group as the ammonium salt (strongly acidic conditions must be used to tie up all of the amine) or as an amide will suppress the nitrogen oxidation effectively (for a detailed discussion of chemoselective dioxirane oxidation see ref. 15). A typical example is shown in Eq. 89.¹⁹² Unlike for alcohols, the α -hydroxylation of an amine is rare. One such example is shown in Eq. 90,⁹³ for which the hydroxylation is made possible by protection of the amine as a carbamate.



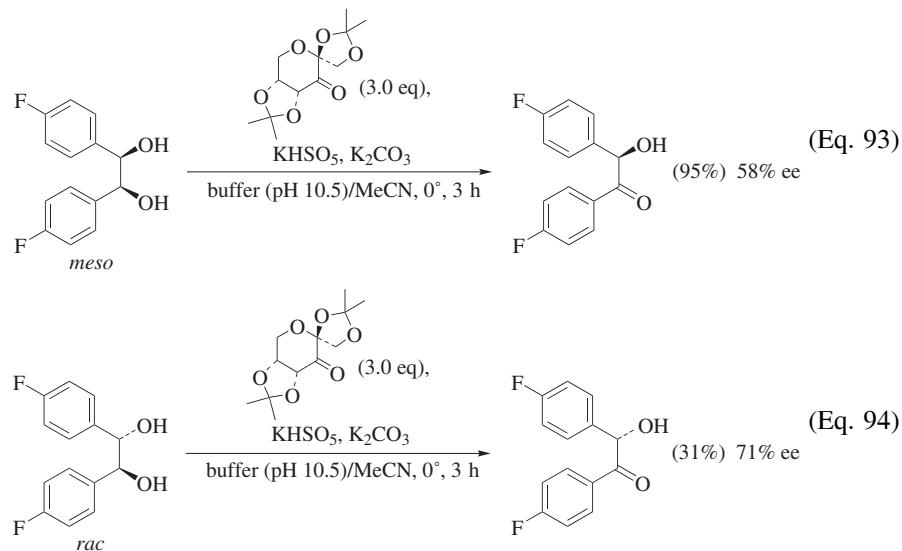
The acidic C–H bond of 1,3-dicarbonyl compounds is also reactive toward dioxirane (both isolated and in situ generated) oxidation (Eq. 91).¹⁹³ Although the oxidation appears like a C–H insertion, the possibility that epoxidation of the enolate is involved cannot be ruled out. The fact that this oxidation may be catalyzed by either $\text{Ni}(\text{OAc})_2$ or $\text{Ni}(\text{acac})_2$ implies involvement of enolate intermediates.¹⁹⁴



As is evident from the above discussion, C–H oxidation is a highly chemoselective reaction. The chemoselectivity is mainly governed by the reactivity of the chemically different C–H bonds, and sometimes by steric factors when the reactivities are similar. In the special situation illustrated in Eq. 92,¹⁹⁵ an in situ generated intramolecular dioxirane chemoselectively oxidizes the C–H bond at the δ site rather than the usually more reactive tertiary hydrogen (γ site) because of a more favorable concerted six-membered cyclic transition state.¹⁹⁵ Moreover, the equatorial C–H bond is preferentially oxidized such that the trans product dominates.

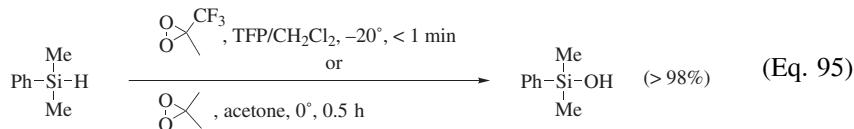


As C–H oxidation by dioxiranes is a stereoselective reaction, an attractive opportunity arises to carry out enantioselective C–H oxidations by employing optically active dioxiranes; however, such asymmetric C–H oxidations by dioxiranes are still largely unexplored. The only known example of enantioselective C–H oxidation appears to be the oxidation of vicinal diols by an *in situ* generated fructose-derived dioxirane.^{196,197} Through either the desymmetrization of meso-diols (Eq. 93) or the kinetic resolution of racemic diols (Eq. 94), enantioenriched α -hydroxy ketones may be obtained in up to 71% ee.¹⁹⁷ The desymmetrization of the acetals of meso-diols leads to higher enantioselectivities compared with that of meso-diols, but the conversion is lower because of their reduced reactivity.¹⁹⁷

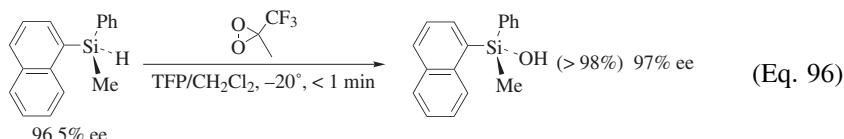


Since presently not much is known about enantioselective C–H oxidation with optically active dioxiranes, more research in this important area is needed. Analogous to the recent development of dioxirane-mediated asymmetric epoxidations, we expect progress in asymmetric C–H functionalization with chiral dioxiranes in the near future. The problem resides in designing more persistent and reactive optically active ketones as the dioxirane precursors.

Silanes. The Si–H bond in silanes is weaker than the C–H bond in alkanes; therefore, the oxidation of silanes is more facile. Nevertheless, only a few examples of silane oxidation by dioxiranes are known. Oxidation of dimethylphenylsilane by TFD (isol.)³⁹ or DMD (isol.)¹⁹⁸ affords the silanol in high yield, as shown in Eq. 95. As in the case of C–H oxidation, TFD is significantly more reactive than DMD toward the Si–H bond. The mild and neutral conditions lead exclusively to silanol product without any formation of disiloxane.



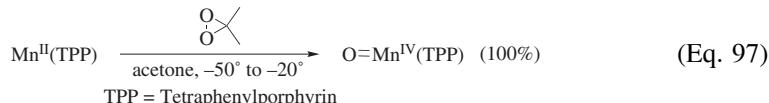
Like C–H oxidation, Si–H oxidation of silanes by dioxirane is also stereoselective. As displayed in Eq. 96, the original configuration of the silane is preserved during the oxidation.³⁹ The hydroxylation of silanes has also been applied to organometallic substrates (see the following section).



Organometallic Compounds

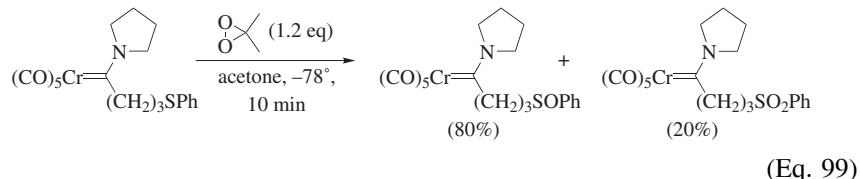
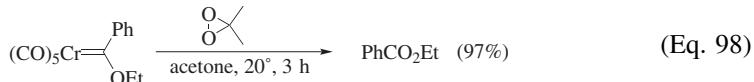
Oxidation of organometallic compounds by dioxiranes is usually more complex since both the metal center as well as the organic ligands may be oxidized. The examples presented in this section include both types of oxidations. Unless redox chemistry at the metal center complicates matters, the more electron-rich organic ligand in the organometallic complex usually undergoes direct oxidation (epoxidation, heteroatom oxidation, σ -bond insertion) by the dioxirane more readily than the metal center. In the case of highly reactive electron-rich alkenes, direct non-selective epoxidation prevails.

Dioxirane oxidation of the metal center leads to a higher oxidation state of the metal. For example, the DMD oxidation of a manganese(II) porphyrin complex at subambient temperature leads to the manganese(IV) derivative in quantitative yield (Eq. 97).¹⁹⁹ Analogously, manganese(III) and iron complexes are oxidized under similar conditions.¹⁹⁹ The use of DMD (isol.) as a stoichiometric oxygen donor in the Jacobsen–Katsuki epoxidation with the manganese-salen catalyst enables the enantioselective epoxidation of prochiral olefins under homogeneous conditions.^{200–203} Since the oxidation of the manganese is much faster than the epoxidation of the olefin, good to excellent enantiomeric excesses are obtained for the epoxides.^{200–203}

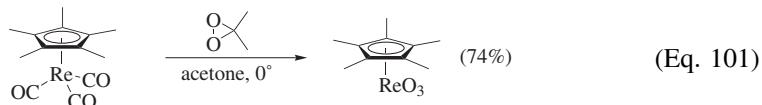
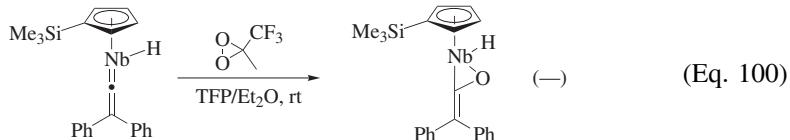


Dioxirane oxidation of metal–carbene complexes usually leads to demetallation.^{204–207} A specific example of such an oxidation by DMD (isol.) is shown in Eq. 98.²⁰⁴ When the ligands of the metal complex contain a functionality that is more prone to oxidation, demetallation may be suppressed (Eq. 99).²⁰⁸ With

even an excess of DMD (2.2 equiv.), a mixture of sulfoxide and the sulfone products is formed exclusively (93% yield) without demetallation.²⁰⁸

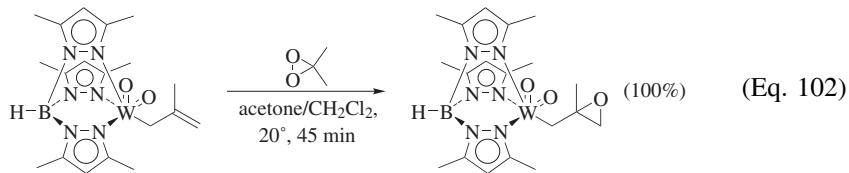


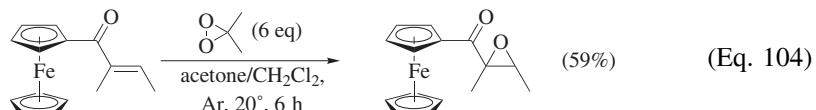
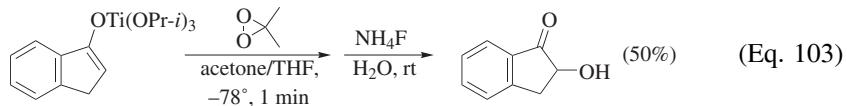
In an unusual example, the niobium complex shown in Eq. 100 is oxidized by TFP (isol.) to the metallaoxirane.²⁰⁹ Selective oxidative decarbonylation reactions of several rhenium and molybdenum carbonyl complexes by DMD (isol.) have also been observed; a particular case for rhenium is given in Eq. 101.²¹⁰



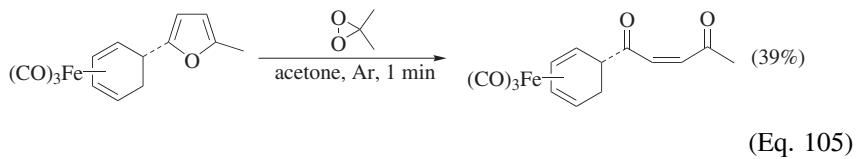
The dioxirane oxidation of ligands in organometallic complexes is more abundant. The chemical nature of the ligand determines whether the oxidation takes place at a π bond (epoxidation), at a lone pair (heteroatom oxidation), or at a σ bond (Si–H insertion).

Organometallic substrates with ligands that contain a reactive C=C double bond may undergo epoxidation. For example, the tungsten complex shown in Eq. 102 is epoxidized by DMD (isol.) in quantitative yield at ambient temperature.²¹¹ Similarly, titanium enolates are functionalized by DMD (isol.) to the corresponding α -hydroxy ketones after acidic workup (Eq. 103).²¹² When enantiomerically pure enolates bearing titanium TADDOLates as chiral ligands are subjected to this oxidation, enantiomerically enriched α -hydroxy ketones are obtained.²¹² If the metal complex is sufficiently robust, even electron-poor double bonds may be epoxidized under more strenuous conditions, as illustrated for the ferrocene derivative shown in Eq. 104.²¹³

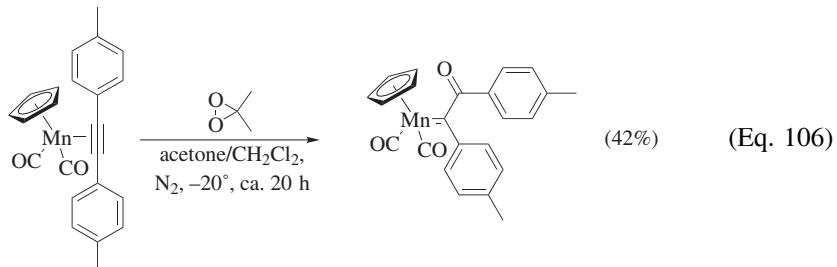




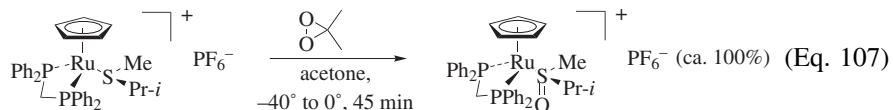
When the C=C double bond is, however, directly coordinated to the metal center, the reactivity drops. For example, oxidation of an iron complex by DMD (isol.) takes place only at the more electron-rich furan ring (Eq. 105).²¹⁴ Thus, the iron-tricarbonyl fragment may be utilized as an oxidatively resistant protecting group for the 1,3-diene functionality.

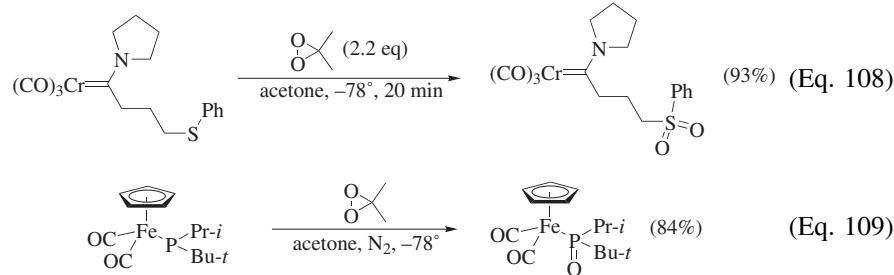


Dioxirane oxidation of cyclopentadiene, ligands widely used in organometallic complexes, has not been reported. Apparently, the complexed cyclopentadiene ligand resists dioxirane oxidation. In contrast, the metal-coordinated triple bond in a manganese-acetylene complex is oxidized by DMD (isol.) to a manganese-carbene complex, as illustrated in Eq. 106.²¹⁵

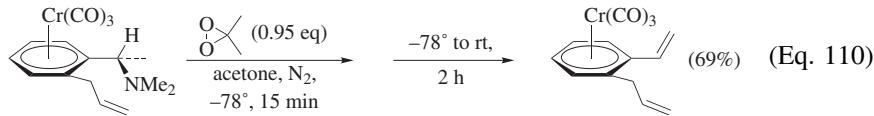


For ligands with a heteroatom functionality (sulfur, phosphorus, or nitrogen), the heteroatom is usually the preferred site of dioxirane oxidation. These oxidations usually follow the general trends presented in the section on Heteroatom Substrates (see above); sulfides are oxidized to sulfoxides (Eq. 107)¹²⁷ and/or sulfones (Eq. 108),²⁰⁸ and phosphines to phosphine oxides (Eq. 109).²¹⁶

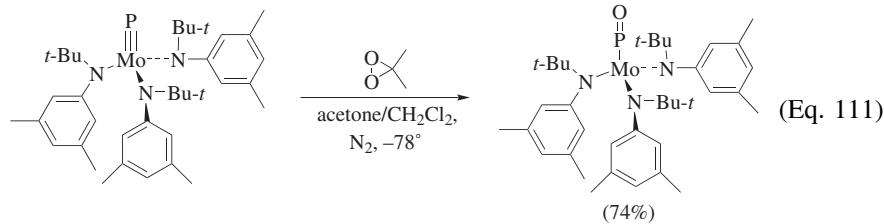




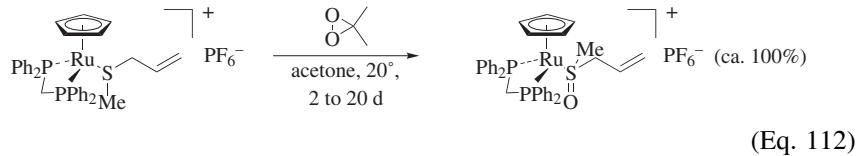
A tertiary amine ligand affords the *N*-oxide with DMD (isol.), which may eliminate hydroxylamine on warming to room temperature, thus generating the vinyl group in the final product (Eq. 110).²¹⁷ This result illustrates that the nitrogen functionality is more readily oxidized than an alkenyl double bond.



Notably, oxidation of a molybdenum complex having a molybdenum-phosphorus triple bond occurs at the trivalent phosphorus ligand, affording the corresponding complex with a P=O functionality (Eq. 111).²¹⁸

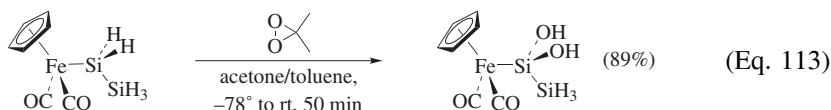


DMD (isol.) mediated oxidation of a ruthenium complex having both sulfide and double-bond functionalities reveals once again that the sulfur atom is more prone to oxidation than the C=C double bond, even though the sulfide functionality is coordinated to the metal center (Eq. 112).²¹⁹ The corresponding epoxide may only be obtained once the sulfur atom has been functionalized.²¹⁹

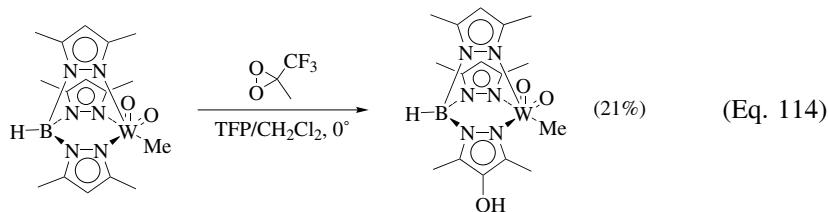


Insertion of oxygen into Si–H with DMD or TFD when Si–H is a component of an organometallic substrate has also been documented. For example, organometallic complexes with silane ligands are successfully hydroxylated by

DMD (isol.).^{220–227} A preparatively valuable example of the regioselective double hydroxylation of a ferriodisilane is shown in Eq. 113.²²⁷



Insertion into a CH bond of a ligand belonging to an organometallic compound is much more difficult. The only case known to date is the TFD (isol.) oxidation of the tungsten–boron complex in Eq. 114,²¹¹ in which hydroxylation of the pyrazole ligand occurs.



COMPARISON WITH OTHER METHODS

The three reaction types of dioxiranes presented in this chapter, namely π -bond oxidation (epoxidation) of allenes, acetylenes, and arenes, lone-pair oxidation of heteroatom substrates (N, S, P heteroatoms), and σ -bond oxidation (CH/SiH insertions) of alkanes and silanes, are quite different in their nature. Consequently, in comparing the dioxirane performance with other oxidants, it is convenient and even essential, to deal with these three classes separately in this subsection. It should, however, be kept in mind that the general features are quite similar, such that considerable overlap in the oxidative behavior exists for these substrates.

Allenes, Acetylenes, and Arenes

The dioxirane oxidation of cumulenes, acetylenes, and aromatic compounds all entail initial formation of epoxides. Some of these epoxides are rather labile and the final oxidation product may be structurally altered. Such functionalizations are to be classified as epoxidation reactions, which have been thoroughly covered in a previous chapter on dioxirane chemistry.¹⁵ The interested reader should consult that coverage for details; herein we reiterate only the more specifically applicable features in regard to oxidants other than dioxiranes.

As cumulenes and arenes are more sluggishly epoxidized than alkenes, potent oxidizing agents must be employed. For example, perhydrates (hexafluoroacetone/H₂O₂),^{228,229} oxaziridines,^{230–232} and the Payne oxidation reagents (MeCN/H₂O₂/HO[–])^{233–235} are hardly suitable. In addition, oxidations catalyzed by most transition metals (Co, Cr, Mn, Mo, Ti, V, W) are relatively ineffective for these substrates. An exception is rhenium, which in the form of methyltrioxorhenium

(MTO), efficiently oxidizes cumulenes and arenes, with the advantage that the MTO/H₂O₂ oxidant operates catalytically.⁴⁰

It is most unfortunate that the usually highly efficient enantioselective Jacobsen–Katsuki epoxidation with chiral manganese-salen complexes is not applicable to functionalize cumulenes and arenes to the corresponding optically active oxidation products. Similarly, the optically active ketones (such as Shi's fructose-derived ketone^{132,236}) employed in the catalytic, enantioselective, *in situ* mode of epoxidation are also ineffective for these substrates because of their low oxidative reactivity.

Peracids (most frequently *m*CPBA) are usually employed for the oxidation of cumulenes, acetylenes, and arenes, but as already pointed out,^{77–86} isolated dioxiranes are more advantageous for the preparation of labile epoxides. The disadvantage of peracids resides in the fact that acid-sensitive substrates and/or products must be avoided. When the acidity is buffered, the substrate and resulting epoxide must resist hydrolysis. Such limitations are not an issue when isolated dioxiranes are used, but the *in situ* mode of generating dioxirane chemistry is subject to the same disadvantages as for peracids. The benefits of dioxirane chemistry should be conspicuous for the oxidation of alenes, acetylenes, and arenes.

Heteroatom Substrates

Of the substrates considered in this chapter, those with heteroatoms are the easiest to oxidize, such that many oxidizing agents are available. For some heteroatoms, particularly divalent sulfur/selenium and more so trivalent phosphorus compounds, even H₂O₂ without activation will do, although the rate of oxidation is relatively slow. In the context of reactivity, dioxiranes present no definite advantages as heteroatom oxidants over the traditional ones such as peracids²³⁷ and transition-metal catalysts.²³⁸ (For a detailed comparison of the reactivity and selectivity of the methyltrioxorhenium (MTO) catalyst with dioxiranes, see a recent review.⁴⁰)

On the contrary, overoxidation by the more reactive dioxiranes may be a more serious problem to control. Whereas sp³-type (amines, hydroxylamine, hydrazines) and sp²-type (imines, oximes, hydrazone, heteroarenes) nitrogen-containing substances are readily oxidized to a plethora of products, the direct oxidation of the sp-type nitrogen atom in nitriles to the corresponding nitrile oxides is still a difficult task even for the highly reactive TFD. Similarly, the oxidative functionalization of amides and imides lacks suitable oxidizing agents, since neither dioxiranes nor traditional oxidants serve this purpose.

A unique chemical property of dioxiranes is their propensity to oxidize oxygen-type nucleophiles (e.g., HO₂[−], RO₂[−], RC(O)O₂[−], ClO[−]) to molecular oxygen; the latter is formed in the singlet-excited state, namely singlet oxygen.^{26,27} This unusual transformation appears not to have an equivalent among other oxidants. It is a consequence of the high electrophilic character of the dioxiranes, which makes them amenable for attack by the oxygen-centered nucleophile on the peroxide bond of the dioxirane. Some amine N-oxides¹⁶⁵ also engage in this type of reaction and are deoxygenated into singlet-excited molecular oxygen and the free amine, again a unique chemical behavior of dioxiranes.

As for enantioselective oxidations, specifically sulfoxidation, the chiral dioxiranes, such as Shi's fructose-based dioxirane,^{132,236} are inferior to the asymmetric oxygen transfer catalyzed by transition metals, namely the Ti(OR)₄/*t*-BuO₂H oxidant (Kagan sulfoxidation²³⁹). The ability, however, to achieve the asymmetric efficiency delivered by oxidative enzymes²⁴⁰ and microorganisms^{241,242} is still a formidable task in oxidation chemistry, particularly for chiral dioxiranes. Nevertheless, sulfoxides of high enantiomeric purity may be obtained through the sequence of desymmetrizing a prochiral sulfide by complexation with a transition metal based chiral auxiliary, followed by DMD oxidation, and final removal of the chiral auxiliary.¹²⁶ Such methodology should be able to compete in efficacy with the established protocols such as the Kagan enantioselective sulfoxidation.²³⁹

The dioxirane-related oxaziridines, which in optically active form deliver sulfoxides with enantioselectivities up to 98% ee, are effective for asymmetric sulfoxidation.^{243,244} Oxaziridinium salts also show promise and offer potential, but, as yet, enantioselectivity of only about 35% ee has been achieved.²⁴⁵

Alkanes and Silanes

Indisputably, the greatest challenge in oxidation chemistry is still the direct functionalization of unactivated C–H bonds. It is especially desirable to carry out such insertion reactions enantioselectively under catalytic conditions. Nature has perfected oxygen-atom insertions into C–H bonds by developing efficacious enzymes for this purpose, namely the oxidases and oxygenases.²⁴⁶ Along these lines, biomimetic oxidants based on chemical catalysts have been developed,²⁴⁷ most notably for the remote hydroxylation of steroids.^{248–250}

Although as yet the dioxiranes do not offer a general method for the enantioselective functionalization of hydrocarbons, it should be appreciated that these readily accessible oxidants, especially the simple structures DMD and TFD, work as impressively as they do. In this context, we reiterate that such non-metal-catalyzed C–H insertions by dioxiranes may take place highly stereoselectively as, for example, with complete retention of configuration in the hydroxylation of (*R*)-2-phenylbutane (see Scheme 5) by DMD.³⁷ Indeed, even a few asymmetric C–H oxidations with optically active dioxiranes, such as Shi's fructose-derived system,^{196,197} have been reported to occur in substantial enantiomeric excess, under quasi-catalytic conditions. These simple metal-free functionalizations of alkanes approach the efficiency of enzymatic C–H insertions. However, their catalytic efficiency still needs to be improved. The future challenges in dioxirane chemistry lie in enhancing the catalytic reactivity of these oxidants to achieve high enantioselectivity.

There are only a few alternative chemical methods that are competitive with dioxiranes; most comprise metal-catalyzed and radical-type C–H oxidations. One such method is the so-called "Gif oxidation,"²⁵¹ which is of limited synthetic utility because complex product mixtures are usually obtained.²⁵² A detailed comparison of metal-catalyzed C–H insertion with methyltrioxorhenium (MTO) and with dioxiranes has been made recently.⁴⁰ Generally, the performance (reactivity, selectivity) of the dioxiranes is better, but the MTO/H₂O₂ oxidant offers excellent catalytic efficiency. An effective nonmetal-type C–H oxidation of alcohols

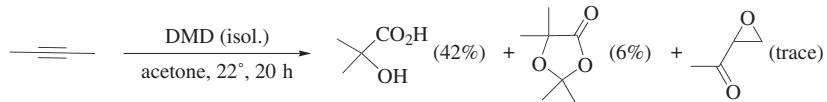
to ketones is catalyzed by the TEMPO nitroxyl radical, which has the advantage over dioxiranes that C=C double bonds may be present, since this reagent does not effect epoxidation.^{253–263} In fact, this method may be used for the kinetic resolution of secondary alcohols to afford ee values of up to 98% by engaging chiral binaphthyl-based nitroxyl radicals.²⁶⁴

Silanes are more readily oxidized than alkanes, since the Si–H bond (ca. 77 kcal/mol) is considerably weaker than the C–H bond (ca. 99 kcal/mol). The advantages of dioxiranes for oxygen insertion into Si–H bonds has been amply emphasized;^{39,198} a competitive alternative is the catalytic MTO/H₂O₂ oxidant.⁴⁰ For oxidation of optically active silanes, the urea/H₂O₂ adduct (UHP) should be employed instead of hydrogen peroxide to obtain enantioselectivities comparable to those of dioxiranes.¹⁹⁹

EXPERIMENTAL CONDITIONS

Caution! The dioxiranes DMD and TFD are volatile peroxides and must be handled with care. The oxidations should be carried out in a hood with good ventilation. Inhalation and direct exposure to skin must be avoided! Although no explosions have been reported for dioxiranes, all safety precautions should be employed!

EXPERIMENTAL PROCEDURES

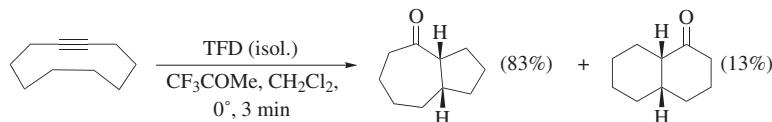


2-Hydroxy-2-methylpropanoic Acid [Oxidation of an Alkyne with DMD (isol.)].⁶³ To a magnetically stirred solution of 2-butyne (216 mg, 4.00 mmol) in acetone (5.0 mL) in a 250-mL flask, was added a solution of DMD in acetone (140 mL, 0.060 M, 8.40 mmol) at room temperature (ca. 22°). The progress of the reaction was followed by GLC analysis, which indicated the presence of three products in the ratio of 10:15:75. After 20 hours, the excess acetone was removed on a rotary evaporator (20°, 15 mmHg), the dark yellow residue (25 mL) was subjected to fractional distillation (80°, 5 mmHg) to afford a colorless material which solidified. The solid was recrystallized from CH₂Cl₂/hexane to give 174 mg (42%) of 2-hydroxy-2-methylpropanoic acid as colorless needles, mp 77–79°; ¹H NMR (CDCl₃) δ 1.50 (s, 6H), 6.30 (br s, 2H); ¹³C NMR (CDCl₃): δ 27.0, 72.2, 181.4; EIMS *m/z* (%): 89 (5), 59 (100), 45 (7), 44 (4), 43 (53).

The yellow distillate contained two other products, which were separated by preparative GLC. One of the products was obtained in trace amount and identified

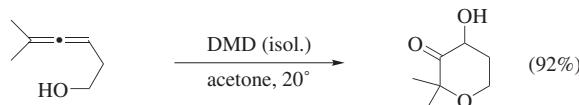
as 1-oxiranylethanone: ^1H NMR (CDCl_3) δ 2.06 (s, 3H), 2.90 (dd, $J = 5.7, 2.5$ Hz, 1H), 3.01 (dd, $J = 5.7, 4.7$ Hz, 1H), 3.40 (dd, $J = 4.6, 2.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 23.7, 45.8, 53.7, 205.5. EIMS m/z (%): 87 ($\text{M} + \text{H}$, 1), 86 (M^+ , 17), 85 (13), 71 (18), 55 (7), 53 (1), 44 (3), 43 (100).

The other product, 2,2,5,5-tetramethyl-1,3-dioxolane-4-one, was isolated by distillation (80° , 5 mmHg) as a colorless liquid (18 mg, 6%); IR (KBr) 2990, 2936, 1797, 1466, 1380, 1301, 1192, 1076, 1015, 931, 868, 838 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.48 (s, 6H), 1.58 (s, 6H); ^{13}C NMR (CDCl_3) δ 26.5, 28.6, 77.2, 109.3, 175.7; EIMS m/z (%): 130 (1.3), 129 ($\text{M}-\text{CH}_3$, 22), 101 (20), 100 (8), 59 (81), 58 (39), 43 (100).



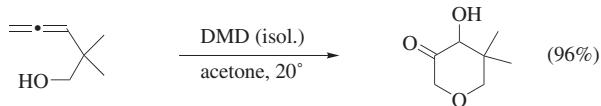
cis-Bicyclo[5.3.0]decan-2-one [Oxidation of an Alkyne with TFD (isol.)].⁶⁴

A 25-mL flask was charged with cyclooctyne (136 mg, 1.00 mmol) and a trifluoroacetone solution of TFD (isol.) (20.0 mL, 0.010 M, 2.00 mmol) at 0° . After magnetic stirring for 3 minutes, the volatiles were removed on a rotary evaporator (10° , 15 mmHg), and the residue was purified by column chromatography on silica gel, to give the title compound (126 mg, 83%); ^{13}C NMR (50 MHz, CDCl_3) δ 21.0, 21.7, 22.1, 23.1, 28.0, 29.7, 43.4, 58.3, 59.2, 206.5. Further elution resulted in isolation of *cis*-bicyclo[4.4.0]decan-2-one (22 mg, 13%); ^{13}C NMR (50 MHz, CDCl_3) δ 24.5, 25.4, 26.2, 27.8, 32.5, 32.2, 40.4, 43.2, 54.6, 214.0.

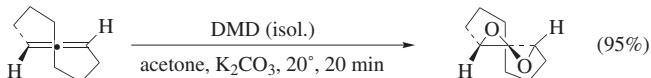


6-Hydroxy-2,2-dimethyl-3-oxacyclohexanone [Oxidation of an Allene with DMD (isol.)].⁵⁷

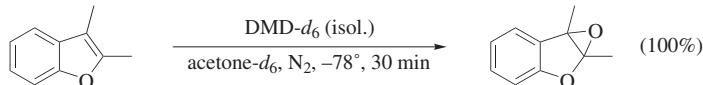
A 25-mL flask at 20° was charged with 5-methyl-3,4-hexadien-1-ol (22 mg, 0.20 mmol) and a solution of DMD (12.0 mL, 0.100 M, 1.20 mmol) under vigorous stirring. Removal of the solvent on a rotary evaporator (20° , 15 mmHg), followed by chromatographic purification on silica gel, afforded the title compound as a colorless liquid (26 mg, 92%); IR 3425, 1720, 1158, 1076 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.37 (s, 3H), 1.39 (s, 3H), 1.99 (m, 1H), 2.51 (m, 1H), 3.20–3.80 (br s, 1H), 3.87 (ddd, $J = 13.0, 5.0, 2.0$ Hz, 1H), 4.05 (ddd, $J = 13.0, 12.0, 4.0$ Hz, 1H), 4.55 (dd, $J = 12.0, 7.0$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 22.6, 23.8, 36.3, 59.0, 70.1, 80.3, 212.0. EIMS m/z (%): 145 (14), 127 (9), 116 (10), 99 (2), 87 (11), 85 (5), 83 (100), 71 (3). HRMS calcd for $\text{C}_7\text{H}_{13}\text{O}_3$ ($\text{M} + \text{H}$), 145.0860, found 145.0865.



6-Hydroxy-5,5-dimethyl-3-oxacyclohexanone [Oxidation of an Allene with DMD (isol.)].⁵⁷ A 25-mL flask was charged at 20° with 2,2-dimethyl-3,4-pentadien-1-ol (20 mg, 0.180 mmol) and a solution of DMD (18.0 mL, 0.100 M, 1.80 mmol) under vigorous magnetic stirring. Removal of the excess solvent on a rotary evaporator (20°, 15 mmHg), followed by chromatographic purification on silica gel afforded 6-hydroxy-5,5-dimethyl-3-oxacyclohexanone as a colorless liquid (25 mg, 96%); IR 3460, 1727, 1248, 1106 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.94 (s, 3H), 1.08 (s, 3H), 3.40–3.50 (br s, 1H), 3.63 (dd, *J* = 15.0, 12.0 Hz, 2H), 4.00 (dd, *J* = 14.4, 1.2 Hz, 1H), 4.02 (br s, 1H), 4.13 (dd, *J* = 14.4, 0.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 17.7, 22.6, 42.8, 72.7, 76.4, 81.0, 206.9. EIMS *m/z* (%): 145 (23), 144 (16), 127 (4), 101 (5), 85 (37), 71 (100). HRMS calcd for C₇H₁₃O₃ (M + H), 145.0860, found 145.0865.

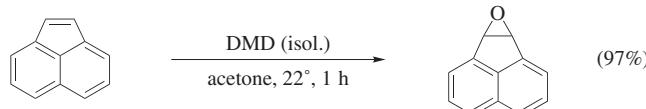


2,5-Hexamethylene-1,4-dioxaspiro[2.2]pentane [Diepoxydation of a Cyclic Allene with DMD (isol.)].¹⁶ To a stirred solution of DMD (0.100 M, 4.44 mmol) in acetone (40.0 mL) dried over K₂CO₃, was added the cyclic allene (112 mg, 0.900 mmol) at 20°. Stirring was continued for 20 minutes at the same temperature. The solvent was removed on a rotary evaporator (20°, 15 mmHg), and the product was separated from the K₂CO₃ by triturating with ether (3 × 10 mL). The combined ether triturations were filtered, dried (MgSO₄), and concentrated (20°, 15 mmHg) to give the title compound (135 mg, 95%) as a colorless oil; IR 1626, 1605 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.35–1.42 (m, 6H), 1.49–1.54 (m, 2H), 1.69–1.74 (m, 2H), 2.12–2.18 (m, 2H), 3.75 (dd, *J* = 6.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 20.1, 24.7, 27.4, 60.1, 84.3; EIMS *m/z* (%): 154 (8), 130 (29), 98 (100), 82 (83), 69 (65). HRMS calcd for C₉H₁₄O₂, 154.0994, found 154.1000.



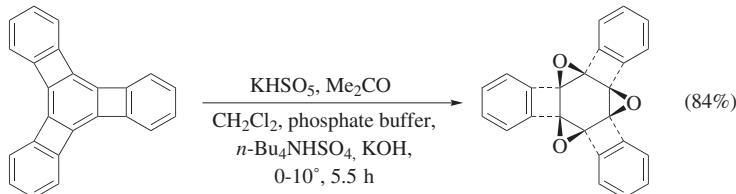
2,3-Epoxy-2,3-dihydro-2,3-dimethylbenzo[*b*]furan [Epoxidation of a Benzfuran with DMD-*d*₆ (isol.)].⁸⁷ A 5-mm NMR tube was charged with an acetone-*d*₆ solution of 2,3-dimethylbenzo[*b*]furan (113 μL, 0.220 M, 25 μmol) at -78° under a N₂ atmosphere. By means of a syringe, a well-dried (over 4 Å molecular sieves) DMD-*d*₆ (isol.) solution in acetone-*d*₆ (500 μL, 0.0500 M, 25 μmol) was added rapidly at -78°. After 30 minutes, the NMR tube was

submitted to low-temperature (-50°) ^{13}C -NMR spectroscopy, which revealed that the olefinic carbon resonances in 2,3-dimethylbenzo[*b*]furan were replaced by the characteristic epoxide resonances for the product. At temperatures higher than 0° , complete decomposition of the epoxide occurred within 30 minutes.



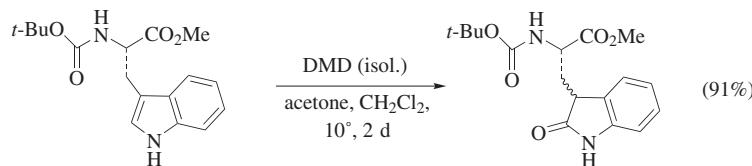
1,2-Epoxyacenaphthene [Epoxidation of an Arene with DMD (isol.)].²⁶⁵

To a magnetically stirred solution of acenaphthylene (611 mg, 4.02 mmol) in acetone (5.0 mL) was added an acetone solution of DMD (66.0 mL, 0.0620 M, 4.09 mmol) at room temperature (ca. 20°). The progress of the reaction was monitored by GLC, which indicated that acenaphthylene was converted into its 1,2-epoxide within one hour. Removal of the solvent on a rotary evaporator (20° , 15 mmHg) afforded a white solid, which was taken up into CH_2Cl_2 (30 mL) and dried over Na_2SO_4 . After removal of the drying agent, the solvent was removed on a rotary evaporator first at 20° , 15 mmHg and subsequently at 20° , 5 mmHg, to give the analytically pure oxide (654 mg, 97%), mp 83–84°; ^1H NMR (CDCl_3) δ 4.81 (s, 2H), 7.39–7.77 (m, 6H).



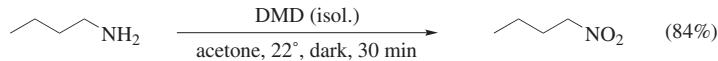
Bisbenzo[3',4']cyclobuta[1',2':1,2:1'',2'':3,4]biphenyleno[1,8b-b:2,3-b':4,4a-b'']trisoxirene [Epoxidation of an Arene with DMD (in situ)].⁶⁷ To a solution of tris(benzocyclobutadieno)cyclohexatriene (1.50 g, 5.06 mmol) in an acetone/ CH_2Cl_2 mixture (350 mL, 5 : 2 v/v) contained in a 1000-mL three-necked flask were added phosphate buffer (50 mL) and tetra-*n*-butylammonium hydrogen sulfate (200 mg, 0.590 mmol). A solution of potassium monoperoxysulfate (46.0 g, 30.2 mmol) in water (225 mL) was added dropwise under vigorous magnetic stirring at 0–10° over 1.5 hours. The pH was maintained at 7.5–8.5 by the dropwise addition of an aqueous solution of KOH (2–3%). The reaction mixture was stirred for an additional 4 hours and then mixed with an equal volume of ice-cold water. The reaction mixture was extracted with CH_2Cl_2 (1 × 150 mL), the extract was washed with ice-cold water (3 × 100 mL), and the combined organic layers were dried (K_2CO_3). The solvent was removed on a rotary evaporator (20°, 15 mmHg) and the solid residue was purified by preparative TLC on silica gel with CH_2Cl_2 /hexane (1 : 1) as eluent. Recrystallization from the same solvent mixture gave the oxide as colorless plates (1.48 g, 84%), mp 180–182°;

IR (KBr) 1613, 1512, 1495, 1463, 1430, 1339, 1261, 1154, 1094, 1003, 918, 861, 802, 751 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (m, 6H), 7.46 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 76.3, 122.6, 131.5, 143.71. EIMS *m/z* (%): 348 (M⁺, 11), 316 (8), 261 (10), 248 (9), 176 (21), 175 (100), 174 (11), 156 (61), 135 (22), 127 (20), 123 (30), 121 (22), 107 (18), 85 (11), 73 (38).

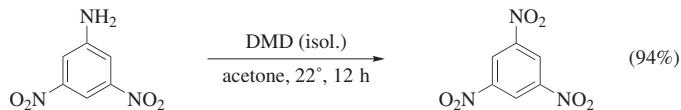


Methyl Boc-β-(2,3-dihydro-2-oxo-indol-3-yl)alaninate [Oxidation of an Indole with DMD (isol.)].⁹³ A 10-mL flask equipped with a magnetic stirring bar was charged with a solution of Boc-Trp-OMe (292 mg, 0.910 mmol) in CH₂Cl₂ (5.0 mL). After cooling to 10° by means of an ice bath, a freshly prepared acetone solution of DMD (23.0 mL, 0.100 M, 2.30 mmol) was added. Stirring was continued for 2 days at 10°. The solvent was removed (10°, 15 mmHg) and the residue was purified by flash column chromatography on silica gel, with a mixture of EtOAc and hexane as eluent, to afford two diastereoisomers (A : B = 1 : 1, 91% yield). Diastereomer A: [α]²⁵_D -221.4° (*c* 1.0, CHCl₃); ¹H NMR (200 MHz, CDCl₃) δ 1.38 (s, 9H), 2.39–2.57 (m, 2H), 3.76 (s, 3H), 4.19–4.32 (m, 1H), 5.44 (s, 1H), 6.59–6.62 (m, 1H), 6.63–6.84 (m, 1H), 7.09–7.20 (m, 1H), 7.21–7.31 (m, 2H); ¹³C NMR (50 MHz, CDCl₃): δ 28.2, 41.4, 52.3, 59.8, 81.2, 84.3, 110.5, 119.4, 123.2, 130.3, 148.3, 154.1, 173.9, 175.2; EIMS *m/z* (%): 334 (M⁺, 18). Anal. Calcd for C₁₇H₂₂N₂O₅: C, 61.06, H, 6.63, N, 8.38. Found: C, 61.0, H, 6.59, N, 8.15.

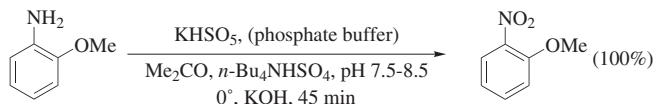
Diastereomer B: [α]²⁵_D +83.6° (*c* 1.0, CHCl₃); ¹H NMR (200 MHz, CDCl₃) δ 1.42 (s, 9H), 2.57–2.64 (m, 2H), 3.64 (s, 3H), 4.58–4.78 (m, 1H), 5.30–5.45 (m, 1H), 6.88–7.05 (m, 2H), 7.12–7.32 (m, 2H); ¹³C NMR (50 MHz, CDCl₃): δ 28.2, 42.1, 52.2, 61.8, 81.6, 98.6, 115.1, 121.9, 123.2, 130.2, 149.1, 154.5, 172.4, 173.9; EIMS *m/z* (%): 334 (M⁺, 16). Anal. Calcd for C₁₇H₂₂N₂O₅: C, 61.06, H, 6.63, N, 8.38. Found: C, 61.10, H, 6.63, N, 8.19.



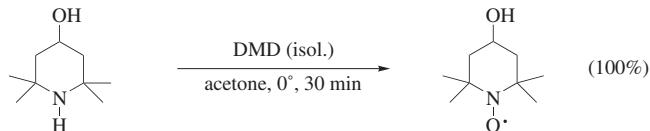
1-Nitrobutane [Oxidation of a Primary Aliphatic Amine with DMD (isol.)].²⁶⁶ A 150-mL flask was charged with a solution of *n*-butylamine (52 mg, 0.700 mmol) in acetone (5.0 mL), and an acetone solution of DMD (95.0 mL, 0.050 M, 4.80 mmol). The mixture was stirred at room temperature (ca. 20°) for 30 minutes in the dark. The solvent was removed on a rotary evaporator (20°, 20 mmHg), to afford the title compound (62 mg, 84%).



1,3,5-Trinitrobenzene [Oxidation of a Primary Aromatic Amine with DMD (isol.)].¹⁰¹ To a stirred solution of 3,5-dinitroaniline (30 mg, 0.165 mmol) in acetone (5.0 mL) was added an acetone solution of DMD (30.0 mL, 0.0600 M, 1.80 mmol) at room temperature (ca. 20°). After the reaction mixture was stirred for 12 hours, excess solvent was removed on a rotary evaporator (20°, 15 mmHg), and the residue was purified by preparative TLC on silica gel with CH₂Cl₂/hexane (1 : 1) as eluent. The product streak was scraped from the plate and extracted from the silica gel with CH₂Cl₂ (15 mL) that contained 5% methanol. Evaporation of the volatiles under reduced pressure (20°, 15 mmHg) gave 1,3,5-trinitrobenzene (33 mg, 94%), mp 121–122°.

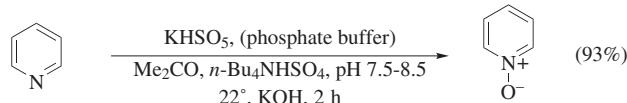


***o*-Nitroanisole [Oxidation of a Primary Aromatic Amine with DMD (in situ)].²⁶⁷** A 500-mL, three-necked round-bottomed flask, fitted with two addition funnels and a pH electrode, was charged with *o*-anisidine (1.10 mL, 10.0 mmol), CH₂Cl₂ (100 mL), acetone (100 mL), an aqueous solution of sodium phosphate (50 mL, 0.080 M), and tetra-*n*-butylammonium hydrogen sulfate (170 mg, 0.500 mmol). In one of the addition funnels was placed an aqueous solution of KHSO₅ (150 mL, 20.0 g, 32.0 mmol), and in the other an aqueous solution of KOH (100 mL, 150 mL). After the mixture was cooled to 0°, the aqueous solution of KHSO₅ was added dropwise over 30 minutes, while maintaining the pH between 7.5–8.5 by dropwise addition of an aqueous solution of KOH (2.00 N). After addition, the mixture was stirred at the same temperature for 15 minutes and then treated with 1 mL of methyl sulfide to destroy residual peroxide. The suspended material was removed by filtration and the organic layer was washed with water (50 mL), dried (MgSO₄), and concentrated (20°, 15 mmHg). The residue was purified by column chromatography on silica gel (50 g) with CH₂Cl₂ as eluent to afford *o*-nitroanisole (1.50 g, 100%).



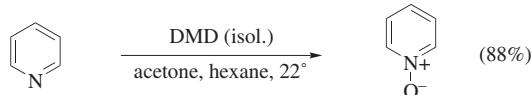
1-Oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine [Oxidation of a Hindered Secondary Amine with DMD (isol.)].⁹⁷ To a magnetically stirred solution of 2,2,6,6-tetramethylpiperidinol (312 mg, 2.00 mmol) in acetone (20 mL) in a

100-mL flask was slowly added a pale yellow stock solution of DMD (60.0 mL, 0.0670 M, 4.00 mmol) at 0° (ice bath). The reaction mixture turned to deep yellow within 10 minutes. After stirring was continued for another 30 minutes, the solvent was removed on a rotary evaporator (20°, 15 mmHg) to afford the nitroxide (354 mg, 100%) as a bright yellow powder, mp 71–72°.



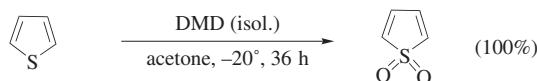
Pyridine N-Oxide, Method A [Oxidation of Pyridine with DMD (in situ)].¹²¹

To a 500-mL, three-necked flask, equipped with a mechanical stirrer, was added pyridine (1.00 g, 12.6 mmol), acetone (5 mL, 68.0 mmol), and phosphate buffer (50 mL). An aqueous solution of potassium monoperoxyxulfate (100 mL, 18.3 g, 29.8 mmol) was added dropwise by means of an addition funnel. Simultaneously, an aqueous solution of KOH (1.00 N) was added in portions to maintain the pH at 7.5–8.0. After completion of the addition, the reaction mixture was stirred for 2 hours, then extracted with CH₂Cl₂ (4 × 30 mL). The combined extracts were dried (MgSO₄) and concentrated (20°, 15 mmHg). The residue was crystallized from a CH₂Cl₂/hexane mixture to afford the pyridine oxide (1.10 g, 93%) as a white crystalline solid, mp 64–65° (lit.²⁶⁸ mp 65–66°); ¹H NMR (60 MHz, CDCl₃) δ 7.30–7.50 (m), 8.3–8.5 (m).



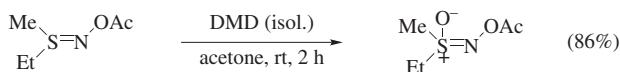
Pyridine N-Oxide, Method B [Oxidation of Pyridine with DMD (isol.)].¹²¹

To a stirred mixture of an acetone solution of pyridine (0.50 mL, 0.200 M, 7.90 mg, 0.10 mmol) and a hexane solution of decane (0.50 mL, 0.100 M) was added an acetone solution of DMD (1.00 mL, 0.116 M, 0.116 mmol) at room temperature (ca. 20°). The solvent was removed (20°, 15 mmHg) leaving pyridine N-oxide (8.4 mg, 88%).

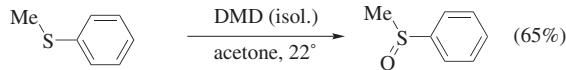


Thiophene 1,1-Dioxide [Oxidation of Thiophene with DMD (isol.)].¹⁴¹ A 50-mL flask was charged with an acetone solution of thiophene (10.0 mL, 84 mg, 1.00 mmol) at –20° and an acetone solution of DMD (isol.) (30 mL, 0.100 M, 3.00 mmol) was added rapidly under magnetic stirring at –20°. Stirring was continued at the same temperature for 36 hours. The solvent and unreacted DMD were removed (below –40°, 5 mmHg) to afford pure thiophene 1,1-dioxide as

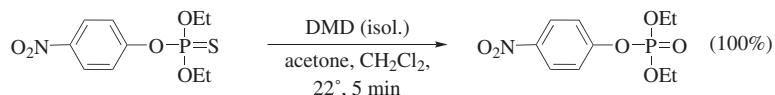
colorless plates (116 mg, ca. 100%); UV (CHCl_3) 245 (870) and 288 (1070) nm; IR (neat) 1152, 1306, 1327, 1530, 3100, 3175 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , -40°) δ 6.53–6.61 (m, 2H), 6.75–6.83 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 , -40°) δ 129.3, 113.1; HRMS calcd for $\text{C}_4\text{H}_4\text{O}_2\text{S}$, 115.9932, found 115.9931.



S-Ethyl-S-methyl-N-(acetyl)sulfoxime [Oxidation of a Sulfilimine with DMD (isol.)].¹⁴⁸ A 25-ml flask, supplied with a magnetic stirrer, was charged with a solution of the substituted sulfilimine (20 mg, 0.150 mmol) in acetone (5 mL). An acetone solution of DMD (4.0 mL, 0.080 M, 0.32 mmol) was added dropwise at 0° . The reaction mixture was stirred for 2 hours at room temperature; the reaction progress was monitored by TLC (silica gel). After complete consumption of the sulfilimine, the solvent was removed (20° , 15 mmHg) and the residue was purified by column chromatography on silica gel with a mixture of $\text{Et}_2\text{O}/\text{MeOH}$ (95 : 5) as eluent, affording the sulfoxime (20 mg, 86%) as an oil; ^1H NMR (300 MHz, CDCl_3) δ 1.40 (t, $J = 7.0$ Hz, 3H), 2.40 (s, 3H), 3.30 (s, 3H), 3.50 (q, $J = 7.0$ Hz, 2H), 7.20–7.80 (m, 4H). Anal. Calcd for $\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$: C, 40.25, H, 7.43, N, 9.39. Found: C, 40.01, H, 7.33, N, 9.46.

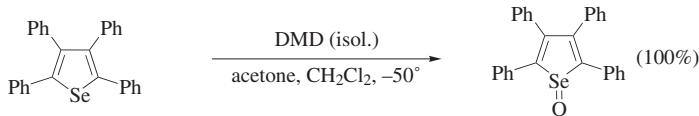


Methyl Phenyl Sulfoxide [Oxidation of a Thioether with DMD (isol.)].¹²¹ A 10-mL flask was charged with a solution of phenyl methyl sulfide (13.6 mg, 0.11 mmol) in acetone (0.50 mL) and an acetone solution of DMD (0.58 mL, 0.189 M, 0.110 mmol) at ca. 20° . The reaction mixture was stirred at room temperature (ca. 22°) until consumption of the sulfide was complete as determined by GC analysis. The solvent was removed under reduced pressure (20° , 15 mmHg) and the crude product was purified by preparative TLC on silica gel by elution with a mixture of hexane and EtOAc to afford the solid phenyl methyl sulfoxide (11 mg, 65%).

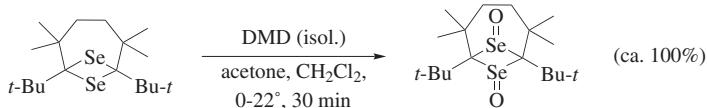


Diethyl 4-Nitrophenylphosphate [Oxidation of a Thiophosphate with DMD (isol.)].¹⁵⁰ An acetone solution of DMD (200 mL, 0.100 M, 20.0 mmol), dried over 4 Å molecular sieves, was added rapidly to a magnetically stirred dry CH_2Cl_2 solution of *O,O*-diethyl *O*-(4-nitrophenyl)thiophosphate (10.0 mL, 29 mg, 0.100 mmol) at room temperature (ca. 20°). After standing for 5 minutes, the crude

reaction mixture was diluted with pentane (10 mL) and dried (MgSO_4). The drying agent was removed by filtration and washed with pentane (5 mL), and the filtrate was concentrated on a rotary evaporator (20° , 15 mmHg), affording the title compound (27 mg) in quantitative yield; ^1H NMR (300 MHz, CDCl_3) δ 1.38 (t, $J = 7.0$ Hz, 3H), 1.39 (t, $J = 7.0$ Hz, 3H), 4.25 (q, $J = 7.0$ Hz, 2H), 4.32 (q, $J = 7.0$ Hz, 2H), 7.38 (dd, $J = 9.0$ Hz, 1.0 Hz, 2H), 8.24 (dd, $J = 9.0, 1.0$ Hz, 2H); ^{13}C NMR (300 MHz, CDCl_3) δ 15.9, 16.1, 65.2, 65.3, 120.4, 125.0, 148.2, 155.7; ^{31}P NMR δ -6.6.



Tetraphenylselenophene 1-Oxide [Oxidation of a Selenophene with DMD (isol.)].¹⁵⁵ A cold (-50°) acetone solution of DMD (11.50 mL, 0.086 M, 1.00 mmol) was added to a cold (-50°), vigorously stirred dry CH_2Cl_2 solution of tetraphenylselenophene (2.0 mL, 435 mg, 1.00 mmol). After complete addition, the solvent was removed (-40° , 0.001 mmHg), to afford the title compound (451 mg) in quantitative yield; IR (KBr) 3056, 1596, 1573, 1487, 1444, 817, 788, 761, 743, 710, 693 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.91 (d, $J = 7.2$ Hz, 4H), 7.10 (t, $J = 7.2$ Hz, 4H), 7.16 (t, $J = 7.2$ Hz, 2H), 7.19–7.27 (m, 6H), 7.29–7.36 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 128.0, 128.1, 128.6, 128.8, 129.4, 129.5, 131.9, 134.7, 147.2, 150.0; ^{77}Se NMR (76 MHz, CDCl_3) δ 1014. Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{OSe}$: C, 74.50, H, 4.47. Found: C, 73.98, H, 4.44.

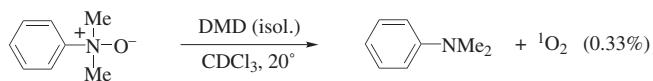


1,6-Di-*tert*-butyl-2,2,5,5-tetramethyl-7,8-diselenabicyclo[4.1.1]octane 7-*endo*, 8-*endo*-Dioxide [Oxidation of a Selenoether with DMD (isol.)].¹³⁴ To a stirred solution of the starting diselenetane (65 mg, 0.160 mmol) in CH_2Cl_2 (10 mL) was added an acetone solution of DMD (5.0 mL, 0.082 M, 0.410 mmol) in three portions at 0° . The mixture was warmed to room temperature (ca. 20°) and magnetically stirred for 30 minutes. The solvent was removed (20° , 20 mmHg) to give spectroscopically pure title compound (70 mg, ca. 100%) as a colorless powder, which decomposed above 80° ; IR (KBr) 824 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.23–1.30 (m, 2H), 1.47 (s, 6H), 1.51 (s, 18H), 1.73 (s, 6H), 4.30–4.37 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 28.4, 31.6, 35.4, 38.8, 43.9, 49.0, 97.3. Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{Se}_2\text{O}_2$: C, 49.09, H, 7.78. Found: C, 48.63, H, 7.74.

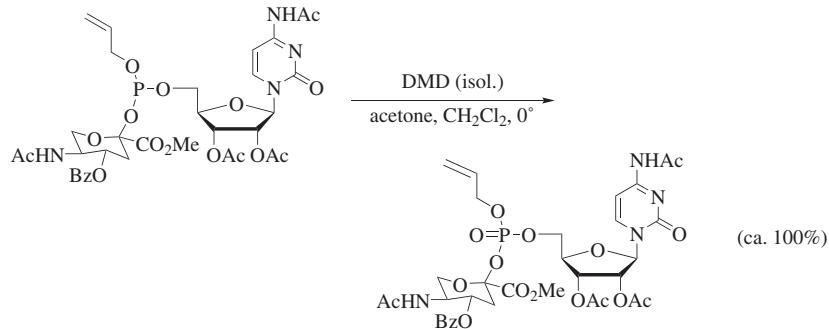


Triphenylphosphine Oxide [Oxidation of a Phosphine with DMD (isol.)].¹²¹

To a stirred solution of triphenylphosphine (26 mg, 0.100 mmol) in acetone (0.50 mL) was added a freshly prepared acetone solution of DMD (0.50 mL, 0.185 M, 6.9 mg, 0.0900 mmol) at room temperature (ca. 20°). Capillary GC was used to monitor the reaction progress by injecting 1.0-μL aliquots of the reaction mixture at intervals of 15–30 minutes (the peak areas of the triphenylphosphine and its oxide product were compared). Removal of the solvent (20°, 15 mmHg) afforded triphenylphosphine oxide (27.8 mg, ca. 100%).

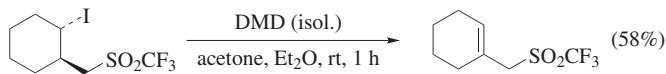


Singlet-Oxygen Generation by Oxidation of *N,N*-Dimethylaniline *N*-Oxide with DMD (isol.).¹⁶⁵ To a stirred solution of *N,N*-dimethylaniline *N*-oxide in CDCl₃ (1.0 mL, 0.50 mM) was added a CDCl₃ solution of DMD (0.080 M, 3 equiv.) at 20°. The reaction mixture was magnetically stirred at this temperature for 10 minutes. The consumption of the dioxirane was monitored by means of the peroxide test (KI/HOAc), while the amount of singlet oxygen (0.33%) was determined by its characteristic IR chemiluminescence at 1268 nm using a photodiode detector.

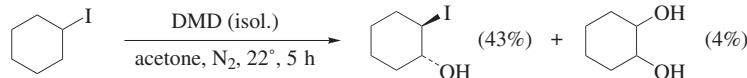


[(2*S*,4*S*,5*S*)-5-Acetylamo-4-benzoyloxy-2-methoxycarbonyltetrahydro-pyran-2-yl] Propen-2-yl *N*-Acetyl-2',3'-di-*O*-acetyl-5'-cytidylate [Oxidation of a Phosphite to a Phosphate with DMD (isol.)].¹⁵⁸ To a cold (0°) stirred solution of the starting phosphite (9.7 mg, 0.0120 mmol) in CH₂Cl₂ (1 mL) was added an acetone solution of DMD (162 μL, 0.083 M, 0.0310 mmol) at 0°. After 10 minutes, the reaction mixture was concentrated on a rotary evaporator (0°, 15 mmHg) to give the title compound (9.9 mg, 100%) as a colorless foam (the product was contaminated with the α-linked diastereomer); ¹H NMR (500 MHz, CDCl₃) δ 1.89 (s, 4.3H), 1.91 (s, 3.2H), 2.02 (s, 6.6H), 2.08 (s, 12.0H), 2.15 (s, 15.2H), 2.22 (s, 4.4H), 2.25 (s, 3.7H), 2.74 (dd, *J* = 13.5, 4.8 Hz, 1H), 2.92 (dd, *J* = 13.7, 4.5 Hz, 1.4H), 3.32 (dd, *J* = 14.9, 4.4 Hz, 0.2H), 3.76–3.80

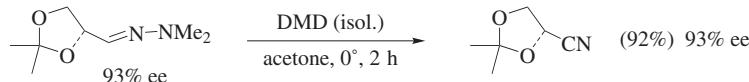
(m, 1.8H), 3.80 (m, 1.8H), 3.82 (s, 3.4H), 3.85–3.90 (m, 1.8H), 4.18–4.22 (m, 2.6H), 4.29–4.49 (m, 10.2H), 4.54–4.63 (m, 4.0H), 4.69 (t, J = 7.4 Hz, 2.0H), 5.26–5.40 (m, 6.6H), 5.44 (d, J = 3.6 Hz, 2.5H), 5.47–5.54 (m, 1.5H), 5.64 (dd, J = 4.8, 4.0 Hz, 1.0H), 5.89–6.02 (m, 2.6H), 6.24 (d, J = 2.8 Hz, 1.0H), 6.37 (d, J = 6.2 Hz, 0.9H), 6.67 (d, J = 7.7 Hz, 0.8H), 6.95 (d, J = 8.7 Hz, 0.8H), 7.36–7.48 (m, 7.9H), 7.53–7.58 (m, 2.5H), 7.83 (d, J = 7.3 Hz, 0.5H), 7.92–8.02 (m, 5.4H), 8.56 (d, J = 7.7 Hz, 1.1H), 8.90 (s, 1.2H), 9.12 (s, 0.9H); ^{31}P NMR (203 Hz, CDCl_3) δ –4.54, –4.60.



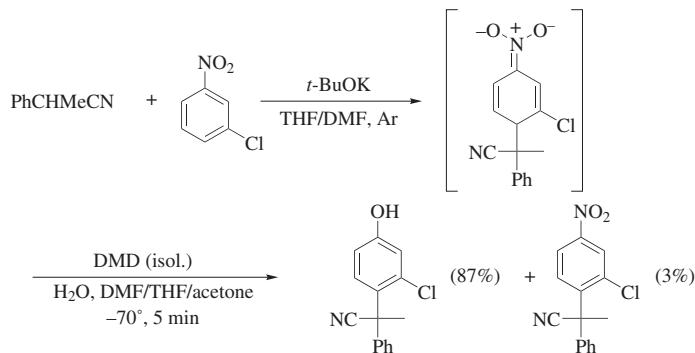
1-[Trifluoromethylsulfonyl]methylcyclohexene [Oxidation of an Iodo-alkane with DMD (isol.)].¹⁶⁹ A 10-mL flask, equipped with a magnetic stirring bar, was charged at 25° with 356 mg (1.00 mmol) of *trans*-1-iodo-2-[(trifluoromethyl)sulfonyl]methylcyclohexane in ether (5 mL) and an acetone solution of DMD (20.0 mL, 0.100 M, 2.00 mmol). After the mixture was stirred at 25° for 1 hour, the solvent was removed (10°, 15 mmHg) and the product was dried to give the title alkene (132 mg, 58%) as a colorless oil.



***trans*-2-Iodocyclohexanol [Oxidation of Iodocyclohexane with DMD (isol.)].¹⁶⁸** A 25-mL, round-bottomed flask was charged with an acetone solution of DMD (11.0 mL, 0.090 M, 1.0 mmol) at ca. 20° under a N_2 atmosphere. While stirring magnetically, the cyclohexyl iodide (210 mg, 1.00 mmol) was added. After five hours, GLC analysis indicated formation of *trans*-2-iodocyclohexanol (102 mg, 43%) and 1,2-cyclohexanediol (5 mg, 4%).

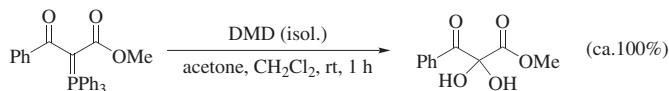


(S)-4-Cyano-2,2-dimethyl-1,3-dioxalane [Conversion of a Hydrazone into a Nitrile with DMD (isol.)].¹¹³ A cold (0°) solution of DMD (0.100 M, 1.00 mmol) in acetone (10.0 mL) was added to a cold (0°) acetone solution of (+)-2,3-*O*-isopropylidene-d-glyceraldehyde *N,N*-dimethylhydrazone (5 mL, 86 mg, 0.50 mmol, enantiomeric purity 93%) with vigorous magnetic stirring. The reaction progress was monitored by GLC analysis, which indicated that the starting material was converted into the nitrile product within 2 hours. Removal of the acetone on a rotary evaporator (20°, 15 mmHg) afforded the title compound (58 mg, 92%); $[\alpha]_D + 1.36$ (*c* 1.33, CHCl_3), 93% optically pure.



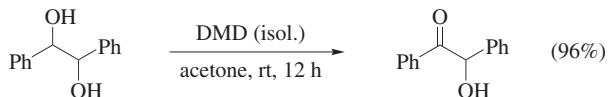
2-(2-Chloro-4-hydroxyphenyl)-2-phenylpropionitrile [Tandem Nucleophilic Addition/Conversion of a Nitrobenzene into a Phenol with DMD (isol.)].¹¹⁰

An oven dried, 100-mL, three-necked, round-bottom flask, equipped with a magnetic stirring bar, was charged with *t*-BuOK (123 mg, 1.10 mmol) and THF (20 mL) at -70° under an argon gas atmosphere. A solution of 2-phenylpropionitrile (131 mg, 1.00 mmol) and 1-chloro-3-nitrobenzene (157 mg, 1.00 mmol) in DMF (1.0 mL) was added at -70° within 2 minutes via syringe. The resulting mixture was magnetically stirred for 5 minutes, and a precooled (-70°) acetone solution of DMD (14.5 mL, 1.20 mmol, 0.0830 M) was added in one portion. After 5 minutes, H_2O (18.0 μL , 1.00 mmol) was added. The mixture was stirred for an additional 5 minutes, hydrolyzed with saturated aqueous NH_4Cl (1.0 mL), raised to 20° , and dried over MgSO_4 . The drying agent was removed by filtration, washed with THF (3 \times 20 mL), and the solvent was evaporated (30° , 12 mmHg). The residue was purified by chromatography on silica gel (4 : 1 hexane/EtOAc, followed by 2 : 1 hexane/EtOAc as eluents) to give the nitro compound (8.6 mg, 3%) as a minor product, and the title phenol (223 mg, 87%) as colorless flakes, mp 180–182°; IR (KBr) 3375, 2236, 1607, 1575, 1495, 1430, 1312, 1291, 1215 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 2.09 (s, 3H), 5.69 (br s, 1H), 6.81–6.89 (dd, J = 8.6, 2.6 Hz, 1H), 6.91–6.94 (d, J = 2.6 Hz, 1H), 7.20–7.39 (m, 5H), 7.42–7.50 (d, J = 8.6 Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 29.6, 44.8, 113.9, 118.9, 122.0, 125.8, 127.5, 128.6, 128.8, 129.0, 135.3, 141.3, 156.5; EIMS m/z (%): 257 (M^+), 242 (100), 222, 215, 207, 206, 195, 177, 165, 152, 89, 77. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{ClNO}$: C, 69.91, H, 4.69, N, 5.43, Cl, 13.76. Found: C, 69.74, H, 4.43, N, 5.29, Cl, 13.83.

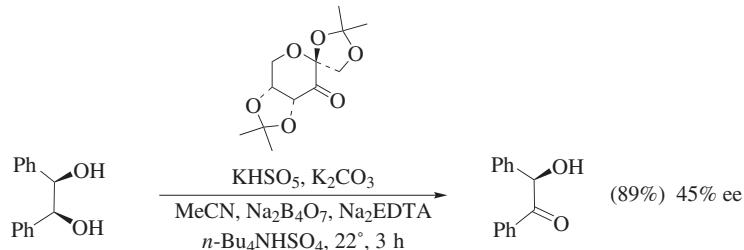


Methyl 3-Phenyl-2,2-dihydroxy-3-oxopropionate [Oxidation of a Phosphorane to a Ketone Hydrate with DMD (isol.)].¹⁵⁹ A 25-mL, round-bottomed flask was charged with a solution of methyl-3-oxo-3-phenyl-2-(triphenylphosphoranylidene)propionate (219 mg, 0.500 mmol) in CH_2Cl_2 (2.0 mL). Under

vigorous magnetic stirring, an acetone solution of DMD (15.0 mL, 1.5 mmol, 0.100 M) was added and the stirring continued at room temperature for one hour until all the starting material had been consumed as monitored by TLC. The reaction mixture was concentrated (20°, 15 mmHg) and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 1 : 1 as eluent) to give the product as a yellow oil (105 mg, ca. 100%); IR (neat) 3600–3300, 3060, 2940, 1760, 1750, 1690, 1600, 1450, 1440, 1230, 1130, 1100, 1010 cm⁻¹; ¹H NMR (CDCl₃) δ 3.66 (s, 3H), 5.81 (br s, 2H), 7.38–7.44 (m, 2H), 7.54–7.58 (m, 1H), 8.05–8.08 (m, 2H); ¹³C NMR (CDCl₃) δ 53.4, 91.9, 128.6, 129.0, 129.8, 131.1, 170.1, 191.4; HRMS (M + H) calcd for C₁₀H₁₀O₅, 211.0603, found 211.0606.

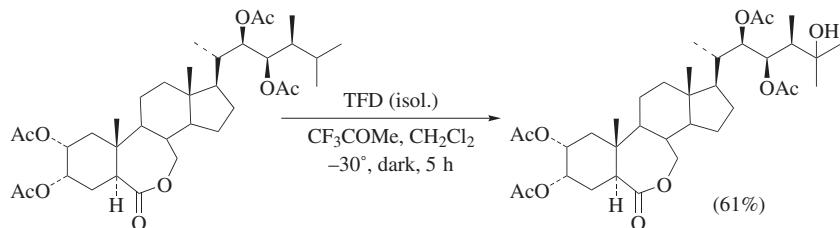


Benzoin. Method A [Oxidation of a Benzyl Alcohol to an Aryl Ketone with DMD (isol.)].²⁶⁹ A 25-mL flask was charged with hydrobenzoin (214 mg, 1.00 mmol) in acetone (1.0 mL) at room temperature, and then a solution (at ca. 20°) of DMD (1.50 mmol, 0.080 M) in acetone (19.0 mL) was added rapidly under vigorous magnetic stirring. The solvent was removed by distillation (20°, 15 mmHg) on a Vigreux column, and the residue was purified by flash column chromatography on silica gel with 1 : 1 hexane/EtOAc as eluent, to afford the benzoin (204 mg, 96%).

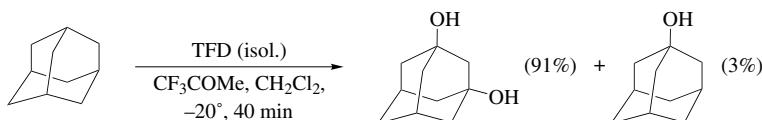


(R)-Benzoin. Method B [Catalytic Asymmetric Oxidation of Hydrobenzoin].¹⁹⁷ To a MeCN solution of *meso*-hydrobenzoin (1.5 mL, 21.4 mg, 0.100 mmol) was added the ketone catalyst 1,2:4,5-bis-O-(1-methylallylidene)- β -D-*erythro*-2,3-hexodiulo-2,6-pyranose (77.5 mg, 0.300 mmol), Bu₄NHSO₄ (1.5 mg, 4.0 μ mol), and Na₂B₄O₇ (1.0 mL, 0.050 M) in aqueous Na₂EDTA (4×10^{-4} M) while stirring magnetically at 0°. Solutions of potassium monoperoxy sulfate (92.0 mg, 0.150 mmol) and K₂CO₃ (87.0 mg, 0.630 mmol), each in an aqueous solution (0.65 mL) of Na₂EDTA (4×10^{-4} M), were added simultaneously using syringes over a period of 2 hours. The mixture was stirred for another hour and then diluted with H₂O (20 mL), extracted with ether (3 \times 20 mL), washed with H₂O (2 \times 10 mL), and dried over MgSO₄. After removal of the solvent on a rotary evaporator (20°, 20 mmHg), the residue was purified by

column chromatography (silica gel) to give the recovered ketone (40–60%) and benzoin (18.9 mg, 89%), with an ee value of 45% for the R enantiomer.

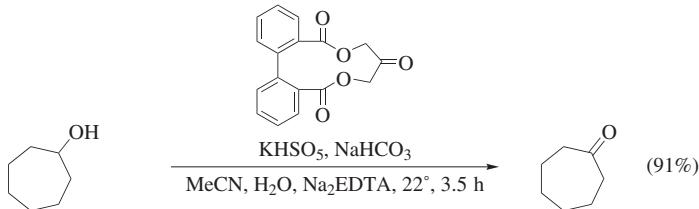


2,3,22,23-Tetra-*O*-acetyl-25-hydroxybrassinolide [Hydroxylation of a Tertiary Carbon Center with TFD (isol.)].²⁷⁰ To a stirred solution of 2,3,22,23-tetra-*O*-acetylbrassinolide (20 mg, 0.0300 mmol) in dry CH₂Cl₂ (0.40 mL) was added dropwise a trifluoroacetone solution of TFD (0.20 mL, 0.50 M, 0.10 mmol) at –30°. The reaction mixture was stirred magnetically in the dark for 5 hours at –30°. The solvent was removed on a rotary evaporator (20°, 15 mmHg), and the residue was purified by flash chromatography on silica gel (2 : 1 hexane/EtOAc as eluent) to give the title compound (12.5 mg, 61%) as colorless needles, mp 226–229°; ¹H NMR (600 MHz, CDCl₃) δ 0.73 (s, 3H), 0.98 (s, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 7.3 Hz, 3H), 1.15 (s, 3H), 1.16 (m, 1H), 1.18 (m, 2H), 1.22 (s, 3H), 1.25 (m, 1H), 1.27 (m, 1H), 1.28 (m, 1H), 1.41 (m, 1H), 1.62 (m, 2H), 1.66 (dq, *J* = 7.3, 1.0 Hz, 1H), 1.68 (m, 1H) 1.73 (m, 1H), 1.75 (s, 1H), 1.76 (m, 1H), 1.92 (m, 1H), 1.93 (m, 1H), 1.98 (m, 1H), 2.00 (s, 6H), 2.02 (s, 3H), 2.09 (m, 1H), 2.11 (s, 3H), 2.29 (ddd, *J* = 15.1, 12.2, 2.4 Hz, 1H), 2.99 (dd, *J* = 12.2, 4.4 Hz, 1H), 4.04 (dd, *J* = 12.2, 9.3 Hz, 1H), 4.12 (dd, *J* = 12.2, 1.0 Hz, 1H), 4.87 (ddd, *J* = 12.2, 4.4, 2.4 Hz, 1H), 5.12 (dd, *J* = 9.3, 1.0 Hz, 1H), 5.37 (m, 1H), 5.49 (dd, *J* = 9.3, 1.0 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 9.1, 11.7, 12.7, 15.5, 20.8, 21.1, 21.2, 22.2, 24.7, 26.6, 28.1, 28.6, 29.3, 37.1, 38.4, 38.9, 39.2, 39.4, 42.1, 42.5, 43.4, 51.3, 52.4, 58.4, 68.0, 68.9, 70.4, 72.3, 72.4, 75.5, 170.0, 170.2, 170.5, 171.0, 175.0; HRMS (FAB) (*M* + H) calcd for C₃₆H₅₇O₁₁, 665.3901, found, 665.3900.

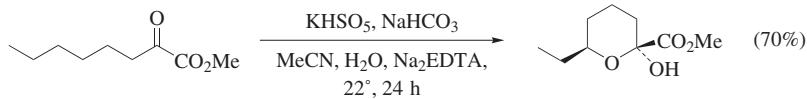


1,3-Dihydroxyadamantane [Dihydroxylation of Adamantane with TFD (isol.)].¹⁷⁸ A solution of TFD (4.60 mL, 0.50 M, 2.30 mmol) in trifluoroacetone/CH₂Cl₂ (2 : 1 v/v) at –20° was added to a solution of adamantane (136 mg, 0.100 mmol) in CH₂Cl₂ (5 mL) also at –20°, while stirring vigorously magnetically. The progress of the reaction was followed by GLC analysis, which indicated that 97% of the adamantane was converted to its hydroxylated products in 40 minutes. Removal of the solvent on a rotary evaporator (–20°, 15 mmHg)

afforded a mixture of the 1,3-dihydroxyadamantane (156 mg, 91%) and the monohydroxy adamantan (4.6 mg, 3%).

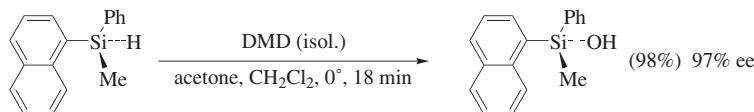


Cycloheptanone [Oxidation of a Secondary Alcohol to a Ketone under In Situ Catalytic Conditions].⁵² To a vigorously stirred solution of cycloheptanol (38.4 mg, 0.300 mmol) in MeCN (1.5 mL), was added an aqueous Na₂EDTA solution (4×10^{-4} M) of 7*H*-dibenzo[*g,i*]-1,5-dioxacycloundecin-5,8,11(9*H*)-trione (catalyst, 1.0 mL, 17.6 mg, 0.0600 mmol) at room temperature (ca. 20°). A mixture of KHSO₅ (282 mg, 0.600 mmol) and NaHCO₃ (156 mg) was added in portions, and consumption of the alcohol was complete after 4 hours as confirmed by GLC analysis. The reaction mixture was poured into water (20 mL), extracted with CH₂Cl₂ (3 × 30 mL), and dried (Na₂SO₄). After removal of the solvent on a rotary evaporator (20°, 15 mmHg), the residue was purified by flash column chromatography (Et₃N-buffered silica gel) to give cycloheptanone (34.4 mg, 91%).

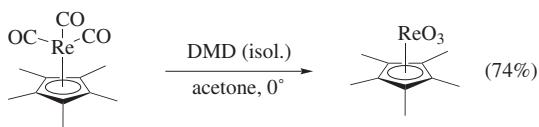


Methyl (S*,S*)-6-Ethyl-2-hydroxytetrahydropyran-2-carboxylate [Hydroxylation of a Secondary Carbon Center under In Situ Catalytic Conditions].¹⁹⁵

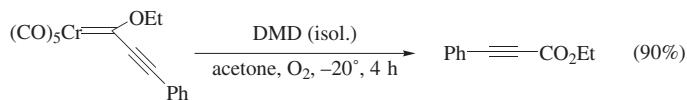
To a magnetically stirred MeCN solution (30 mL) of methyl-2-oxo-octanoate (86 mg, 0.50 mmol) was added an aqueous Na₂EDTA solution (20 mL, 4×10^{-4} M), followed by a mixture of KHSO₅ (1.54 g, 2.5 mmol) and NaHCO₃ (0.65 g) at ca. 20° over a period of 1 hour. After stirring for 24 hours, the reaction mixture was poured into brine (10 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were dried (MgSO₄), and the solvent was removed on a rotary evaporator (20°, 15 mmHg). The residue was purified by flash column chromatography on silica gel (1 : 4 EtOAc/hexane as eluent) to give the title compound (66 mg, 70%) as a colorless syrup; ¹H NMR (300 MHz, CDCl₃) δ 0.89 (t, *J* = 7.5 Hz, 3H), 1.20–1.74 (m, 6H), 1.79–1.97 (m, 2H), 3.60 (s, 1H), 3.82 (s, 3H), 3.85 (m, 1H); ¹³C NMR (68 MHz, CDCl₃) δ 9.8, 18.4, 28.8, 30.0, 30.4, 53.1, 72.5, 94.8, 171.7; EIMS *m/z* (%): 171 (M⁺ – OH, 14), 130 (12), 129 (100), 111 (41).



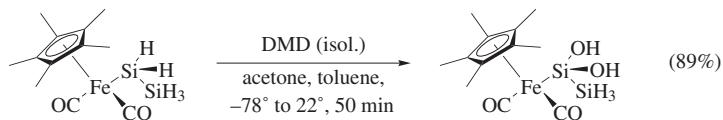
(R)-Methylphenyl(1-naphthyl)silanol [Hydroxylation of a Silane with TFD (isol.)].³⁹ A cold (-20°) 1,1,1-trifluoropropanone solution of TFD (80.0 mL, 0.500 M, 4.00 mmol) was rapidly added to a cold (-20°) solution of 96.5% optically pure (*R*)-methylphenyl(1-naphthyl)silane (0.992 g, 4.00 mmol) in dry CH_2Cl_2 (30 mL). Capillary GC analysis indicated complete consumption of the silane immediately on addition of the oxidant. Removal of the solvent on a rotary evaporator ($10-20^\circ$, 80–100 mmHg) afforded very pure (97% ee) silanol (1.03 g, 98%).



(η^5 -Pentamethylcyclopentadienyl)trioxorhenium [Oxidation of a Rhenium Complex with DMD (isol.)].²¹⁰ A 100-ml flask, equipped with a magnetic stirring bar, was charged with a chilled (0°) anhydrous acetone solution of $\text{Cp}^*\text{Re}(\text{CO})_3$ (20 mL, 80 mg, 0.20 mmol) and an acetone solution of DMD (25.0 mL, 0.05 M, 1.25 mmol) was added dropwise at 0° . The reaction terminated within a few minutes under immediate gas evolution, accompanied by a slight darkening of the pale yellow solution. The solvent was removed on a rotary evaporator (20° , 15 mmHg) until a volume of ca. 3 mL remained. Hexane (15 mL) was added to the residue, and the resulting solution cooled to 0° for 3 hours to afford the title compound (54 mg, 74%) as yellow needles; IR (KBr) 913 and 878 cm^{-1} .



Ethyl Phenylpropiolate [Oxidation of a Fischer Carbene Complex with DMD (isol.)].²⁰⁵ To a vigorously stirred acetone solution of the Fischer carbene complex (10 mL, 99 mg, 0.28 mmol), previously filtered over Celite and protected from light at -20° , was added an acetone solution of DMD (13.6 mL, 0.041 M, 0.56 mmol) dropwise over 4 hours. The reaction progress was monitored by TLC (silica gel), which indicated complete consumption of the complex within minutes. The solvent was evaporated (room temperature, 20 mmHg), the residue taken up in CH_2Cl_2 (10 mL), and the chromium oxides were removed by filtration through Celite. The solvent was removed on a rotary evaporator (room temperature, 20 mmHg) to afford pure ethyl phenylpropiolate (44 mg, 90%).



[Dicarbonyl(η^5 -pentamethylcyclopentadienyl)ferrio]-1,1-dihydroxydisilane [Hydroxylation of an Iron-Complexed Silane with DMD (isol.)].²²⁷ A cold (-78°) acetone solution of DMD (11.0 mL, 1.3 M, 0.84 mmol) was added to a solution of $\text{Me}_5\text{Cp}(\text{CO})_2\text{FeSi}_2\text{H}_5$ (130 mg, 0.420 mmol) in toluene (5 mL) at -78° while stirring magnetically. After complete addition (ca. 10 minutes), the color of the reaction mixture changed from yellow to orange. Subsequently, the temperature of the reaction mixture was raised to ca. 20° and after 80 minutes a material precipitated. The solvent was removed (20° , 15 mmHg), the residue was washed with pentane (10 mL) and dried over MgSO_4 to give the title compound (98 mg, 89%) as a yellow powder, mp 65 – 66° ; IR (toluene) 1931, 1986, 2107, 3479 cm^{-1} ; ^1H NMR (400 MHz, benzene- d_6) δ 3.57 (s, 1J (SiH) = 182 Hz, 3H), 2.28 (br s, 2H), 1.58 (s, 15H); ^{13}C NMR (100 MHZ, benzene- d_6) δ 9.7, 95.7, 215.9; ^{29}Si NMR (benzene- d_6) δ –95.26 (s), 96.70 (s). Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{FeO}_4\text{Si}_2$: C, 42.35, H, 5.92. Found C, 42.26, H, 6.01.

TABULAR SURVEY

The oxidation of allenes, alkynes, arenes, heteroatom substrates, alkanes and silanes, and organometallic compounds is presented in the appended tables. The tabular survey covers the literature reported through March, 2005.

The tables are arranged in the order of the discussion in the section on Scope and Limitations. Thus, the data on the oxidation of allenes and alkynes, arenes, heteroatom substrates, alkanes and silanes, and organometallic compounds by isolated dioxiranes (DMD and TFD) are presented in Tables 1A, 2A, 3A–3E, 4A, 5A, 5E, and 6. Oxidations with *in situ* generated dioxiranes of allenes, alkynes, arenes, heteroatom substrates, and alkanes are shown in Tables 1B, 2B, 3F–H, 4B, and 5C. Regioselective oxidations of alkanes by isolated dioxiranes are compiled in Table 5B. Asymmetric oxidations of alkanes by *in situ* generated dioxiranes are shown in Table 5D. Miscellaneous oxidations are presented in Table 7.

The entries within each table are arranged in order of increasing carbon number of the substrates. The carbon count is based on the total number of carbon atoms. Yields of products are given in parentheses, and an em-dash (—) indicates that no yield was reported in the original reference. Data on conversion (% conv.) are included in the product column, preferentially in subtables, and labeled as such. Ratios of different products or diastereomers are given without parentheses. For those reactions that were carried out both with and without a co-solvent, the cosolvent is enclosed in parentheses to indicate that its use is optional.

The following abbreviations are used in the tables:

Ac	acetyl
Ad	adamantyl
Bn	benzyl
Bz	benzoyl
Boc	<i>tert</i> -butyloxycarbonyl

Cbz	benzyloxycarbonyl
Cp	cyclopentadienyl
Cy	cyclohexyl
de	diastereomeric excess
DEK	diethyl ketone
DMD	dimethyldioxirane
DMD (in situ)	in situ generated dioxirane
DMD (isol.)	isolated dimethyldioxirane in acetone
DMD- <i>d</i> ₆ (isol.)	isolated hexadeuterated dimethyldioxirane in acetone- <i>d</i> ₆
DMIPS	dimethylisopropylsilyl
DMM	dimethoxymethane
dr	diastereomeric ratio
EDTA	ethylenediaminetetraacetic acid
Na ₂ EDTA	disodium salt of ethylenediaminetetraacetic acid
F112	1,1,1,2-tetrachlorodifluoroethane
ee	enantiomeric excess
LDA	lithium diisopropylamide
Ms	methanesulfonyl
MOM	methoxymethyl
Naph	naphthyl
NPhth	<i>N</i> -phthalimido
Oxone®	potassium monoperoxysulfate (2KHSO ₅ •KHSO ₄ •K ₂ SO ₄)
PMB	<i>p</i> -methoxybenzyl
PMP	<i>p</i> -methoxyphenyl
PG	protecting group
PPTS	pyridinium <i>p</i> -toluenesulfonate
TAS	tris(dimethylamino)sulfonium difluorotrimethylsiliconate
TBDPS	<i>tert</i> -butyldiphenylsilyl
TBS	<i>tert</i> -butyldimethylsilyl
TES	triethylsilyl
Tf	trifluoromethanesulfonyl (triflyl)
TFD	methyl(trifluoromethyl)dioxirane
TFD (in situ)	in situ generated methyl(trifluoromethyl)dioxirane
TFD (isol.)	isolated methyl(trifluoromethyl)dioxirane
TFP	1,1,1-trifluoro-2-propanone
TIPS	triisopropylsilyl
TMP	tetramesitylporphyrin
TMS	trimethylsilyl
Tp	hydridotris(1-pyrazoylborate)
Tp*	3,5-dimethylhydridotris(1-pyrazoylborate)
TPP	tetraphenylporphyrin
TPS	triphenylsilyl
Ts	<i>p</i> -toluenesulfonyl

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄ 	DMD, acetone, rt, 20 h		63
C ₅ 	DMD, acetone, rt, 10 min		56, 57, 60
C ₅₋₇ 	DMD, acetone, rt, 10 min	 I: II: R ¹ , R ² , n, Product: Me, H, 1, I (55) H, Me, 1, II (89) Me, H, 2, I (92)	56
C ₆ 	DMD, acetone, rt, 140 h		63
	DMD, acetone, rt, 5 min		56, 57, 60
	DMD, acetone, CH ₂ Cl ₂ , TsOH, rt, 10 min		56, 57, 60
	1. Lewis acid/ligand (pre-mixed, 9.0 eq), furan 2. DMD (3-5 eq), CH ₂ Cl ₂ , 8-10 h	 I: II:	271

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63

Ligand	eq	Lewis Acid (eq)	Temp	I	% ee	II	% ee
	1.3	Zn(OTf) ₂ (1.1)	-55°	(0)	—	(48)	8
	1.3	Zn(OTf) ₂ (1.1)	-55°	(0)	—	(58)	2
	1.3	Zn(OTf) ₂ (1.1)	-55°	(0)	—	(70)	21
	1.0	Co(OAc) ₂ •4H ₂ O (1.1)	-55°	(0)	—	(—)	—
1	1.0	Co(OAc) ₂ •4H ₂ O (0.25)	-55°	(0)	—	(46)	1
	0.25	—	-78°	(0)	—	(40)	3
	1.3	Sn(OTf) ₂ (1.1)	-55°	(0)	—	(48)	5
2	0.32	MgI ₂ (0.25)	-78°	(0)	—	(46)	3
2	1.1	Cu(OTf) ₂ (0.85)	-55°	(62)	78	(0)	—
2	0.32	Cu(OTf) ₂ (0.25)	-78°	(46)	74	(0)	—

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.
C ₆	(continued from previous page)					
	Ligand 	eq	Cu(OTf) ₂ (1.1)	-55°	(53) 22 (0) —	
		0.32	Cu(OTf) ₂ (0.25)	-78°	(0) — (46) 10	
		0.32	Cu(OTf) ₂ (0.25)	-78°	(54) 61 (0) —	
		0.32	Cu(OTf) ₂ (0.25)	-78°	(46) 82 (0) —	
		0.32	Cu(OTf) ₂ (0.25)	-78°	(46) 90 (0) —	
		0.12	Cu(OTf) ₂ (0.10)	-78°	(76) 59 (0) —	
		0.32	Cu(OTf) ₂ (0.25)	-78°	(84) 2 (0) —	

44

	+	1.	CuOTf ₂ (25 mol%), Ph (32 mol%), 3.4 Å MS		I S (syn) + II S (anti) + III	271
Y				I + II + III	Additive I + II I:II III % ee	
O			W = O; R = H		(90) 1:1 (0) 92	
O			AgSbF ₆	(91) 1:1 (0)	99	
O			—	(0) — (87)	82	
CH ₂			—	(60) 1:1 (0)	58	
(CH ₂) ₂			—	(47) 1:1 (0)	14	
Y = O	+	"		I + II (90), I:II = 1:1, 43% ee		271
			W = CH ₂ ; Additive = AgSbF ₆			
Y = O	+	R		I + II	Additive I + II I:II % ee	
		Me			(37) (4:1) —	
		Me	W = O	AgSbF ₆	(88) (20:1) 71	
		CO ₂ Me		—	(33) (100:0) —	
		CO ₂ Me	AgSbF ₆	(61)	(100:0) 67	
Y = O	+	"		I + II (81), 36% ee		271
			W = O			
Y = O	+	R		I + II	Additive I + II I:II % ee	
		Me			AgSbF ₆ (91) (0:100) 99	
		Br	W = O	AgSbF ₆	(58) (1:14) 84	
		CH ₂ OTPS	AgSbF ₆	(66)	(1:2.3) 92	

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TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₆		DMD (6–10 eq), acetone, rt, 0.5–2 h		272
		DMD, TsOH, acetone		56
		DMD, acetone	 I: R^1 Me, R^2 H, R^3 H (76) II: R^1 Me, R^2 Me, R^3 Me (96) I + II: R^1 n-Pr, R^2 H, R^3 Me (84) 40:60	60
96				
C ₇		DMD, acetone, rt, 20 h	 t-Bu-C ₂ H ₃ (6) + (18) OAc + (40) + (4) + (3) + (9)	63
		DMD, acetone, rt		57
		DMD, acetone, CH ₂ Cl ₂ , TsOH, rt, 10 min	(79) + (10)	57
97				
		DMD, acetone, H ₂ O		59
		DMD, acetone, TsOH		59
		DMD, acetone, MeOH	 (35) +	59
		DMD, acetone		60
		DMD, acetone		58
		DMD, acetone		56
		DMD, acetone, rt		57
		DMD, acetone, rt		57
		DMD, acetone, rt, 15 min	 I: + (85), I:II = 25:75	56, 57, 60

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.																																																
C ₇		DMD, acetone, K ₂ CO ₃	(—) + (53)	58																																																
		DMD (6-10 eq), K ₂ CO ₃ , acetone, rt, 0.5-2 h	(68)	272																																																
88		DMD (6-10 eq), acetone, rt, 0.5-2 h	(87)	272																																																
		DMD (6-10 eq), NaHCO ₃ , acetone, rt, 0.5-2 h	(52) + (10)	272																																																
		DMD (6-10 eq), acetone, NaHCO ₃ , rt, 0.5-2 h	(52)	272																																																
		DMD (6-10 eq), acetone, TsOH, rt, 0.5-2 h	(84) + (43) + (32)	272																																																
C ₇₋₈		DMD, acetone	(21)	58																																																
C ₇₋₉		DMD, acetone	or $\frac{n}{1} \text{ I } (87)$ $\frac{n}{2} \text{ II } (82)$ $\frac{n}{3} \text{ II } (91)$	60																																																
69		DMD, acetone		56																																																
		DMD, acetone, rt		57																																																
C ₇₋₁₁		DMD, acetone	+	55																																																
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>n</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>1 (88)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>1 (48)</td> </tr> <tr> <td>H</td> <td>H</td> <td>2 (55)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>2 (75)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>2 (65)</td> </tr> </tbody> </table> <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(55)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>(65)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>(75)</td> </tr> </tbody> </table>	R ¹	R ²	n	Me	H	1 (88)	H	Me	1 (48)	H	H	2 (55)	Me	H	2 (75)	H	Me	2 (65)	R ¹	R ²	H	H	(55)	H	Me	(65)	Me	H	(75)																				
R ¹	R ²	n																																																		
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R ¹	R ²	R ³	R ⁴	Temp	Time	I + II	I:II																																													
Me	Me	Me	Me	-50°	30 min	(44)	50:50																																													
Me	Me	n-Bu	H	rt	10 min	(95)	90:10																																													
Me	Me	t-Bu	H	rt	10 min	(84)	100:0																																													
n-Bu	n-Bu	H	H	-40°	1.5 h	(80)	50:50																																													
n-Oct	H	H	H	-40°	2.5 h	(50)	83:17																																													

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
<chem>C8</chem>		DMD (6-10 eq), acetone, rt, 0.5 to 2 h	 I (92)	272
		DMD (6-10 eq), NaHCO ₃ , acetone, rt, 0.5-2 h	I (54) + II (28)	272
<chem>70</chem>	<chem>Ph-C#C</chem>	DMD, acetone, CH ₂ Cl ₂ , 0°, 6 h	<chem>PhCHO</chem> (12) + PhCHO (38)	64
		TFD, TFP, CH ₂ Cl ₂ , 0°, 7 min	<chem>PhCHO</chem> (49)	64
<chem>70</chem>		DMD, acetone, CH ₂ Cl ₂ , MeOH, 3 Å MS	 I (47) + II (27)	59
		DMD, acetone, H ₂ O	 III (58) + IV (29)	59
<chem>71</chem>		DMD, acetone, H ₂ O	 V (68)	59
		DMD, acetone, MeOH	 VI (51)	59
<chem>71</chem>		DMD, acetone (dry)	 VII (17)	59
		DMD, acetone, rt	 VIII (65)	57
<chem>71</chem>		DMD, acetone, rt	 I + II (67), I : II = 1.2:1	57
		DMD, acetone, rt	 I + II (80), I : II = 1.3:1	57
<chem>71</chem>		DMD, acetone, rt	 IX (88)	57
		DMD, acetone, CH ₂ Cl ₂ , TsOH, rt, 1.7 h	 X + I + II (50), I : II = 5:1	57

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
<chem>C8.9</chem>	DMD (6-10 eq), acetone, rt, 0.5-2 h	 I 1 (82) II 2 (71)	272
	DMD (6-10 eq), Cs2CO3, acetone, rt, 0.5-2 h	 I 1 (100) II 2 (83)	272
<chem>C9</chem>	DMD, acetone, K2CO3, rt, 20 min	 (95)	16
	DMD (6-10 eq), acetone, NaHCO3, rt, 0.5-2 h	 I (44) + II (11) + III (11)	272
<chem>C7.2</chem>	DMD (6-10 eq), acetone, TsOH, rt, 0.5-2 h	 I + II (88), I : II = 1:4	272
	DMD, acetone, rt	 (66)	57
	DMD, acetone, KOAc, rt	 (63)	57
<chem>C7.3</chem>	1. NaHCO3 2. DMD, acetone	 I (44) + II (11)	60
	DMD, acetone; TsOH, K2CO3, or Cs2CO3	 I (—) + II (—)	60
	DMD (6-10 eq), K2CO3, acetone, rt, 0.5 to 2 h	 (18)	272
<chem>C7.3</chem>	DMD, acetone, H2O	 I + II (83), I : II = 50:50	59
	DMD, acetone, MeOH, K2CO3	 (83)	59
	DMD, acetone, MeOH, CH2Cl2, TsOH, 3 Å MS	 (80)	59

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.																																																															
C ₉		DMD, acetone (dry), CH ₂ Cl ₂ , 3 Å MS		59																																																															
		DMD, acetone, H ₂ O		59																																																															
		DMD, acetone, K ₂ CO ₃ , rt	 I: R-O-C(=O)-C(R)(R')-O-R II: R-O-C(=O)-C(R)(R')-O-C(=O)-O-R III: R-O-C(=O)-C(R)(R')-O-C(=O)-O-C(=O)-O-R Time: n-Pr 20 min, i-Pr 20 min, t-Bu 25 min Yield: I:II:III (99), (75), (98)	16																																																															
74																																																																			
C ₉		DMD, acetone, rt		57																																																															
C ₉₋₂₁		DMD (2-3 eq), acetone, THF, -40 to 50°	 I: R ¹ -C(=O)-C(R ²)(R ³)-O-C(=O)-C(R ¹)(R ²)-O-C(=O)-C(R ³)(R ⁴)-Z II: R ¹ -C(=O)-C(R ²)(R ³)-O-C(=O)-C(R ¹)(R ²)-O-C(=O)-C(R ³)(R ⁴)-Z	273																																																															
<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Y</th> <th>Z</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>i-Pr</td> <td>O</td> <td>O</td> <td>(70)</td> <td>55:45</td> </tr> <tr> <td>H</td> <td>H</td> <td>Ph</td> <td>O</td> <td>CH₂</td> <td>(40)</td> <td>> 95.5</td> </tr> <tr> <td>H</td> <td>H</td> <td>PhCH₂</td> <td>O</td> <td>O</td> <td>(67)</td> <td>77:23</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Ph</td> <td>NMe</td> <td>O</td> <td>(60)</td> <td>> 95.5</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Ph</td> <td>NMe</td> <td>CH₂</td> <td>(83)</td> <td>> 95.4</td> </tr> <tr> <td>H</td> <td>H</td> <td>Ph₂CH</td> <td>O</td> <td>O</td> <td>(74)</td> <td>> 95.5</td> </tr> <tr> <td>H</td> <td>H</td> <td>Ph₂CH</td> <td>O</td> <td>CH₂</td> <td>(62)</td> <td>93:7</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>i-Pr</td> <td>O</td> <td>O</td> <td>(72)</td> <td>94:6</td> </tr> </tbody> </table>					R ¹	R ²	R ³	Y	Z	I + II	I:II	H	H	i-Pr	O	O	(70)	55:45	H	H	Ph	O	CH ₂	(40)	> 95.5	H	H	PhCH ₂	O	O	(67)	77:23	Me	H	Ph	NMe	O	(60)	> 95.5	Me	H	Ph	NMe	CH ₂	(83)	> 95.4	H	H	Ph ₂ CH	O	O	(74)	> 95.5	H	H	Ph ₂ CH	O	CH ₂	(62)	93:7	Ph	Ph	i-Pr	O	O	(72)	94:6
R ¹	R ²	R ³	Y	Z	I + II	I:II																																																													
H	H	i-Pr	O	O	(70)	55:45																																																													
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Ph	Ph	i-Pr	O	O	(72)	94:6																																																													
C ₁₀		TFD, TFP, CH ₂ Cl ₂ , 0°, 3 min		64																																																															
		DMD (1 eq), acetone, rt		61																																																															
	t-Bu—C≡C—Bu-t	DMD, acetone, rt, 140 h		63																																																															
75																																																																			
		DMD (6-10 eq), acetone, rt, 0.5-2 h		272																																																															

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₁₀		DMD (6-10 eq), Na ₂ CO ₃ , acetone, rt, 0.5-2 h	(37) + (9)	272
76		DMD, acetone, rt	(70)	57
76		DMD, acetone, rt	I + II (75), I:II = 2.5:1	57
76		DMD, acetone, rt	I + II (56)	56, 57, 60
76		DMD, acetone, rt	I (36) + II (23) + III (13)	56, 57
		DMD (dry), acetone, rt	I (5) + II (38) + III (33)	57
77		DMD, acetone, K ₂ CO ₃ , rt, 10 min	(96)	56, 57
77		DMD (excess), acetone, rt, 24 h	II (—)	61
77		DMD, acetone, CH ₂ Cl ₂ , MeOH, 3 Å MS	I (25) + II (60)	59
77		DMD, acetone, MeOH, CH ₂ Cl ₂	I (32) + II (—) + III (—) II:III = 80:20	59
77		DMD, acetone (dry), CH ₂ Cl ₂ , 3 Å MS	I + II (—)	59
		DMD, acetone, CH ₂ Cl ₂ , TsOH, H ₂ O	(72)	59

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.																																																												
C ₁₀		DMD, acetone, rt		57																																																												
		DMD (6-10 eq), acetone, rt, 0.5-2 h		272																																																												
C ₁₁		DMD, acetone, rt, 24 h	 I + II + III + IV (—), I:II:III:IV = 26:30:28:16	61																																																												
78		DMD, acetone, H ₂ O		59																																																												
		DMD, acetone, MgSO ₄ , rt	 I + II + III (100), I:II:III = 3.4:1:1.4	57																																																												
		DMD (2-5 eq), acetone, CH ₂ Cl ₂	 I + II (100), I:II = 2.4:1	274																																																												
C ₁₂		DMD, acetone, rt		57																																																												
		DMD, acetone, K ₂ CO ₃ , rt, 45 min	 I + II (100), I:II = 2.4:1	16																																																												
		DMD, acetone, K ₂ CO ₃ , rt, 12 min		57																																																												
79		DMD (2-3 eq), additive (2 eq), acetone	 I + II (75:25), I:II = 75:25	273																																																												
			<table border="1"> <thead> <tr> <th>Temp</th> <th>Solvent</th> <th>Additive</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>-40°</td> <td>CH₂Cl₂</td> <td>—</td> <td>(75)</td> <td>75:25</td> </tr> <tr> <td>-40°</td> <td>Et₂O</td> <td>—</td> <td>(77)</td> <td>75:25</td> </tr> <tr> <td>-40°</td> <td>MeCN</td> <td>—</td> <td>(< 10)</td> <td>—</td> </tr> <tr> <td>-40°</td> <td>THF</td> <td>—</td> <td>(80)</td> <td>75:25</td> </tr> <tr> <td>rt</td> <td>THF</td> <td>—</td> <td>(80)</td> <td>75:25</td> </tr> <tr> <td>-78°</td> <td>THF</td> <td>—</td> <td>(70)</td> <td>82:18</td> </tr> <tr> <td>-40°</td> <td>THF</td> <td>LiClO₄</td> <td>(81)</td> <td>75:25</td> </tr> <tr> <td>-40°</td> <td>THF</td> <td>MgBr₂</td> <td>(< 10)</td> <td>—</td> </tr> <tr> <td>rt</td> <td>THF</td> <td>ZnCl₂</td> <td>(40)</td> <td>90:10</td> </tr> <tr> <td>-40°</td> <td>THF</td> <td>ZnCl₂</td> <td>(77)</td> <td>94:6</td> </tr> <tr> <td>-78°</td> <td>THF</td> <td>ZnCl₂</td> <td>(80)</td> <td>> 96:4</td> </tr> </tbody> </table>	Temp	Solvent	Additive	I + II	I:II	-40°	CH ₂ Cl ₂	—	(75)	75:25	-40°	Et ₂ O	—	(77)	75:25	-40°	MeCN	—	(< 10)	—	-40°	THF	—	(80)	75:25	rt	THF	—	(80)	75:25	-78°	THF	—	(70)	82:18	-40°	THF	LiClO ₄	(81)	75:25	-40°	THF	MgBr ₂	(< 10)	—	rt	THF	ZnCl ₂	(40)	90:10	-40°	THF	ZnCl ₂	(77)	94:6	-78°	THF	ZnCl ₂	(80)	> 96:4	
Temp	Solvent	Additive	I + II	I:II																																																												
-40°	CH ₂ Cl ₂	—	(75)	75:25																																																												
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TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)					Refs.
	DMD (2-5 eq), acetone, CH ₂ Cl ₂						274
	Addition Method	Additive	Y	n	Temp	I + II	I:II
	syringe-pumped	—	O	0	-45°	(82)	> 96:4
	syringe-pumped	—	O	0	rt	(77)	> 96:4
	cannulated	—	O	0	-45°	(75)	> 96:4
	cannulated	—	O	1	-45°	(75)	> 96:4
	cannulated	ZnCl ₂	O	1	-78°	(30)	95:5
	syringe-pumped	—	O	2	-45°	(30)	87:13
	syringe-pumped	—	O	2	rt	(70)	83:17
	syringe-pumped	—	O	3	rt	(57)	70:30
	syringe-pumped	—	CH ₂	1	rt	(90)	87:13
	cannulated	—	CH ₂	1	-45°	(85)	93:7
	syringe-pumped	—	CH ₂	3	rt	(40)	52:48
	DMD, acetone, TsOH		(42)				58
	DMD, acetone, NaHCO ₃ , rt		(93)				57
	DMD, acetone, NaHCO ₃ , -78° to rt, 5 h		(45)				57
	DMD (excess), acetone		$\frac{n}{1 (56)}$				58
			$\frac{n}{2 (52)}$				
	DMD, acetone, CH ₂ Cl ₂ , 0°, 8 h		(15)	+ Ph ₂ C=O	II (29)		64
	TFD, TFP, CH ₂ Cl ₂ , 0°, 6 min		I (25) + II (49)				64
	DMD, acetone, CH ₂ Cl ₂ , TsOH		(2)	+	(33)		58
	DMD, acetone, K ₂ CO ₃		(—)	+	(47) I:II = 1:1.6		58
	DMD, acetone, NaHCO ₃ , -50 to 10°			+	(85) I:II = 1.1:1		57
	DMD, acetone, NaHCO ₃ , -40 to 20°, 6 h		(—)				57
	DMD, acetone, K ₂ CO ₃ , rt			+	I + II (91), I:II = 9:1		57

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.																				
C ₁₄		DMD, acetone, rt		57																				
C ₁₄₋₁₈		DMD (2-3 eq), acetone, CH ₂ Cl ₂ , -45°		274																				
			<table border="1"> <thead> <tr> <th>R</th> <th>n</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>t-Bu</td> <td>0</td> <td>(80)</td> <td>(14)</td> </tr> <tr> <td>Bn</td> <td>0</td> <td>(75)</td> <td>(—)</td> </tr> <tr> <td>t-Bu</td> <td>1</td> <td>(< 5)</td> <td>(—)</td> </tr> <tr> <td>Bn</td> <td>1</td> <td>(< 5)</td> <td>(—)</td> </tr> </tbody> </table>	R	n	I	II	t-Bu	0	(80)	(14)	Bn	0	(75)	(—)	t-Bu	1	(< 5)	(—)	Bn	1	(< 5)	(—)	
R	n	I	II																					
t-Bu	0	(80)	(14)																					
Bn	0	(75)	(—)																					
t-Bu	1	(< 5)	(—)																					
Bn	1	(< 5)	(—)																					
C ₁₅		DMD, acetone, NaHCO ₃		58																				
		DMD, acetone, TsOH		58																				
		DMD, acetone, K ₂ CO ₃		58																				
C ₁₆		DMD, acetone, rt		57																				
	n-C ₇ H ₁₅ -C≡C-C ₇ H ₁₅ -n	DMD, acetone, CH ₂ Cl ₂ , 0°, 8 h		64																				
		TFD, TFP, CH ₂ Cl ₂ , 0°, 7 min		64																				
		DMD, acetone, NaHCO ₃ , rt		57																				
83		DMD, acetone, rt, 1 h		57																				
		DMD, acetone, rt		57																				
		DMD, acetone, rt		57																				

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₁₆		DMD (2-5 eq), acetone, -40°, 2 h	 I (88) I + II (70), I:II = 75:25	275 275
		DMD (2-5 eq), acetone, PPTS (0.5 eq), -40°, 2 h	 I + II (65) dr 95:5	275
C ₁₇		DMD (2-5 eq) cannulated, acetone/CH ₂ Cl ₂ , -78°, 5-15 min	 I (46)	276
		1. DMD, acetone 2. TBDPSCl, imadazole, CH ₂ Cl ₂ , 2 h	 Temp ratio at C-2 rt 1:1 -45° 2:1 -78° 2:1	275
		DMD (2-5 eq) syringe-pumped, acetone, CH ₂ Cl ₂ , -45°	 I + II (65), I:II = 53:47	274
C ₁₈		DMD (2-5 eq) syringe-pumped, acetone/CH ₂ Cl ₂ , -45°	 Additive I + II I:II — (20) 58:42 ZnCl ₂ (47) 60:40	274
			 Additive I + II I:II — (20) 58:42 ZnCl ₂ (47) 60:40	274
C ₁₉		DMD (2-5 eq), acetone, CH ₂ Cl ₂ , -78°, 10 min	 I (45) dr 95:5	276
		DMD (2-5 eq), acetone, CH ₂ Cl ₂ , -78°, 30 min	 I (75) dr 95:5	276
C ₂₂		DMD, acetone, CH ₂ Cl ₂ , dark, 5 min	 I (38)	62
		1. DMD, acetone, CH ₂ Cl ₂ , K ₂ CO ₃ , N ₂ , rt, 1 h 2. m-CPBA, CH ₂ Cl ₂ , rt, 18 h	 I (—) II (11)	62
		DMD, acetone, CH ₂ Cl ₂ , AcOH, rt, 3 h	 I (63)	62

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (*Continued*)

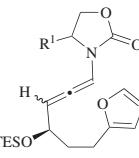
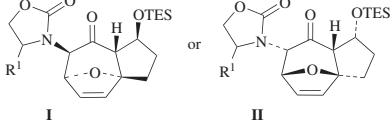
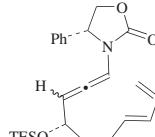
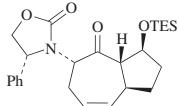
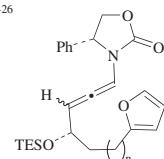
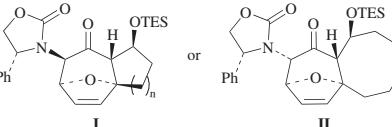
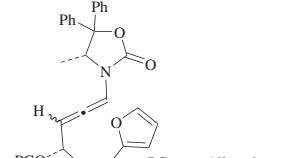
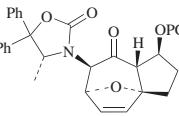
	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₂₂₋₂₆		DMD (2.5 eq), acetone, CH ₂ Cl ₂ , -78°, 5-15 min	 I or II	276
	<u>R¹</u>	Allene isomer	<u>I</u> <u>II</u> <u>dr</u>	
	(R)-Bn	P/M 3:1	(65) (—) 71:29	
	(S)-Ph	P/M 1:1	(—) (60) 90:10	
	(S)-Pr-i	P	(—) (60) 95:5	
	(S)-Pr-i	M	(—) (60) 95:5	
C ₂₅		DMD (2.5 eq), acetone, CH ₂ Cl ₂ , -78°, 5-15 min	 <u>dr</u>	276
	<u>Allene isomer</u>			
	M		(30) < 5:95	
	P		(34) < 5:95	
C ₂₅₋₂₆		DMD (2.5 eq), acetone, CH ₂ Cl ₂ , -78°, 5-15 min	 I or II	276
	<u>n</u>	Allene isomer	<u>I</u> <u>II</u> <u>dr</u>	
	1	P	(60) (—) 90:10	
	1	M	(75) (—) 90:10	
	2	P/M 1:1	(65) (—) 93:7	
	3	P/M 1:1	(—) 55 < 5:95	
C ₂₈₋₃₂		DMD (2.5 eq), acetone, CH ₂ Cl ₂ , -78°, 5-15 min	 (78)	276
	<u>PG</u>	Allene isomer		
	TES	P/M 2.5:1	(83)	
	Ac	P/M 2.5:1		

TABLE 1B. OXIDATION OF ALLENES AND ALKYNES BY IN SITU GENERATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆		Oxone®, NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h	(42)	272
C ₇		Oxone®, NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h	(72)	272
88		Oxone®, NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h	(67)	272
C ₈		Oxone®, NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h	(74)	272
Ph— \equiv		Oxone®, acetone, phosphate buffer (pH 7.5), CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 10°, 40 h	PhCHO I (6) + PhCO ₂ H II (15) + PhCH ₂ CO ₂ H III (52)	64
		Oxone®, acetone, phosphate buffer (pH 7.5), CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 10°, 8 h	I (25) + II (20) + III (19)	64
C ₉		Oxone®, NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h	(—)	272
C ₁₀		Oxone®, NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h	(76)	272
86		Oxone®, NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h		272
C ₁₄		Oxone®, NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h	(—)	272
Ph— \equiv —Ph		Oxone®, acetone, phosphate buffer (pH 7.5), CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 5°, 60 h		64
		Oxone®, acetone, phosphate buffer (pH 7.5), CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 5°, 12 h	I (12) + II (44) + III (6)	64

TABLE 1B. OXIDATION OF ALLENES AND ALKYNES BY IN SITU GENERATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₆		Oxone®, acetone, CH ₂ Cl ₂ , H ₂ O (1:1:2), rt, 2-3 h	(40)	275
	$n\text{-C}_7\text{H}_{15}\text{---C}_7\text{H}_{15\text{-}n}$	Oxone®, acetone, phosphate buffer (pH 7.5), CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 5°, 16 h	$n\text{-C}_6\text{H}_{13}\text{---C}_7\text{H}_{15\text{-}n}$ (56) + $n\text{-C}_7\text{H}_{15}\text{---C}_7\text{H}_{15\text{-}n}$ (12)	64

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄		1. DMD, acetone, 0°, 30 min 2. Ph ₃ PC(Me)CHO, CH ₂ Cl ₂ , acetone, 0° to rt, 3 h	OHC- (84)	75
C ₄₋₁₀		DMD, acetone, rt	O= (> 95)	73
			R ¹ R ²	
			H H	
			Me H	
			Me Me	
			H AcOCH ₂	
			H AcOCH ₂	
			AcOCH ₂ CH(OMe) ₂	
			H C(Me) ₂ OTMS	
C ₅		1. DMD, acetone, 0°, 30 min 2. Ph ₃ PCHCHO, CH ₂ Cl ₂ , acetone, 0° to rt, 3 h	O= (73)	75
C ₅₋₆		DMD, acetone, rt	O=H- (> 95)	73
			R ¹ R ²	
			H H	
			H Me	
			Me H	
			CH ₂ OH H	
C ₆		TFD, TFP, F113, 0°, 6 h	I + II (4), I:II = 1:1.5	65
			+	
			II	
		TFD, acetone, TFP, -20°, 1 h	(70)	277

96

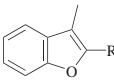
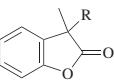
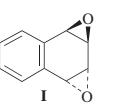
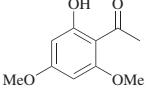
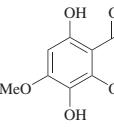
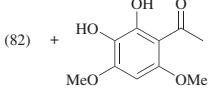
TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

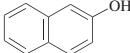
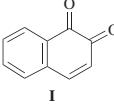
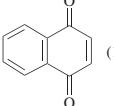
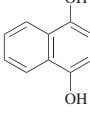
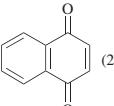
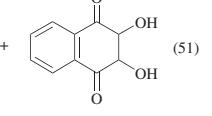
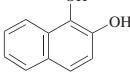
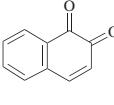
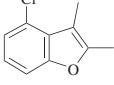
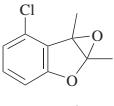
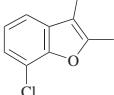
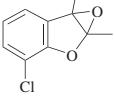
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆		+ NaCl DMD, acetone, 10% H ₂ SO ₄ , rt, 1 min		278
C ₆₋₈		+ HX DMD, acetone, rt, 1 min	R X H Br (95) H Cl (90) Me Br (95) Me Cl (95)	278
			I	
			R X H Br (95) H Cl (90) Me Br (95) Me Cl (95)	
			I	
			R X H Br (78) H Cl (85) Me Br (85) Me Cl (90)	
			I	
			R X H Br (78) H Cl (85) Me Br (85) Me Cl (90)	
92				

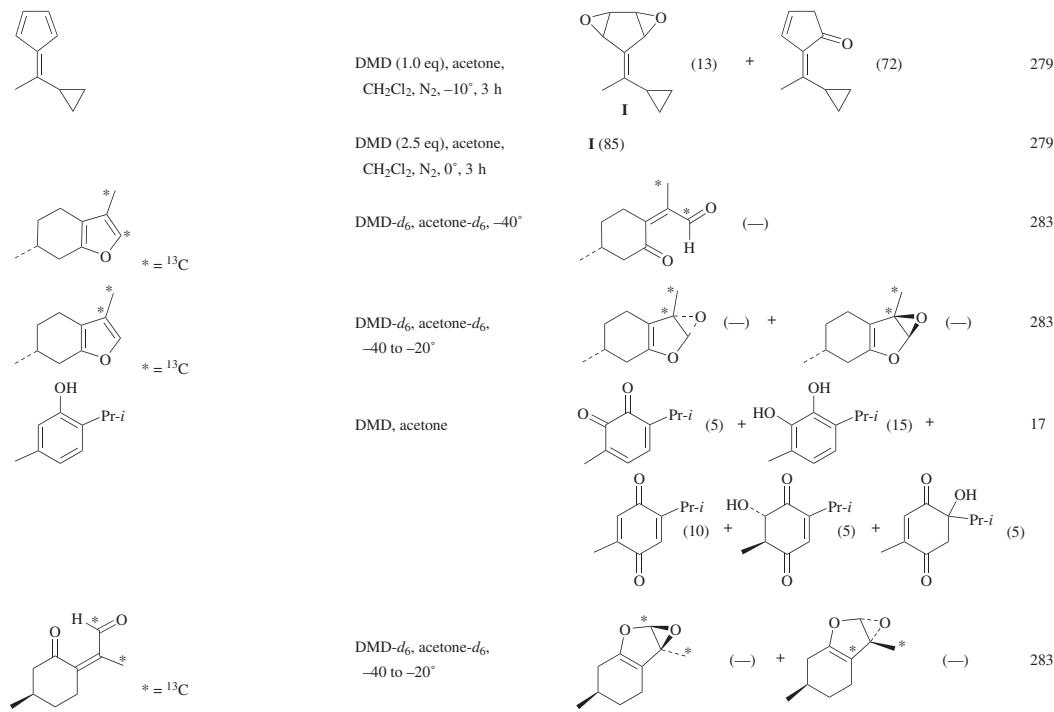
C ₇		1. DMD, acetone, 0°, 30 min 2. Ph ₃ PCHCO ₂ Et, CH ₂ Cl ₂ , acetone, 0° to rt, 3 h		(84)	75
		1. DMD, acetone, 0°, 30 min 2. Ph ₃ PCHCO ₂ Et, CH ₂ Cl ₂ , acetone, 0° to rt, 3 h		(84)	75
		DMD (1.1 eq), acetone, CH ₂ Cl ₂ , N ₂ , -10°, 3 h		(70) + (30) I	279
		DMD (2.5 eq), acetone, CH ₂ Cl ₂ , N ₂ , 0°, 3 h	I (91)		279
		DMD, acetone, 10% H ₂ SO ₄ , rt, 1 min		I + II	278
		DMD, acetone, 10% H ₂ SO ₄ , rt, 1 min	I	Cl (96) Br (82)	278
				(51)	280
93		DMD, CH ₂ Cl ₂ , 0° to rt, 2 h		(85)	75
		1. DMD, acetone, 0°, 30 min 2. Ph ₃ PC(Me)CHO, CH ₂ Cl ₂ , acetone, 0° to rt, 3 h			
C ₈		DMD, CH ₂ Cl ₂ , 0° to rt, 2 h		(51)	280
		1. DMD, acetone, 0°, 30 min 2. Ph ₃ PC(Me)CHO, CH ₂ Cl ₂ , acetone, 0° to rt, 3 h		(85)	75

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.	
C ₈		DMD, acetone, rt		(>95)	73
C ₈₋₁₄		DMD (1.5 eq), acetone, CH ₂ Cl ₂ , rt, 1.5 h		R Bn (73) Me (70) MOM (60) SO ₂ NMe ₂ (—)	281
C ₉		DMD, acetone, 1 h		(96)	265
94		DMD, acetone, CH ₂ Cl ₂ , N ₂ , 20°, 19 h		(35)	89
		DMD-d ₆ , acetone-d ₆ , N ₂ , -55°, 4 h		(—)	89
C ₉₋₁₀		DMD, acid, acetone, 0°, N ₂		I + II + III	282

R^1	R^2	R^3	Acid	Time	I	II	III	
MeO	H	Me	—	360 min	(—)	(3)	(11)	
MeO	H	Me	H_2SO_4	60 min	(—)	(8)	(2)	
H	MeO	Me	—	300 min	(—)	(—)	(12)	
H	MeO	Me	H_2SO_4	45 min	(1)	(35)	(5)	
H	MeO	Me	$H_3PMo_{12}O_{40}$	300 min	(1)	(38)	(2)	
Me	MeO	MeO	—	30 min	(26)	(—)	(—)	
Me	MeO	MeO	H_2SO_4	60 min	(—)	(50)	(—)	
Me	MeO	MeO	$H_3PMo_{12}O_{40}$	30 min	(—)	(23)	(—)	
Me	MeO	MeO	H_3PO_4	30 min	(—)	(51)	(—)	
Me	MeO	MeO	CF_3CO_2H	30 min	(—)	(46)	(—)	
Me	MeO	MeO	AcOH	30 min	(6)	(16)	(—)	
MeO	MeO	Me	—	390 min	complex mixture			
MeO	MeO	Me	H_2SO_4	240 min	(11)	(14)	(—)	
C_{9-17}								89
C_{10}			DMD, acetone, CH_2Cl_2 , N_2					89
C_{10}			TFD, CH_2Cl_2 , TFP, -20°, 30 min					65
					(82)			
C_{10}			DMD, CH_2Cl_2 , 0° to rt, 10 min					280
					(82) + 			
TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)								

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		DMD, acetone	 I (38)	17
		DMD, acetone	 (17) + I (14)	17
		DMD, acetone, Ar, 20°, 24 h	 (27) +  (51)	66
		DMD, acetone	 (100)	17
		DMD, acetone, N_2 , -40°, 11 h	 (41)	79
		DMD, acetone, N_2 , -40°, 9 h	 (72)	79

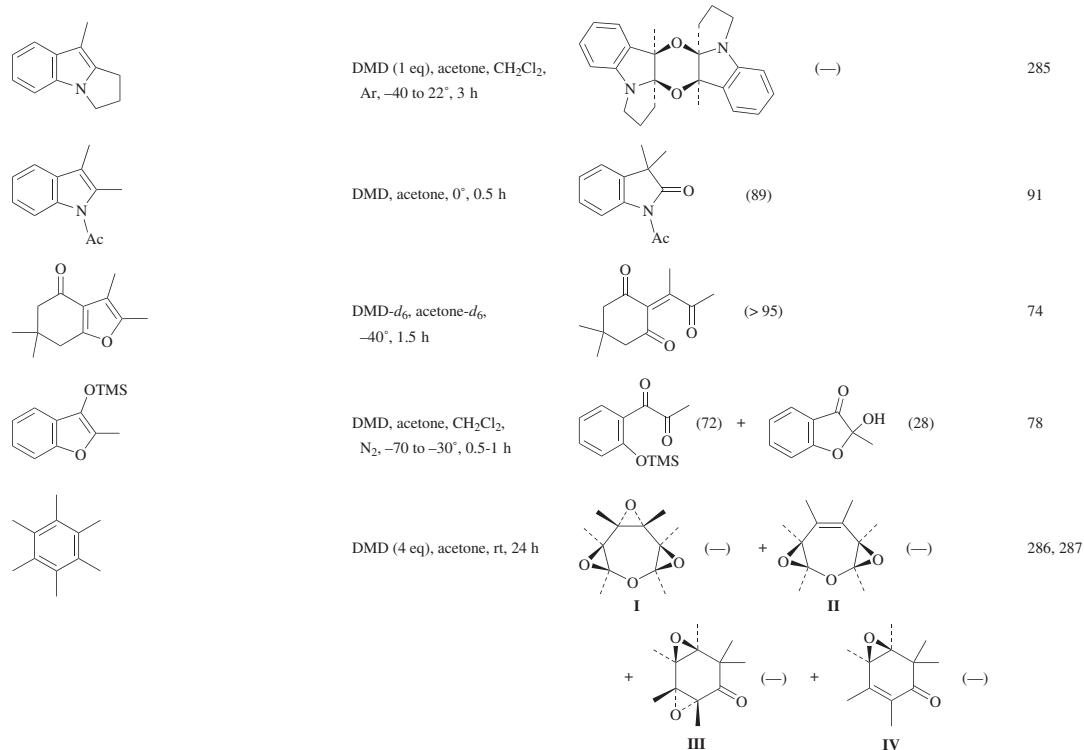
TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₀		DMD, acetone, Ar, 20°, 1.5 h	 (72) + (11)	66
		DMD, acetone	 (77)	17
C₁₀₋₁₁		DMD, acetone, CH ₂ Cl ₂ , N ₂ , -78 to -20°, 0.5 to 3 h	 (100) $\begin{array}{ccc} \text{R}^1 & \text{R}^2 & \text{R}^3 \\ \text{H} & \text{H} & \text{H} \\ \text{Me} & \text{H} & \text{H} \\ \text{H} & \text{Me} & \text{H} \\ \text{H} & \text{H} & \text{Me} \end{array}$	77, 79
C₁₀₋₁₂		DMD-d ₆ , acetone-d ₆ , N ₂ , -78°, 0.5 h	 R = H, OAc (100)	87
		DMD, acetone, N ₂ , -40°, 11-12 h	 (100) $\begin{array}{cc} \text{R}^1 & \text{R}^2 \\ \text{Cl} & \text{H} \\ \text{H} & \text{Cl} \\ \text{H} & \text{Ac} \end{array}$	79
C₁₀₋₁₈		DMD, acetone, CH ₂ Cl ₂ , N ₂	 I + II	82

	R ¹	R ²	R ³	R ⁴	Temp	Time	% Convn	Products	
	Cl	H	H	H	-20°	10 h	>95	I	
	H	Cl	H	H	-35°	6 h	79	I	
	H	H	Cl	H	-20°	9 h	71	I	
	H	H	H	Cl	-20°	8 h	92	I	
	H	H	H	H	-40°	7 h	>95	I	
	Me	H	H	H	-45°	3 h	95	I	
	H	Me	H	H	-50°	2 h	>95	I+II (31:69)	
	H	H	Me	H	-40°	3 h	>95	I	
	H	H	H	Me	-35°	4 h	>95	I	
	H	MeO	H	H	-60°	0.5 h	>95	II	
	H	H	t-Bu	H	-30°	2 h	>95	I	
	H	t-Bu	H	t-Bu	-45°	3 h	>95	I	
C ₁₁					DMD, acetone, CH ₂ Cl ₂ , 0°, 9 h		(99)		83
					DMD, acetone, CH ₂ Cl ₂ , -78°		I + II (> 98%), I : II = 11:1		92
					DMD, acetone, CH ₂ Cl ₂ , -78°		I + II (> 98%), I : II = 10:1		92
					DMD, acetone, CH ₂ Cl ₂ , N ₂ , -78 to -20°, 3 h		(80)		79

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₁₁		1. DMD, acetone, 0°, 30 min 2. Ph ₃ PCHCHO, CH ₂ Cl ₂ , acetone, 0° to rt, 3 h		75
		DMD, acetone, -70 to -20°, 3 to 5 h		I II 4-MeO (100) (—) 5-MeO (34) (66) 6-MeO (—) (100) 7-MeO (57) (43) 81
		DMD, acetone, Ar, 20°, 24 h		(45) + (28) 66
100		TFD, TFP, CH ₂ Cl ₂ , N ₂ , -78 to -40°		R Time H 30 min (100) MeO 2 h (100) 84
C ₁₂		DMD, acetone, 20°, 24 h		(29) 284
		DMD, acetone, rt, 1 h		(97) 265
		DMD, acetone, MeOH, rt, 19 h		(83) 85

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
	DMD (5 eq), acetone, rt, 48 h	 I (51) + II (0) + III (19) + IV (0) + V (7.5) + VI (3)	286, 287
			VII (6.4) + VIII (5)
	DMD (2 eq), acetone, rt, 5 h	I (5) + II (29) + IV (5) + III (traces)	286, 287
	DMD (6 eq), acetone, -25°, 72 h	I (—) + II (—) + IV (—) + V (—) + III (traces) + VII (traces)	286, 287
	DMD (6 eq), acetone, NaHCO ₃ , rt, dark, 64 h	I (—) + II (—) + III (—), I:II:III = 58:27:15	286, 287
	DMD (> 6 eq), acetone, NaHCO ₃ , rt, dark, > 76 h	I (—) + III (—), I:III = 90:10	286, 287
	Dry DMD (6 eq), acetone, rt, 96 h	I (—) + II (—) + VII (—), I:II:VII = 58:15:27	286, 287
	DMD (6 eq), acetone, TsOH, rt, 96 h	I (—) + III (—) + V (traces) + VII (traces), I:III = 15:85	286, 287

		DMD, acetone, CH ₂ Cl ₂ , 10°, 2 d		93
		DMD-d ₆ , acetone-d ₆ , -40°, 10-30 min		288
		DMD, acetone, CH ₂ Cl ₂ , -78°		92
C ₁₂₋₁₇		DMD-d ₆ , acetone-d ₆ , -70 to -40°, 10-30 min		90
C ₁₃		DMD, acetone, rt		73

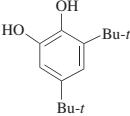
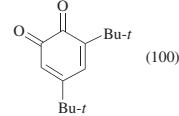
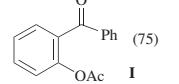
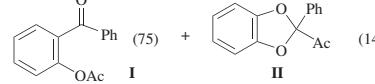
TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (*Continued*)

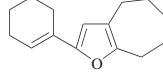
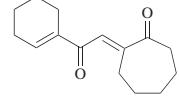
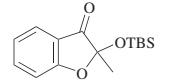
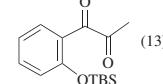
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃		DMD (1.0 eq), acetone, CH ₂ Cl ₂ , N ₂ , -10°, 3 h	 I	279
		DMD (3.1 eq), acetone, CH ₂ Cl ₂ , N ₂ , 0°, 4 h		279
		DMD, acetone, H ₂ O		289
		DMD, acetone, CH ₂ Cl ₂ , N ₂ , 0°, 3 h		89
C ₁₄		DMD, acetone, CH ₂ Cl ₂ , -20°		290
		DMD, acetone, CH ₂ Cl ₂ , -78°, 20 min	 I	291
		DMD, acetone, MeCN, 26°	 I	121

	Ethylmethylidioxirane, 2-butanone, MeCN, rt	I (—)	121
	TFD, TFP, -20°, 5 min	I (74)	173
	DMD, acetone, 22°, 20 h	I (—)	173
	TFD, CH ₂ Cl ₂ , TFP, -20°, 8 min	I (96)	65
	TFD, CH ₂ Cl ₂ , TFP, 0°, 30 min	 (80)	65
	DMD, acetone	 (77)	17
	DMD, acetone, CH ₂ Cl ₂ , N ₂ , -78° to -20°, 16 h	 (100)	84
	DMD, acetone, CH ₂ Cl ₂ , N ₂ , -78° to -20°, 22 h	 (100)	84
	DMD, acetone, CH ₂ Cl ₂ , 20°	 (99)	91

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
^{C₁₄} 	DMD, acetone, 0°, 0.5 h	 I (75)	91
	DMD, acetone, CH ₂ Cl ₂ , -78°	I (100)	92
	TFD, TFP, CH ₂ Cl ₂ , N ₂ , 0°, 1 min	 I (4) + II (23) + III (67)	277
	DMD, acetone, CH ₂ Cl ₂ , N ₂ , 0°, 48 h	 II (19) + III (13) + IV (2)	277
	DMD, acetone	 (46) + V (20)	17
	DMD, acetone	 (55)	17

	DMD, acetone		(100)	17
	DMD, acetone, CH_2Cl_2 , N_2 , -20° , 2 d		(75)	292
			(14)	292

	DMD, acetone, CH_2Cl_2 , -20°		(—)	290
	DMD, acetone, CH_2Cl_2 , -78° , 1 h		(74)	83
			(13)	83

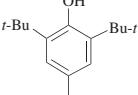
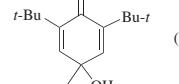
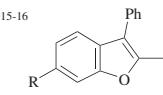
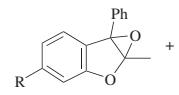
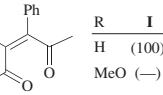
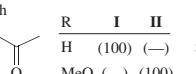
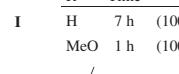
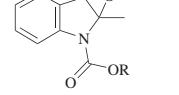
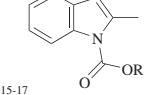
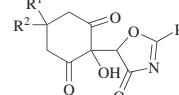
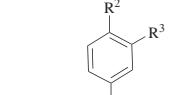
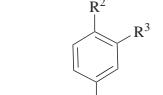
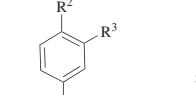
	DMD, acetone		(13)	17

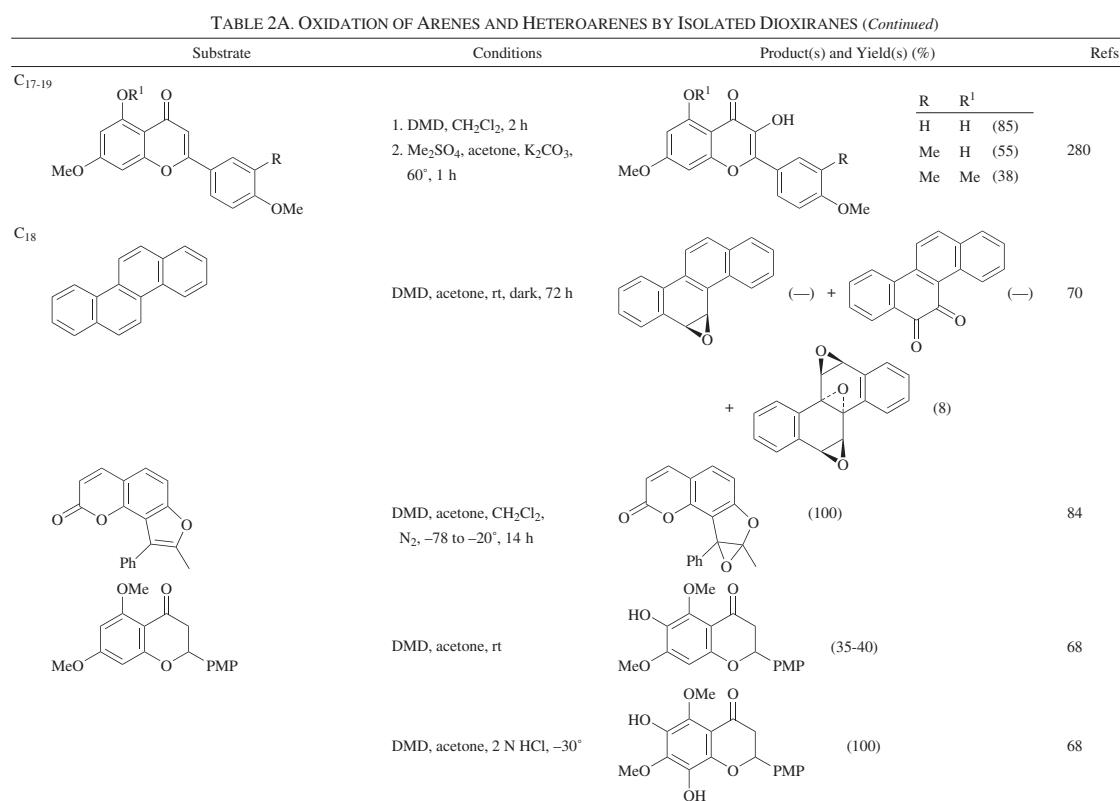
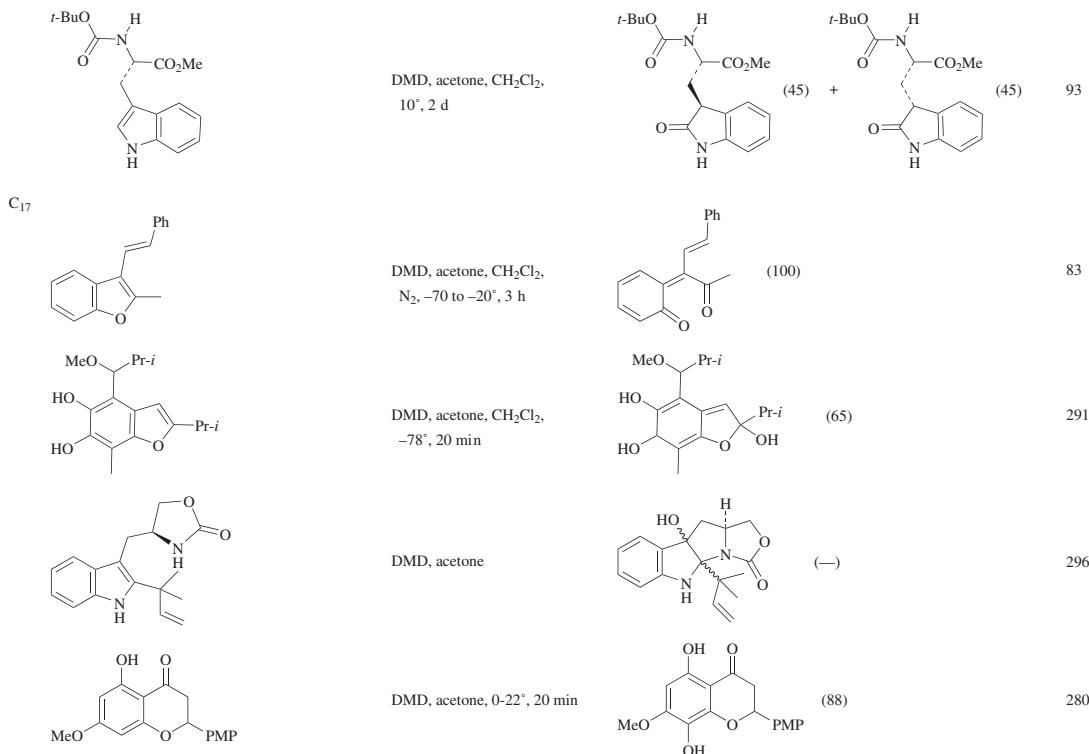
TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, -70 to -20° , 4 h	 + 	 80
	DMD, acetone, N_2 , -78 to -10°		 293
	DMD, acetone, CH_2Cl_2 , N_2 , -78 to -20° , 3 h		 294
	DMD, acetone, CH_2Cl_2 , -78° , 10-20 min; 20° , 60-140 min		 295
	DMD, acetone, N_2	 + 	 86

	R ¹	R ²	R ³		Temp	Time	I	II	
	H	H	H		-78° to -10°	7 h	(> 95)	(—)	
	MeO	H	NO ₂		-78° to -20°	3 h	(—)	(> 95)	
	MeO	H	H		-78° to -20°	1 h	(—)	(> 95)	
	Ac	H	H		-78° to 0°	14 h	(—)	(—)	
	MeO	MeO	H		-78° to -20°	1 h	(—)	(> 95)	
C ₁₆				+ HCl	DMD, acetone, rt				278
					DMD, acetone, 0-5°, 12 h			I (—)	69
					TFD (1.1 eq), CH ₂ Cl ₂ , TFP, -20°, 5 min		I (1.2)		65
					TFD (2.2 eq), CH ₂ Cl ₂ , TFP, -20°, 5 min		I (2.4)		65
					DMD, acetone, 0-5°, 12 h			(7)	69
					DMD, acetone, CH ₂ Cl ₂ , N ₂ , -78 to -20°, 5 h			(100)	84

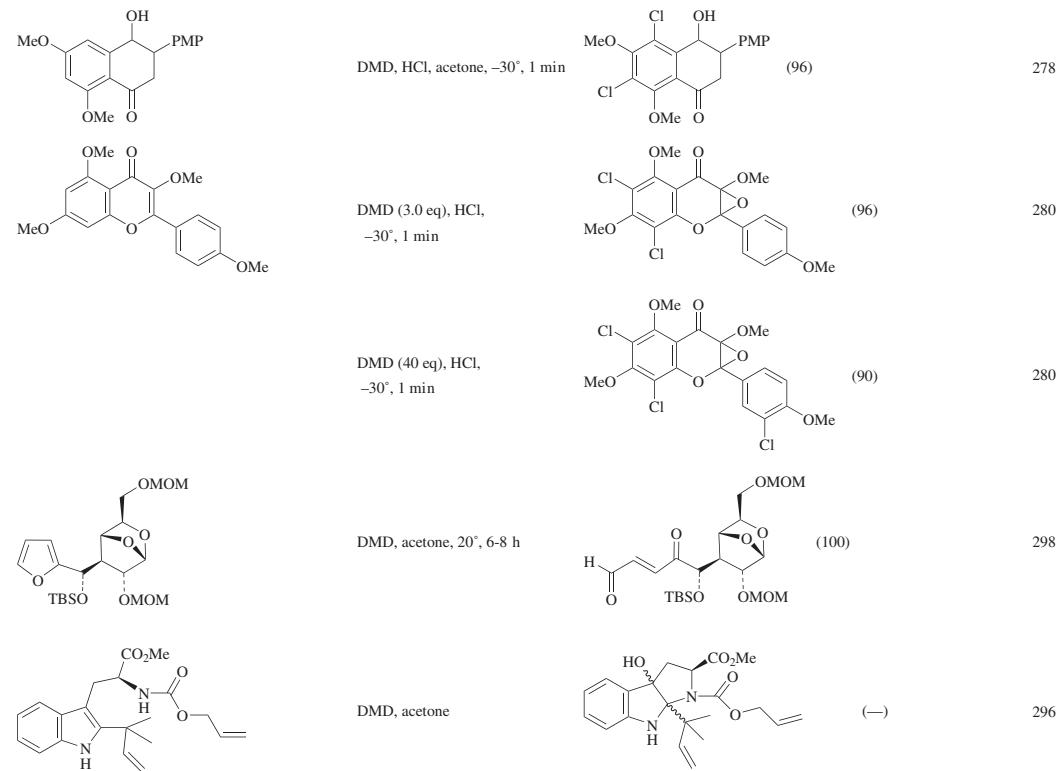
TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (*Continued*)

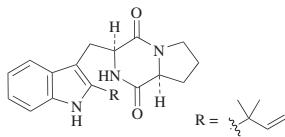
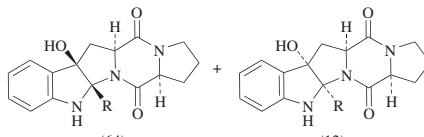
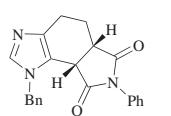
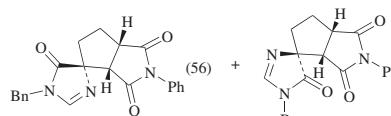
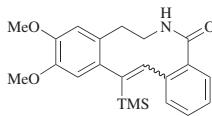
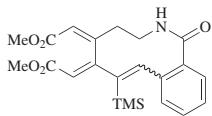
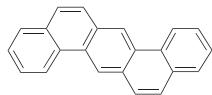
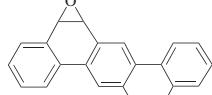
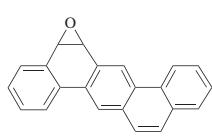
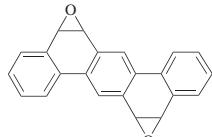
	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₁₆		DMD, acetone, CH ₂ Cl ₂ , N ₂ , -78 to -20°, 7 h		(100) 84
		DMD, acetone, rt		(35-40) 68
		DMD, acetone, 2 N HCl, -30°		(100) 68
		DMD, acetone, 2 N HCl, -30°		(100) 68
		DMD (1.5 eq), acetone, CH ₂ Cl ₂ , rt, 2 h		(40) 281



	DMD, acetone, 0-5°, 12 h		(-)	69
	DMD, acetone, 0-5°, 12 h		(97)	69
	DMD, acetone, 0-5°, 12 h		(18)	69
	DMD (1.0 eq), acetone, CH ₂ Cl ₂ , N ₂ , -10°, 2 h	 (61) + I (14)	279	
	DMD (2.2 eq), acetone, CH ₂ Cl ₂ , N ₂ , 20°, 5 min		(100)	297
	DMD, acetone, rt, 30 min		(100)	297
	DMD, acetone, 2 N HCl, -30°		(100)	68

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₈₋₁₉		DMD, CH ₂ Cl ₂ , 0° to rt, 1 h	 R H (76) OMe (65)	280
		DMD, CH ₂ Cl ₂ , 1 h	 R H (90) OMe (90)	280
C₁₉		DMD, acetone, CH ₂ Cl ₂ , -78°	 I + II (> 98), I:II = 10:1	92
		DMD, CH ₂ Cl ₂ , N ₂ , 30 min	 (86)	280
		DMD, CH ₂ Cl ₂ , 50 min	 (89)	280

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₁	DMD (4 eq), acetone, CH ₂ Cl ₂ , -78 to 0°, 25 h	 (64) + (12)	296
 C ₂₂	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , rt, 2 h	 (56) + (27)	281
 116	TFD, TFP, CH ₂ Cl ₂ , rt, 9 h	 (90)	299, 300
	DMD, acetone, 0-5°, 12 h	 (—)	69
	DMD, acetone, 0-5°, 12 h	 (16)	69

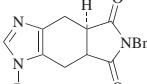
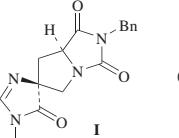
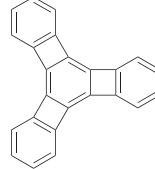
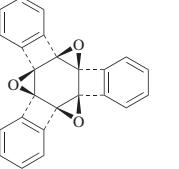
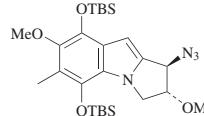
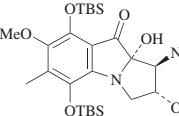
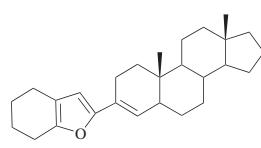
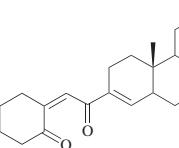
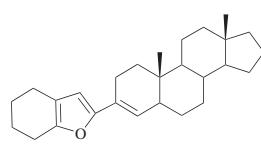
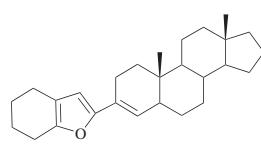
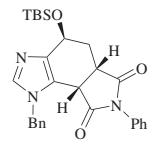
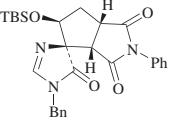
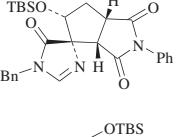
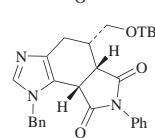
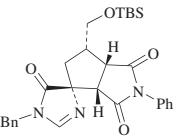
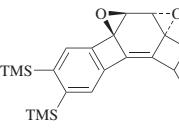
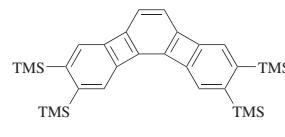
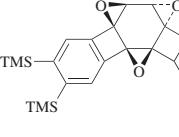
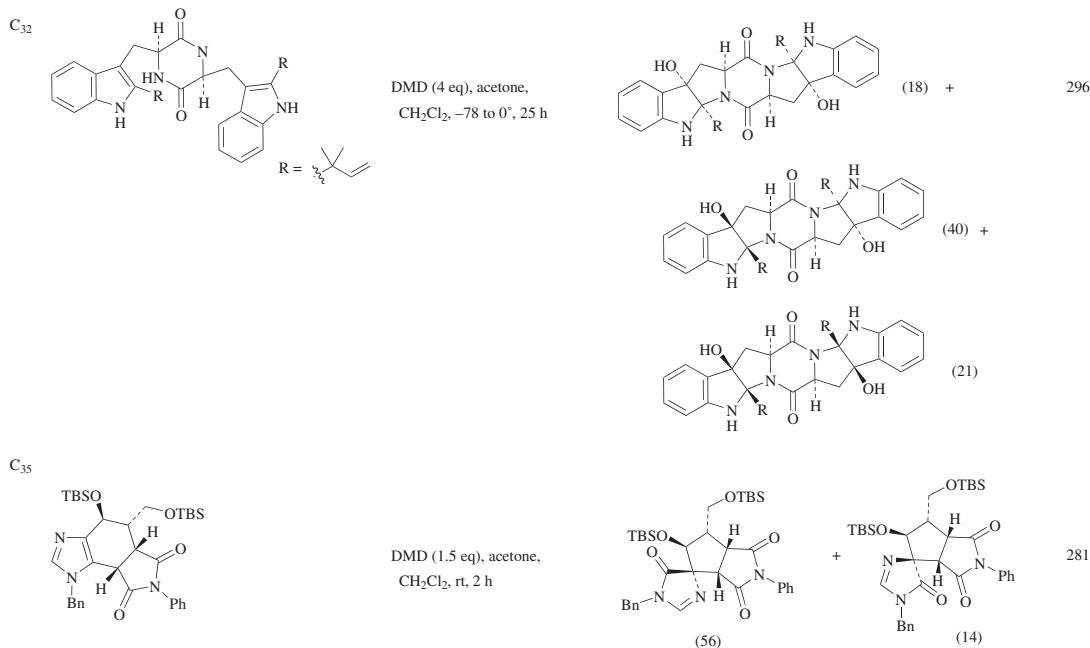
	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , rt, 2 h	 I	(45)	281
		 I (-)		281
	DMD, acetone		(84)	67
	DMD (2.0 eq), acetone, -30 to 0°, 1.5 h		(44)	289
		 Additive — (44) H ₂ O (53)	(53)	289
	DMD, acetone, CH ₂ Cl ₂ , -20°		(56)	289
		 Additive MeOH (56) AcOH (71)	(71)	289
	DMD, acetone, CH ₂ Cl ₂ , -20°	 Additive ClCH ₂ CO ₂ H (66)	(66)	289
		 Additive CF ₃ CO ₂ H (66)	(66)	289
	DMD, acetone, CH ₂ Cl ₂ , -20°		(100)	290

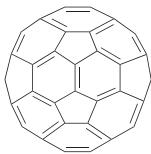
TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , -78°, 2 h	 (82)	281
	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , -78°, 2 h	 (44)	281
	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , rt, 1 h	 (60)	281
	DMD, acetone, rt, 1 h	 (100)	297
	DMD, acetone, rt, 6 h	 (26)	297

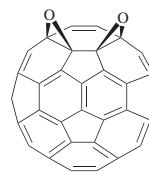
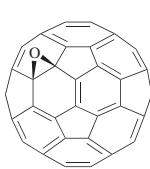
TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C₄₃₋₅₀ 	DMD, acetone, -15°, 0.6 h		301
C₄₃₋₅₃ 	DMD, acetone		301
	R¹ R²	Temp Time	
H Br	-40°	7.5 h	(33-36)
H CF ₃ CO	-30°	36 h	(37)
Bn CHO	-40°	7.5 h	(38)
Bn CO ₂ H	-15°	0.6 h	(30-40)
Bn CH ₂ OAc	-40°	7.5 h	(34)
Bn CF ₃ CO	-30°	20 h	(49)

C₆₀



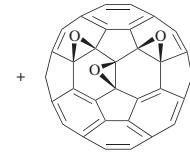
TFD (4 eq), TFP,
1,2-dichlorobenzene,
0°, 6 min



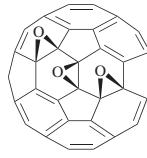
(20) + (21) 72

I

II



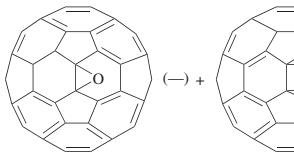
(3.5)



IV

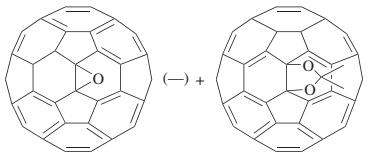
+ isomeric C₆₀O₂ (14.5) + isomeric C₆₀O₃ (10)

TFD (1.2 eq), TFP,
1,2-dichlorobenzene,
0°, 5 min



I (37) + II (8) + isomeric C₆₀O₂ (5.5) 72

DMD, toluene, acetone,
rt, 12 h



(—) + (—) 71

121

TABLE 2B. OXIDATION OF ARENES AND HETEROARENES BY IN SITU GENERATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₁₃₋₁₄		1. (<i>i</i> -Pr) ₃ B, LDA, THF 2. Oxone®, NaOH, acetone, THF, H ₂ O, NaHSO ₃	 R R-C(=O)-C ₆ H ₄ -N(Boc)-C ₆ H ₄ -R	R 5-Me (89) 4-Cl (70) 7-Me (63) 5-Br (62) H (78)
C ₁₅₋₁₆		Oxone®, acetone/H ₂ O (v/v 1:1), NaX, rt	 X X-C(=O)-C ₆ H ₄ -O-C ₆ H ₄ -R	303
122		X (eq) Time	Product	
	H (1) 3 h		6-Br (97)	
	OMe (1) 0.3 h		3',6-Br ₂ (74)	
	H (1) 1 h		6-Cl (85)	
	OMe (4) 0.3 h		3',6-Cl ₂ (55)	
C ₁₆		Oxone®, acetone/H ₂ O (v/v 1:1), NaX, rt		303
	X (eq) Time	I II		
	Br (10) 0.3 h		(97) (—)	
	Br (5) 0.5 h		(—) (98)	
	Cl (4) 6 h		(38) (30)	
	Cl (5) 0.5 h		(—) (98)	
123		Oxone®, acetone/H ₂ O, NaX, rt		303
	Acetone/H ₂ O X (eq) Time	Product		
	5:1 Br (1) 0.5 h		I, 6-Br (19) + 8-Br (79)	
	1:1 Br (1) 0.25 h		II, 5-OMe (58) + II, 5-OH, Br ₂ (36)	
	5:1 Cl (1) 2 h		I, 8-Cl (59) + II, Cl ₂ (16)	
	1:1 Cl (3) 0.25 h		II, Cl ₂ (98)	
123		Oxone®, acetone/H ₂ O (v/v 1:1), NaX (1 eq), rt		303
	Acetone/H ₂ O X Time	Product		
	5:1 Br 45 min		I, 6-Br (98)	
	1:1 Br 45 min		II, Br ₂ (98)	
	1:1 Cl 60 min		I, 6-Cl (30) + 8-Cl (65)	

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₀	NO ₂ ⁻	DMD, acetone, rt, 0.5 h	NO ₃ ⁻ (—)	163
C ₄		DMD, acetone, 0°, 20-30 min	(67)	99
n-BuNH ₂	DMD (x eq), acetone, rt		I (20) ^a II (34) ^a III <5 ^b IV (25)	114
x Additives			II (24) III (36) IV (trace) IV (15)	
5 —			III (16) IV (58) IV (trace) IV (—)	
6 NaHCO ₃				
6 K ₂ CO ₃				
	DMD, acetone, dark, rt, 30 min		III (84)	266
	DMD, acetone, dark, rt, 30 min		(87)	266
t-BuNH	DMD, acetone, dark, rt, 30 min		(90)	266
C ₄₋₅	DMD, acetone, 0°, 20 to 30 min		n 1 (27) 2 (72)	99
C ₄₋₆	DMD, acetone, rt, 18-48 h		R ¹ R ² R ³ R ⁴ H Cl H H (91) Me Cl Me H (81) H Cl Cl H (40)	304
C ₅	DMD, acetone, hexane, rt		I (75)	121
	DMD, acetone, 0°, < 1 h		I (100)	95
	Cyclohexanone dioxirane, cyclohexanone, -20°, 5 min		I (100)	98
	DMD, acetone, 0°, < 1 h		(100)	95
	DMD, acetone, -78°, 30 min		(32)	305
C ₅₋₉	DMD, acetone		R k _{rel} 3-Br 0.104±0.0050 H 3.12±0.12 4-CN 0.0352±0.0035 2-Me 3.12±0.12 3-Me 9.34±0.47 4-Me 10.6±0.53 3,4-Me ₂ 23.0±1.4 3,5-Me ₂ 19.7±1.2 2,6-Me ₂ 0.0415±0.0042 2,4,6-Me ₃ 0.0923±0.0092 1,2-CH=CHCH=CH- 1.08 2,3-CH=CHCH=CH- 5.59±0.28 4-CF ₃ 0.017±0.002 4-OMe 5.36±0.27 4-Ph 1.01±0.06	21, 306

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₅₋₁₂		DMD, acetone, 0°, 20-30 min	R CHO (89) PhCH ₂ O ₂ C (67) 4-AcC ₆ H ₄ (85)	99
C ₆		DMD, acetone, 20°, 1 h	(60)	307
126		DMD, acetone, 20°, 2 h	(98)	307
		DMD, acetone, 20°, 1 h	(98)	307
		DMD, acetone, 20°, 1 h	(100)	308
		DMD, acetone, H ₂ O, rt, 23 h	(82)	101
127		DMD (x eq), acetone, rt	I + II + III + I + II + III + V (—), I:II:III:V = 39:16:trace:39	114
		x	Time	
	3.5	—	—	(40) (21) (trace)
	5	NaHCO ₃	—	(21) (46) (—)
	5	K ₂ CO ₃	—	(25) (33) (—)
	7	CH ₂ Cl ₂	10 min	(20) (48) (—)
	10	—	15 min	(24) (39) (trace)
	10	reverse addition	15 min	10 ^a 50 ^a 40 ^a
	7	—	—	(—) 60 ^a 40 ^a
	7	dark	—	(—) 70 ^a 30 ^a
		DMD (1.2 eq), acetone, -78°, 15 min	V	114
		DMD, acetone, dark, rt, 30 min	III (95) IV	266
		DMD, acetone, rt, 5 h	I + IV (95), I:IV = 60:40	114
		DMD, acetone, rt, 15 min	I + II + III (100), I:II:III = 50:50:trace	114

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₆		DMD, acetone, -45° to rt		100
		DMD, acetone, 0°, 1 h		308
		DMD, acetone, rt, 1 h	 I + II (—), I:II = 90:10	114
128		DMD, acetone, H ₂ O, rt, 30 min	I + II (—), I:II = 26:53	114
	H ₂ N—(CH ₂) ₆ —NH ₂	DMD, acetone, H ₂ O, rt, 24 h	O ₂ N—(CH ₂) ₆ —NO ₂ (20)	101
		DMD, acetone, 0°, 1 h		308
	HCl•H ₂ N—(CH ₂) ₆ —NH ₂ •HCl	DMD, acetone, H ₂ O, rt, 23 h	O ₂ N—(CH ₂) ₆ —NO ₂ (60)	101
C ₆₋₇		DMD, acetone, dark, 22°		101, 266

R ¹	R ²	R ³	R ⁴	R ⁵	Time	
H	H	Cl	H	H	30 min	(97)
Cl	H	Cl	H	Cl	10 h	(98)
F	H	H	H	F	10 h	(96)
H	H	H	H	H	30 min	(97)
NH ₂	H	H	H	H	6 h	(85)
NO ₂	H	H	H	H	6 h	(65)
H	NO ₂	H	H	H	30 min	(97)
H	H	NO ₂	H	H	30 min	(98)
H	NO ₂	H	NO ₂	H	overnight	(94)
H	H	Me	H	H	30 min	(98)
H	H	CF ₃	H	H	2 h	(93)
H	H	CN	H	H	30 min	(90)
H	H	CO ₂ H	H	H	30 min	(95)
H	H	MeO	H	H	30 min	(94)
H	H	Ac	H	H	30 min	(95)

129

C ₇		Cyclohexanone dioxirane, acetone, cyclohexanone, CH ₂ Cl ₂ , -10°, 20 min		98
		DMD, acetone, 0°, < 1 h		95
		DMD, acetone, 0°, < 1 h		95

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₇		DMD, acetone, 0°, 5 min		(57) 309	
		DMD (6 eq), acetone, rt		Additives — (60) — NaHCO ₃ (69) 9:1 K ₂ CO ₃ (65) 8:1	114
		DMD, acetone		(—) 21	
130		DMD, acetone		(—) 21	
		DMD, acetone		I + II (—), I:II = 17:83 21	
130		DMD (x eq), acetone, rt		I + II + III + IV (—), I:II:III:IV = 44:30:26 114	
		DMD (x eq), acetone, rt		I + II + III + IV (—), I:II:III:IV = 44:30:26 114	
C ₇₋₁₅		x Additives		I (20) II (5) III < 5 ^b IV (28)	
		5 —		(20)	
		6 NaHCO ₃		(5)	
C ₇₋₁₅		7 K ₂ CO ₃		< 5 ^b	
		DMD, acetone, rt, 34 min		(28)	
		1. DMD, acetone, H ₂ O, 21°, 3 min 2. rt, 7 h		(81) 101	
131		DMD, acetone, rt, 15 min		(58) 101	
		DMD, acetone, rt, 15 min		I + II + III (—), I:II:III = 44:30:26 114	
C ₇₋₁₅		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		R x Time	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		Me 2.0 24 h (90)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		CH ₂ CN 3.0 60 h (40)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		Et 2.0 24 h (74)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		CH ₂ CCH 3.0 60 h (35)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		n-Pr 2.0 24 h (76)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		CH ₂ CO ₂ Et 3.0 36 h (68)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		n-C ₆ H ₁₃ 2.0 34 h (81)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		Bz 2.0 48 h (0)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		Bn 3.0 60 h (92)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		CH ₂ OPh 3.0 36 h (91)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		CH ₂ CH ₂ Ph 2.2 48 h (92)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		CH(Me)Ph 2.0 48 h (73)	310
		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		n-C ₉ H ₁₉ 3.0 48 h (90)	310

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																							
C ₈		DMD, acetone		21																																																																							
		DMD, acetone		149																																																																							
		DMD, acetone, CH ₂ Cl ₂ , rt, 48 h		101																																																																							
132		DMD, acetone, 0°, < 1 h		95																																																																							
		DMD, acetone, 0°, < 1 h		95																																																																							
		DMD, acetone, 0°, 10 min		96																																																																							
C ₈₋₉		DMD, acetone, 0°, 20-30 min	 n 1 (54) 2 (83)	99																																																																							
		TFD, CH ₂ Cl ₂ , TFP, 0°, 20 min	 R Cl (74) H (68) Me (90) MeO (73)	311																																																																							
		DMD, acetone, 0-5°, dark	 R = Cl, NO ₂ , H, MeO	25																																																																							
C ₈₋₁₁		DMD (1.2 eq), acetone, CH ₂ Cl ₂ , rt, 8 h	 I + II R ² R ¹ R ² R ¹	312																																																																							
133	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>n</th> </tr> </thead> <tbody> <tr> <td>OH</td> <td>NH₂</td> <td>3</td> </tr> <tr> <td>OH</td> <td>NH₂</td> <td>3</td> </tr> <tr> <td>OH</td> <td>H</td> <td>3</td> </tr> <tr> <td>OH</td> <td>NH₂</td> <td>2</td> </tr> <tr> <td>OH</td> <td>NH₂</td> <td>2</td> </tr> <tr> <td>OH</td> <td>NH₂</td> <td>4</td> </tr> <tr> <td>OH</td> <td>NH₂</td> <td>4</td> </tr> <tr> <td>Me</td> <td>NH₂</td> <td>4</td> </tr> <tr> <td>Me</td> <td>NH₂</td> <td>4</td> </tr> <tr> <td>OAc</td> <td>NH₂</td> <td>3</td> </tr> <tr> <td>OAc</td> <td>NH₂</td> <td>3</td> </tr> </tbody> </table> <p style="text-align: center;"> Catalyst A: R³ = OMe, R⁴ = Cl Catalyst B: R³ = Cl, R⁴ = H </p>	R ¹	R ²	n	OH	NH ₂	3	OH	NH ₂	3	OH	H	3	OH	NH ₂	2	OH	NH ₂	2	OH	NH ₂	4	OH	NH ₂	4	Me	NH ₂	4	Me	NH ₂	4	OAc	NH ₂	3	OAc	NH ₂	3	<table border="1"> <thead> <tr> <th>Catalyst</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>(—)</td> <td>(98)</td> </tr> <tr> <td>B</td> <td>(93)</td> <td>(—)</td> </tr> <tr> <td>A</td> <td>(98)</td> <td>(—)</td> </tr> <tr> <td>A</td> <td>(92)</td> <td>(—)</td> </tr> <tr> <td>B</td> <td>(94)</td> <td>(—)</td> </tr> <tr> <td>B</td> <td>(95)</td> <td>(—)</td> </tr> <tr> <td>A</td> <td>(15)</td> <td>(30)</td> </tr> <tr> <td>A</td> <td>(95)</td> <td>(—)</td> </tr> <tr> <td>B</td> <td>(97)</td> <td>(—)</td> </tr> <tr> <td>A</td> <td>(91)</td> <td>(—)</td> </tr> <tr> <td>B</td> <td>(93)</td> <td>(—)</td> </tr> </tbody> </table>	Catalyst	I	II	A	(—)	(98)	B	(93)	(—)	A	(98)	(—)	A	(92)	(—)	B	(94)	(—)	B	(95)	(—)	A	(15)	(30)	A	(95)	(—)	B	(97)	(—)	A	(91)	(—)	B	(93)	(—)	
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TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

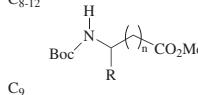
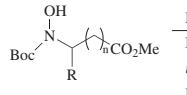
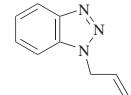
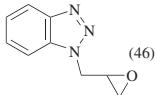
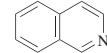
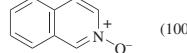
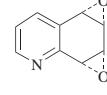
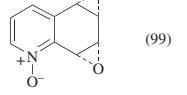
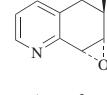
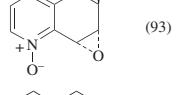
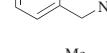
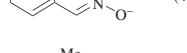
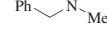
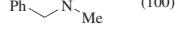
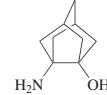
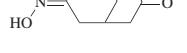
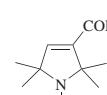
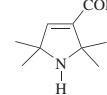
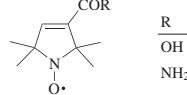
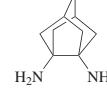
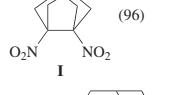
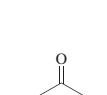
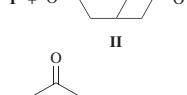
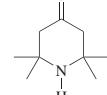
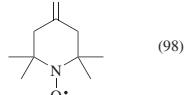
	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
		TFD (x eq), TFP, CH2Cl2, -20 to 0°	 R H 0 2.0 5 h (82) i-Pr 0 3.1 6 h (75) H 4 2.0 8 h (74)	313
		DMD (1.5 eq), acetone, CH2Cl2, 0°, 24 h; rt, 12 h	 (28) + 	310
134		DMD, acetone, 0°, < 1 h	 (100)	95
		DMD, acetone, 10°, 3 h	 (99)	314
		DMD, acetone, 10°, 3 h	 (93)	314
		DMD, acetone, 0°, 20-30 min	 (48)	99
		DMD, acetone, 0°, < 1 h	 (100)	95
135		1. DMD (3 eq), acetone, CH2Cl2, -25° 2. rt, 12-15 h	 (92)	315
		1. DMD (7 eq), acetone, CH2Cl2, -25° 2. rt, 12 to 15 h	 (100)	315
		DMD (2 eq), acetone, 0°, 30 min	 $\frac{R}{OH}$ (94) NH_2 (98)	97
		1. DMD (6 eq), acetone, CH2Cl2, -25° 2. rt, 12 to 15 h	 (100)	315
		1. DMD (10 eq), acetone, CH2Cl2, -25° 2. rt, 12 to 15 h	 I (96)	315
		1. DMD (20 eq), acetone, CH2Cl2, -25° 2. rt, 12 to 15 h	 I + II (100), I : II = 80:20	315
		DMD (2 eq), acetone, 0°, 30 min	 (98)	97

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

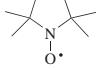
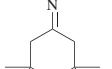
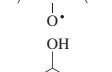
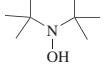
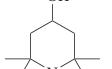
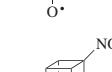
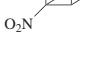
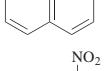
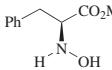
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, 0°, 2 h	 (—)	96
	DMD (2 eq), acetone, 0°, 30 min	 (100)	97
	DMD (2 eq), acetone, 0°, 30 min	 (99)	97
	DMD, acetone, 0°, 2 h	 (99)	96
	DMD (2 eq), acetone, 0°, 30 min	 (100)	97
	DMD, acetone, H2O, dark, N2, rt, 1.5 h	 (85)	316
	DMD, acetone, dark, 22°	 (42) +  (20)	101
	DMD, acetone, H2O, rt, 4 h	 (91)	101
	DMD, acetone, -45° to rt	 (54)	100
	DMD, acetone	 (—)	21
	DMD, acetone	 (—)	317
	DMD, acetone	 (—)	317
	DMD, acetone	 (—)	318

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

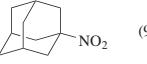
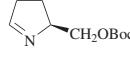
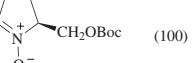
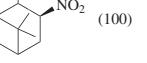
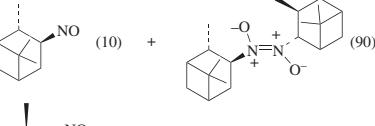
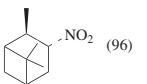
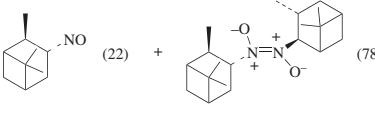
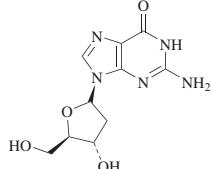
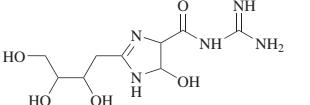
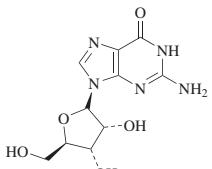
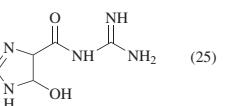
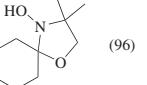
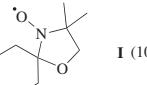
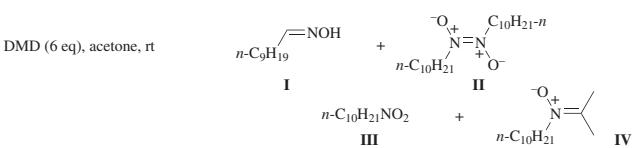
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
		DMD, acetone, dark, rt, 30 min	 (95)	266																				
		TFD (1.2 eq), TFP, CH2Cl2, -78°, 1 h	 (100)	319																				
		DMD, acetone, CH2Cl2, rt, 1 h	 (100)	22																				
		DMD (insufficient amount), acetone, CH2Cl2, rt, 35 min		22																				
138		DMD, acetone, CH2Cl2, rt, 1 h	 (96)	22																				
		DMD (insufficient amount), acetone, CH2Cl2, rt, 35 min		22																				
		DMD (2.5 eq), acetone, 90°, 5 h	 (35)	320																				
		DMD (2.5 eq), acetone, 90°, 5 h	 (25)	320																				
		DMD, acetone, 0°, 2 h	 (96)	96																				
		DMD (2 eq), acetone, 0°, 30 min	 I (100)	97																				
139		Cyclohexanone dioxirane, acetone, cyclohexanone, 20°, 10 min	I (88)	98																				
		Acetone, cyclohexanone, -20°, 10 min	I (88)	98																				
	<i>n</i> -C10H21NH2	DMD (6 eq), acetone, rt		114																				
			<table border="1"> <thead> <tr> <th>Additives</th> <th>I</th> <th>II</th> <th>III</th> <th>IV</th> </tr> </thead> <tbody> <tr> <td>—</td> <td>(51)</td> <td>(18)</td> <td>(8)</td> <td>(3)</td> </tr> <tr> <td>NaHCO3</td> <td>(43)</td> <td>(13)</td> <td>(trace)</td> <td>(17)</td> </tr> <tr> <td>K2CO3</td> <td>(73)</td> <td>(18)</td> <td>(trace)</td> <td>(—)</td> </tr> </tbody> </table>	Additives	I	II	III	IV	—	(51)	(18)	(8)	(3)	NaHCO3	(43)	(13)	(trace)	(17)	K2CO3	(73)	(18)	(trace)	(—)	
Additives	I	II	III	IV																				
—	(51)	(18)	(8)	(3)																				
NaHCO3	(43)	(13)	(trace)	(17)																				
K2CO3	(73)	(18)	(trace)	(—)																				

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																	
C ₁₀₋₂₃		DMD, acetone, 0°, 30 min		321																	
	$\begin{array}{ccc} x & y & R \\ \hline 0 & 2 & \text{Me} \\ 1 & 3 & \text{Me} \\ 6 & 3 & \text{Me} \\ 6 & 3 & [(\text{CH}_2)_2\text{O}]_3\text{Me} \end{array}$																				
C ₁₁		DMD, acetone, 0°, 10 min		322																	
		DMD, acetone, 0°, < 1 h		95																	
		DMD, acetone, CH ₂ Cl ₂ , 0°, 2 h	 <table style="margin-left: auto; margin-right: auto;"> <tr> <td style="text-align: center;">I</td> <td style="text-align: center;">II</td> </tr> <tr> <td style="text-align: center;">R</td> <td style="text-align: center;">I</td> <td style="text-align: center;">II</td> </tr> <tr> <td style="text-align: center;">Br</td> <td style="text-align: center;">(17)</td> <td style="text-align: center;">(56)</td> </tr> <tr> <td style="text-align: center;">Cl</td> <td style="text-align: center;">(15)</td> <td style="text-align: center;">(47)</td> </tr> <tr> <td style="text-align: center;">NO₂</td> <td style="text-align: center;">(23)</td> <td style="text-align: center;">(31)</td> </tr> <tr> <td style="text-align: center;">H</td> <td style="text-align: center;">(12)</td> <td style="text-align: center;">(36)</td> </tr> </table>	I	II	R	I	II	Br	(17)	(56)	Cl	(15)	(47)	NO ₂	(23)	(31)	H	(12)	(36)	102
I	II																				
R	I	II																			
Br	(17)	(56)																			
Cl	(15)	(47)																			
NO ₂	(23)	(31)																			
H	(12)	(36)																			
I+		DMD, acetone, -78°		24																	
		DMD, acetone, rt		323																	
		DMD, acetone, 0°, 10 min		96																	
		DMD, acetone, 0°, 15 min		96																	
		DMD, acetone, 0°, 2 h		96																	
		DMD, acetone		324																	

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.	
C ₁₁₋₁₇ 142		DMD, acetone, 0°, 10 min		R ¹ R ² Cl t-Bu (99) F t-Bu (99) NO ₂ t-Bu (95) H t-Bu (96) CF ₃ t-Bu (98) Me t-Bu (99) MeO t-Bu (98) t-Bu t-Bu (99) Cl Ph (96) H Ph (98) H Bn (96) H 1-Ad (99)	309
C ₁₂		DMD, acetone, H ₂ O, overnight		(>30)	325
		DMD, acetone		(-)	21
		DMD, acetone		(-)	21
		DMD, acetone, dark, rt, 30 min		(96)	266
143		DMD, acetone, 0°, < 1 h		(100)	95
		DMD, acetone, 0°, < 1 h		(100)	95
		DMD, acetone, CH ₂ Cl ₂ , CDCl ₃ , -78°		(-)	95
		DMD, acetone, -78°		(66)	24
		DMD, acetone, -78°		(96)	24
		O ₂ O-, MeCOEt, -78°		(-)	24
		DMD, acetone, -45° to rt		(70)	100

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂		DMD, acetone, rt, 6 h	I (—) + (—) I:II = 90:10	114
		DMD, acetone, 0°, 10 min	(82)	96
		TFD (5 eq), TFP, CH ₂ Cl ₂ , -20 to 0°, 6 h	(57) + (21)	313
C ₁₃		DMD, acetone, 0°, < 1 h	(100)	95
		DMD, acetone, CH ₂ Cl ₂ , 0°, 2 h	(90) + (2)	102
		DMD, acetone, 0°, < 1 h	(100)	95
		DMD, acetone, CH ₂ Cl ₂ , 0°, 2 h	(39)	102
C ₁₃₋₁₆		DMD, acetone, -45° to rt	(76)	100
		DMD, acetone, CH ₂ Cl ₂ , 0°, 2 h	 I: R = Me (71), t-Bu (65) II: R = Me (28), t-Bu (30)	102
		DMD (1.2 eq), acetone, CH ₂ Cl ₂ , rt, 8 h	 I: R ¹ = NH ⁺ R ¹ II: R ¹ = NH ⁺ R ¹	312
C ₁₅		Catalyst A: R ⁵ = OMe, R ⁶ = Cl Catalyst B: R ⁵ = Cl, R ⁶ = H	 A: Ar = R ⁵ -C ₆ H ₃ -R ⁶ B: Ar = R ⁵ -C ₆ H ₃ -R ⁶	
		Catalyst A: R ⁵ = OMe, R ⁶ = Cl Catalyst B: R ⁵ = Cl, R ⁶ = H	 A: Ar = R ⁵ -C ₆ H ₃ -R ⁶ B: Ar = R ⁵ -C ₆ H ₃ -R ⁶	
		Catalyst A: R ⁵ = OMe, R ⁶ = Cl Catalyst B: R ⁵ = Cl, R ⁶ = H	 A: Ar = R ⁵ -C ₆ H ₃ -R ⁶ B: Ar = R ⁵ -C ₆ H ₃ -R ⁶	
		Catalyst A: R ⁵ = OMe, R ⁶ = Cl Catalyst B: R ⁵ = Cl, R ⁶ = H	 A: Ar = R ⁵ -C ₆ H ₃ -R ⁶ B: Ar = R ⁵ -C ₆ H ₃ -R ⁶	
		Catalyst A: R ⁵ = OMe, R ⁶ = Cl Catalyst B: R ⁵ = Cl, R ⁶ = H	 A: Ar = R ⁵ -C ₆ H ₃ -R ⁶ B: Ar = R ⁵ -C ₆ H ₃ -R ⁶	
		Catalyst A: R ⁵ = OMe, R ⁶ = Cl Catalyst B: R ⁵ = Cl, R ⁶ = H	 A: Ar = R ⁵ -C ₆ H ₃ -R ⁶ B: Ar = R ⁵ -C ₆ H ₃ -R ⁶	
		Catalyst A: R ⁵ = OMe, R ⁶ = Cl Catalyst B: R ⁵ = Cl, R ⁶ = H	 A: Ar = R ⁵ -C ₆ H ₃ -R ⁶ B: Ar = R ⁵ -C ₆ H ₃ -R ⁶	

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

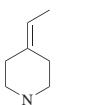
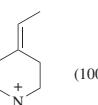
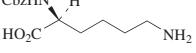
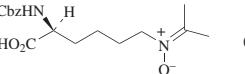
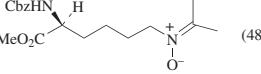
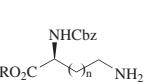
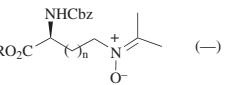
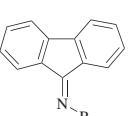
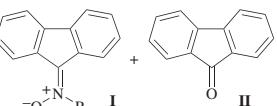
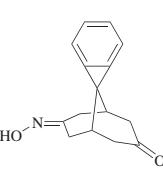
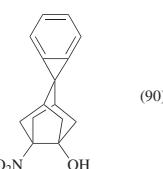
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₁₄		DMD, acetone, 0°, 15 min	 (98)	96	
		Cyclohexanone dioxirane, cyclohexanone, 20°, 5 min	I (68) +  (24)	98	
		Cyclohexanone dioxirane (2 eq), cyclohexanone, 20°, 5 min	II (65)	98	
14		DMD, acetone, 0°, < 1 h	 (100)	95	
		DMD, acetone, 0°, < 1 h	 (100)	95	
		DMD, acetone, 0°, < 1 h	 (100)	95	
		1. SOCl ₂ , MeOH 2. DMD, acetone, -78°	 (48)	326	
		1. SOCl ₂ , MeOH, -5° to rt, overnight 2. NaHCO ₃ , rt 3. DMD, acetone, -78°, 5-10 min	 (48)	327	
C ₁₄₋₁₈		n R 2 Me 3 t-Bu 3 t-Bu	DMD, acetone	 (—)	328
C ₁₄₋₁₉			DMD, acetone, CH ₂ Cl ₂ , 0°, 2 h		102
R I II	Me (91) (5) Et (92) (9) i-Pr (31) (12) t-Bu (4) (14) Ph (43) (—)				
C ₁₅		1. DMD (7 eq), acetone, CH ₂ Cl ₂ , -25° 2. rt, 12-15 h	 (90)	316	
		1. DMD (3 eq), acetone, CH ₂ Cl ₂ , -25° 2. rt, 12-15 h	 (86)	316	
		1. DMD (10 eq), acetone, CH ₂ Cl ₂ , -25° 2. rt, 12-15 h	 (100)	316	
		1. DMD (6 eq), acetone, CH ₂ Cl ₂ , -25° 2. rt, 12-15 h	 (95)	316	
		1. DMD (20 eq), acetone, CH ₂ Cl ₂ , -25° 2. rt, 12-15 h	 (100)	316	

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₁₅		DMD, acetone, 0°, < 1 h		(—)	95
		1. DMD (3 eq), acetone, CH ₂ Cl ₂ , -25° 2. rt, 12-15 h		(100)	316
		1. DMD (6 eq), acetone, CH ₂ Cl ₂ , -25° 2. rt, 12-15 h		(100)	316
		1. DMD (12 eq), acetone, CH ₂ Cl ₂ , -25° 2. rt, 12-15 h		(96)	316
C ₁₆		DMD, acetone, -45° to rt		(—)	100
C ₁₇		DMD, acetone, CH ₂ Cl ₂ , rt		(94)	329
		DMD, acetone, CH ₂ Cl ₂ , rt		I + II (—), I:II = 3.9:1	329
C ₁₈		DMD, acetone, -78°, 10 min		(—)	326
C ₁₉		DMD, CH ₂ Cl ₂ , acetone, -60 to 20°		(—)	330
		1. DMD, CH ₂ Cl ₂ , acetone, 4-5° 2. CF ₃ CO ₂ H or BF ₃ •Et ₂ O		(—)	330

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₂₀		DMD, acetone		331
150		DMD, acetone, -78°		95
		DMD, acetone, 0°, < 1 h	PhCHO (31) +	95
		DMD, acetone, -45° to rt		100
		DMD, acetone, -45° to rt		332
151		1. DMD, acetone, MeOH, rt, overnight 2. Ac ₂ O, pyridine, rt, overnight		333
		DMD, CH ₂ Cl ₂ , acetone, 4-5°		330
C ₂₃		1. DMD, CH ₂ Cl ₂ , acetone, 4-5° 2. CF ₃ CO ₂ H or BF ₃ •Et ₂ O		330
		DMD, acetone, 0°, 20 min		334

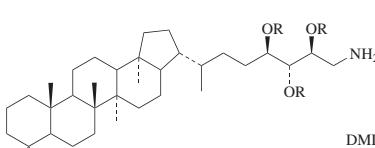
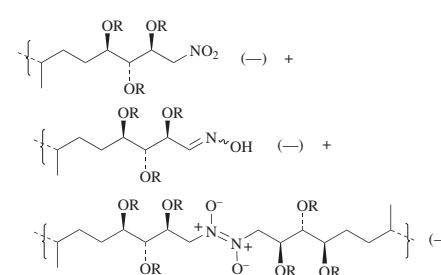
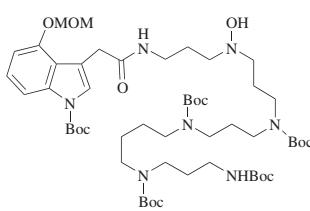
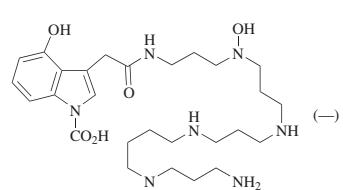
TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	C ₂₃	DMD, acetone, 0° to rt, 4 h	Boc ₂ N—C ₂ O ₂ —N(Boc) ₂ (81)	335
	C ₂₄	DMD, acetone, 0° to rt, 70 min	H ₂ N—C ₂ O ₂ —N(Cbz) ₂ (46)	335
152	C ₂₆	DMD, acetone, MeOH, 30 min	CH ₂ NH ₂ •HCl HO—C ₂ O ₂ —N(Cbz) ₂ (71)	336
	Ph ₃ P=N— 5-(4-chlorophenyl)- 1,2-dioxazoles	DMD, acetone	O ₂ N— 5-(4-chlorophenyl)- 1,2-dioxazoles (—) + Ph ₃ PO (—)	149
	MOMO MeO ₂ C PMB	TFD, CH ₂ Cl ₂ , -22°	MOMO MeO ₂ C PMB (—)	337
	C ₂₇	DMD, acetone, -45° to rt	Ac O ⁺ OH (—)	100
	R = rhamnopyranosyl (2-L)	DMD, acetone, MeOH, rt, overnight	NO ₂ (21)	333
153	R = rhamnopyranosyl (2-L)	DMD, acetone/MeOH, rt, overnight	NO ₂ (36)	333
	AcOCH ₂ AcOCH ₂ CH ₂ OAc	DMD, acetone, overnight	CH ₂ OAc CO ₂ H AcOCH ₂ (—)	325
	C ₂₉	DMD, acetone, -45° to rt	PMBO PhthN MeO HO HN (80)	100

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

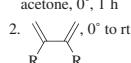
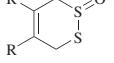
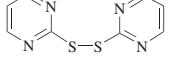
	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₃₁		DMD, acetone, 0°, 2 h	 (97)	96
C ₃₂		DMD, CH ₂ Cl ₂ , sat K ₂ CO ₃ , 0° to rt, 7 h	 I	337
			 II	337
C ₃₄		DMD, CH ₂ Cl ₂ , sat NaHCO ₃ , 0° to rt	I:II = 1:1	337
		DMD, acetone, -20°	 (65)	338
C ₃₈		DMD, acetone, -78° to rt, 24 h	 (83)	339
C ₃₉		DMD, acetone, CH ₂ Cl ₂ , rt, 15 min	 (42)	333
C ₄₅		DMD, acetone, HCl, Ar, 1 h	 (73)	340
C ₄₇		1. DMD, acetone, N ₂ , 0°, 15 min 2. NaCNBH ₃ , AcOH, rt, 2 h	 (33)	340

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅₀	 <p>R = DMIPS</p>	DMD, acetone, CH ₂ Cl ₂ , 20°, 2.5 h	 <p>(—) + (—) + (—)</p>	341
I56		DMD, acetone, HCl, Ar, 1 h	 <p>(—)</p>	340

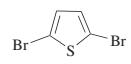
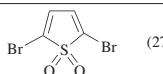
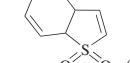
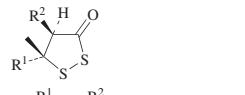
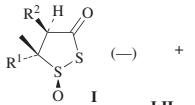
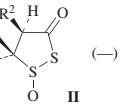
^aThe two products were obtained as a mixture.^bThis value is the ratio of this compound in the crude products.

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₀	³⁴ S ₈	DMD, acetone, CH ₂ Cl ₂ , 0°, 1 h	³⁴ S ₂ O (—)	342
S ₈		1. DMD, CH ₂ Cl ₂ , benzene, acetone, 0°, 1 h 2. 	 R Me (33) Ph (27)	343
C ₂₋₅		DMD, CH ₂ Cl ₂ , benzene, acetone, 0°, 1 h	S ₂ O (—)	343
RSH		1. DMD, acetone, CH ₂ Cl ₂ , N ₂ , -40°, 1 h 2. Air	RSO ₂ H Et (73) n-Pr (74) i-Pr (90) n-Bu (84) t-Bu (95) n-C ₅ H ₁₁ (96)	115
C ₃		DMD, acetone, MeOH, rt	 (81)	142
C ₄		DMD, acetone, MeOH, rt	 (53) +  (15)	142
C ₄		DMD, acetone, CH ₂ Cl ₂ , EtOH, rt	 (53)	143
		DMD, acetone, CH ₂ Cl ₂ , rt	 (77)	143

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TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄		DMD, acetone, several days	 (27)	344
		DMD, acetone, temp 1; solvent removal, temp 2 Temp 1 Time Temp 2 -18° 2 h <-15° -25° 36 h <-25° -25° 6 h <-40°	 I (—) +  II (—) I:II 88:12 91:9 100:0	141, 345, 346,
C ₄₋₁₃		DMD, acetone, CH ₂ Cl ₂ , -78°	 I (—) +  II (—) I:II 2:1 8:1 18:1 5:1 2:1 15:1 8:1	137

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<p>C₄₋₃₀</p>	DMD, acetone, CH ₂ Cl ₂ , rt		<table border="1" style="border-collapse: collapse; text-align: center;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th></th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>H</td> <td>H</td> <td>Br</td> <td>(27)</td> </tr> <tr> <td>Et</td> <td>H</td> <td>H</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>Me</td> <td>(93)</td> </tr> <tr> <td>Et</td> <td>H</td> <td>H</td> <td>Ac</td> <td>(53)</td> </tr> <tr> <td>Bn</td> <td>H</td> <td>H</td> <td>Bn</td> <td>(93)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>Ph</td> <td>Ph</td> <td>(99)</td> </tr> <tr> <td>PhCO</td> <td>Ph</td> <td>Ph</td> <td>Bz</td> <td>(76)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴		Br	H	H	Br	(27)	Et	H	H	H	(—)	Me	H	H	Me	(93)	Et	H	H	Ac	(53)	Bn	H	H	Bn	(93)	Ph	Ph	Ph	Ph	(99)	PhCO	Ph	Ph	Bz	(76)	138
R ¹	R ²	R ³	R ⁴																																									
Br	H	H	Br	(27)																																								
Et	H	H	H	(—)																																								
Me	H	H	Me	(93)																																								
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PhCO	Ph	Ph	Bz	(76)																																								
<p>C₅₋₉</p>	DMD, acetone, CH ₂ Cl ₂ , rt		<table border="1" style="border-collapse: collapse; text-align: center;"> <thead> <tr> <th>R</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(55)</td> <td>(32)</td> </tr> <tr> <td>i-Bu</td> <td>(40)</td> <td>(37)</td> </tr> </tbody> </table>	R	I	II	H	(55)	(32)	i-Bu	(40)	(37)	143																															
R	I	II																																										
H	(55)	(32)																																										
i-Bu	(40)	(37)																																										
<p>C₅₋₁₉</p>	DMD, acetone, rt		<table border="1" style="border-collapse: collapse; text-align: center;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Et</td> <td>Ac</td> <td>2 h (86)</td> </tr> <tr> <td>Me</td> <td>Et</td> <td>Ts</td> <td>4 h (86)</td> </tr> <tr> <td>Me</td> <td>4-ClC₆H₄</td> <td>Ts</td> <td>6 h (49)</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>Ts</td> <td>6 h (72)</td> </tr> <tr> <td>Me</td> <td>4-MeC₆H₄</td> <td>Ts</td> <td>6 h (77)</td> </tr> <tr> <td>Me</td> <td>4-MeOC₆H₄</td> <td>Ts</td> <td>6 h (86)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>Ts</td> <td>6 h (64)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Time	Me	Et	Ac	2 h (86)	Me	Et	Ts	4 h (86)	Me	4-ClC ₆ H ₄	Ts	6 h (49)	Me	Ph	Ts	6 h (72)	Me	4-MeC ₆ H ₄	Ts	6 h (77)	Me	4-MeOC ₆ H ₄	Ts	6 h (86)	Ph	Ph	Ts	6 h (64)	148								
R ¹	R ²	R ³	Time																																									
Me	Et	Ac	2 h (86)																																									
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Me	4-MeOC ₆ H ₄	Ts	6 h (86)																																									
Ph	Ph	Ts	6 h (64)																																									
<p>C₇</p>	DMD (1-2 eq), acetone, rt		(—)	347																																								
	DMD (4 eq), acetone, rt, 2-4 h			(100)	347																																							

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
<p>C₇</p>	TFD, vigorous conditions		(—) +	348												
	DMD, acetone		<table border="1" style="border-collapse: collapse; text-align: center;"> <thead> <tr> <th>R</th> <th>k_R/k_H</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>0.7185</td> </tr> <tr> <td>NO₂</td> <td>0.2762</td> </tr> <tr> <td>H</td> <td>1.0000</td> </tr> <tr> <td>Me</td> <td>1.337</td> </tr> <tr> <td>MeO</td> <td>1.857</td> </tr> </tbody> </table>	R	k _R /k _H	Cl	0.7185	NO ₂	0.2762	H	1.0000	Me	1.337	MeO	1.857	349
R	k _R /k _H															
Cl	0.7185															
NO ₂	0.2762															
H	1.0000															
Me	1.337															
MeO	1.857															
<p>I</p>	DMD, acetone, rt		(65)	121												
<p>II</p>	DMD, CDCl ₃ , minutes		(—)	156, 157												
<p>III</p>	TFD, solvent, 0°		+ (—)	348												
<p>IV</p>	TFD, Solvent		IV : II : III = 42:12:46 IV : III : II = 3.8 IV : II : III = 93:3:4 IV : III : II = 1.3 IV : II : III = 68:9:23 IV : III : II = 2.6 IV : II : III = 71:8:21 IV : III : II = 2.6 IV : II : III = 68:9:23 IV : III : II = 2.6 IV : II : III = 66:18:16 IV : III : II = 0.9	1:1 CH ₂ Cl ₂ 10:1 CH ₂ Cl ₂ 2:1 CH ₂ Cl ₂ 2:1 CH ₂ Cl ₂ /acetone (1:19) 2:1 CH ₂ Cl ₂ /CH ₃ CN (1:19) 2:1 CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:7)												

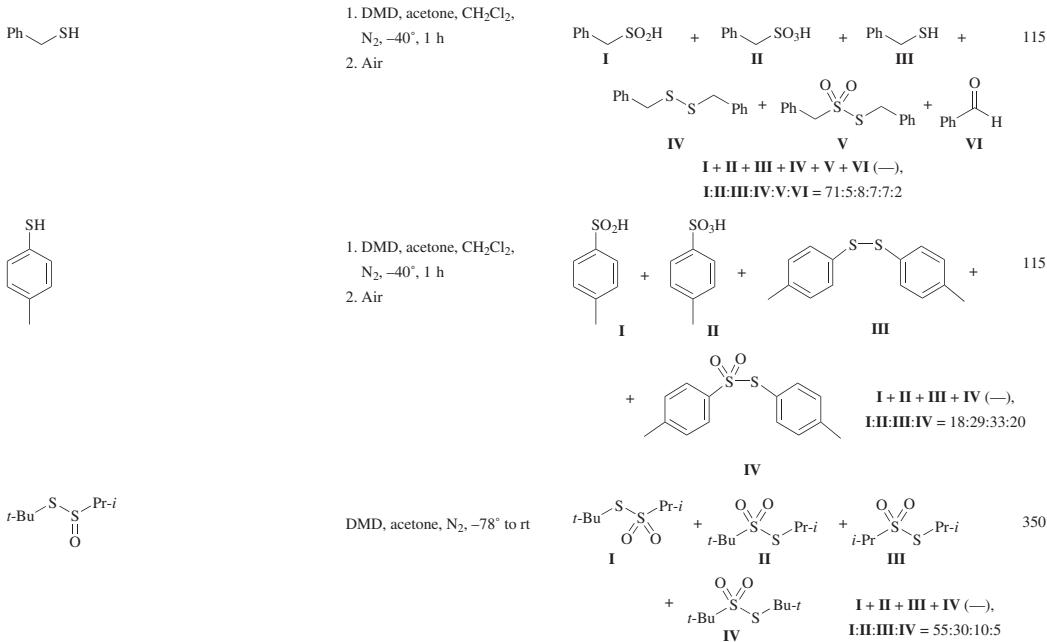


TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (<i>Continued</i>)																				
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																
C ₇		DMD (1.5 eq), CH ₂ Cl ₂ , -50 to 30°, 5 h	 (48) (trace) (trace)	351																
		DMD (2.2 eq), CH ₂ Cl ₂ , 0°, 3 h	I (88)	351																
C ₇₋₈		DMD, CH ₂ Cl ₂ , 0°		351																
		DMD, acetone		(—)	<table> <tr> <td>R</td> <td>k_R/k_H</td> </tr> <tr> <td>Br</td> <td>0.6356</td> </tr> <tr> <td>Cl</td> <td>0.6598</td> </tr> <tr> <td>NO₂</td> <td>0.2093</td> </tr> <tr> <td>H</td> <td>1.0000</td> </tr> <tr> <td>Me</td> <td>1.237</td> </tr> <tr> <td>MeO</td> <td>1.548</td> </tr> </table>	R	k_R/k_H	Br	0.6356	Cl	0.6598	NO ₂	0.2093	H	1.0000	Me	1.237	MeO	1.548	349
R	k_R/k_H																			
Br	0.6356																			
Cl	0.6598																			
NO ₂	0.2093																			
H	1.0000																			
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MeO	1.548																			

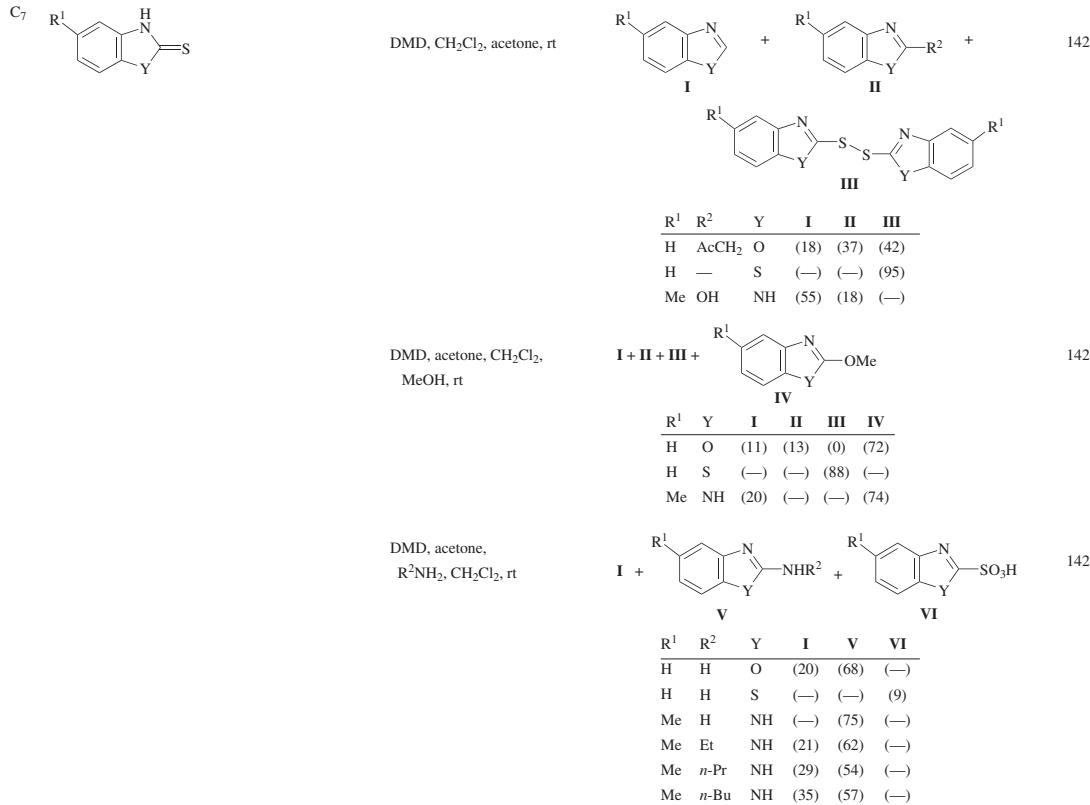


TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)						Refs.
C ₇₋₁₃ R ¹ 'S~R ²	TFD (x eq), TFP, 0°	R ¹ 'S~R ²	I	O=S	R ¹ 'S~R ²	II		352
—ArN(Me)Ar— =	Solvent	R ¹	R ²	x	% Conv.	I	II	II:I
CH ₂ Cl ₂	Ph	Me	0.5	31	(27)	(73)	2.7	
CCl ₄	Ph	Me	0.5	25	(20)	(80)	4.0	
CH ₂ Cl ₂ /acetone (1:19)	Ph	Me	0.5	29	(28)	(72)	2.6	
CH ₂ Cl ₂ /MeCN (1:19)	Ph	Me	0.5	32	(28)	(72)	2.6	
CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:19)	Ph	Me	0.5	34	(53)	(47)	0.9	
CH ₂ Cl ₂ /CF ₃ CO ₂ H (2 eq)	Ph	Me	0.5	40	(50)	(50)	1.0	
CH ₂ Cl ₂ /CF ₃ CO ₂ H (10 eq)	Ph	Me	0.5	41	(66)	(34)	0.53	
CH ₂ Cl ₂ /CF ₃ CO ₂ H (20 eq)	Ph	Me	0.5	53	(73)	(27)	0.36	
CH ₂ Cl ₂ /CF ₃ CO ₂ H (1:19)	Ph	Me	0.5	46	(100)	(—)	0.0	
CH ₂ Cl ₂	Ph	Me	1.0	58	(21)	(79)	3.8	
CH ₂ Cl ₂ /DMSO (1 eq)	Ph	Me	1.0	42	(28)	(72)	2.6	
CH ₂ Cl ₂ /DMSO (3 eq)	Ph	Me	1.0	27	(32)	(68)	2.1	
CH ₂ Cl ₂ /DMSO (5 eq)	Ph	Me	1.0	23	(40)	(60)	1.5	
CH ₂ Cl ₂	4-NCC ₆ H ₄	Me	0.5	31	(45)	(54)	1.2	
CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:19)	4-NCC ₆ H ₄	Me	0.5	44	(77)	(23)	0.3	
CH ₂ Cl ₂	Ph	Ph	0.5	45	(36)	(64)	1.8	
CCl ₄	Ph	Ph	0.5	22	(28)	(72)	2.6	
CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:19)	Ph	Ph	0.5	30	(61)	(39)	0.6	
CH ₂ Cl ₂	—ArN(Me)Ar—	0.5	21	(31)	(69)	2.2		
CCl ₄	—ArN(Me)Ar—	0.5	18	(13)	(87)	6.7		
CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:19)	—ArN(Me)Ar—	0.5	25	(87)	(13)	0.15		
CH ₂ Cl ₂	—ArN(Me)Ar—	1.0	41	(27)	(73)	2.7		
CH ₂ Cl ₂ /CH ₃ CO ₂ H (15:1)	—ArN(Me)Ar—	1.0	52	(42)	(58)	1.4		
CH ₂ Cl ₂ /CH ₃ CO ₂ H (1.7:1)	—ArN(Me)Ar—	1.0	75	(69)	(31)	0.45		
CH ₂ Cl ₂ /t-BuOH (1.7:1)	—ArN(Me)Ar—	1.0	64	(35)	(65)	1.9		

Dioxirane (x eq), CH₂Cl₂,
TFP, acetone, 0°

Dioxirane	R ¹	R ²	x	% Conv.	I	II	II:I
TFD	Ph	CF ₃	0.5	48	(>99)	(—)	(—)
TFD	4-ClC ₆ H ₄	Me	0.5	30	(38)	(62)	1.6
TFD	4-O ₂ NC ₆ H ₄	Me	0.5	35	(47)	(51)	1.1
DMD	Ph	Me	1.0	95	(95)	(5)	<0.1
DMD	Ph	Me	0.5	55	(100)	(—)	0.0
TFD	Ph	Me	1.0	58	(21)	(79)	3.8
TFD	Ph	Me	0.5	31	(27)	(73)	2.7
TFD	Ph	Me	0.33	20	(35)	(65)	1.9
TFD	Ph	Me	0.33 ^a	20	(40)	(60)	1.5
TFD	Ph	Me	0.2	13	(38)	(61)	1.6
TFD	Ph	Me	0.1	7	(43)	(57)	1.3
TFD	4-NCC ₆ H ₄	Me	0.5	34	(46)	(55)	1.2
TFD	4-MeC ₆ H ₄	Me	0.5	27	(24)	(76)	3.2
TFD	4-MeOC ₆ H ₄	Me	0.5	30	(29)	(71)	2.4
DMD	n-Bu	n-Bu	1.0	90	(94)	(6)	<0.1
TFD	n-Bu	n-Bu	1.0	63	(29)	(71)	2.5
TFD	n-Bu	n-Bu	0.33	22	(41)	(59)	1.4
TFD	n-Bu	n-Bu	0.1	7	(43)	(57)	1.3
TFD	Ph	Ph	0.5	45	(36)	(64)	1.8
DMD	—ArN(Me)Ar—	—	0.5	49	(100)	(—)	0.0
TFD	—ArN(Me)Ar—	—	1.0	41	(27)	(73)	2.7
TFD	—ArN(Me)Ar—	—	0.5	21	(31)	(69)	2.2
TFD	—ArN(Me)Ar—	—	0.33	19	(34)	(66)	1.9
DMD	Bn	Bn	1.0	93	(96)	(4)	<0.1
TFD	Bn	Bn	1.0	63	(27)	(73)	2.7
TFD	Bn	Bn	0.5	30	(36)	(64)	1.8
TFD	Bn	Bn	0.33	22	(41)	(59)	1.4
TFD	Bn	Bn	0.1	7	(43)	(57)	1.3

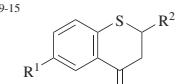
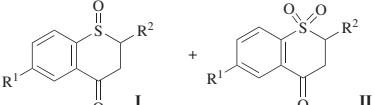
TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions		Product(s) and Yield(s) (%)						Refs.	
C ₇₋₁₄ R ¹ —S—R ²	TFD (x eq), TFP, CH ₂ Cl ₂	O R ¹ —S—R ² I	+ R ¹ —S—O ⁺ R ² II						352	
		R ¹	R ²	x	Temp	% Conv.	I	II	II:I	
		Ph	Me	0.5	0°	31	(27)	(73)	2.7	
		Ph	Me	0.5	-40°	31	(32)	(68)	2.1	
		Ph	Me	0.5	-80°	35	(49)	(51)	1.1	
		Ph	Me	0.33	0°	20	(35)	(65)	1.9	
		Ph	Me	0.33	-40°	22	(41)	(59)	1.4	
		Ph	Me	0.33	-80°	24	(54)	(46)	0.8	
		Bn	Bn	0.5	0°	30	(36)	(64)	1.8	
		Bn	Bn	0.5	-40°	34	(41)	(59)	1.4	
		Bn	Bn	0.5	-80°	38	(58)	(42)	0.7	
C ₇ Ph—S—Me	TFD (1.0 eq), TFP, solvent, additive, 0°								352	
	Additive ^b	Eq	Solvent		% Convn	I	¹⁸ O	II	¹⁸ O	II:I
	CF ₃ C(18O)H ₂ CH ₃	100	CH ₂ Cl ₂ /MeCN (1:4)		56	(34)	(23)	(66)	(12)	1.7
	H ₂ ¹⁸ O	100	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:4)		41	(33)	(11)	(67)	(6)	2.0
	H ₂ ¹⁸ O, CF ₃ CO ₂ H	100, 2.5	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:4)		67	(47)	(21)	(53)	(5)	1.1
	CF ₃ C ¹⁸ O ₂ H	200	CH ₂ Cl ₂		54	(94)	(1.1)	(6)	(0.5)	<0.1
Ph—S—CD ₃ I	+ Ph—S—Me II	Dioxirane (III), solvent, 0°	O Ph—S—CD ₃ IV	+ O Ph—S—CD ₃ V	+ O Ph—S—Me VI	(—)				352
		Dioxirane	Solvent		I:II:III (molar)	I:IV:V	II:VI	I:II	VI:IV	
	DMD	CH ₂ Cl ₂ /acetone (1:1)			1:1:1	13:80:7	93:7	13.4	0.1	
	TFD	CH ₂ Cl ₂			1:1:1	58:11:31	66:34	2.1	2.8	
	TFD	CH ₂ Cl ₂			1:3:1	73:9:18	80:20	2.3	2.0	
	TFD	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:9)			1:1:1	53:21:26	70:30	2.4	1.2	

	DMD, acetone, CH ₂ Cl ₂ , N ₂ , rt, 10 min		(100)	$\begin{array}{ccc} \text{R}^1 & \text{R}^2 & \text{R}^3 \\ \text{Br} & \text{Br} & \text{CO}_2\text{H} \\ \text{Br} & \text{Br} & \text{CH}_2\text{OH} \\ \text{Br} & \text{Br} & \text{CO}_2\text{CH}_2\text{OC(O)Bu-}t \\ \text{Br} & \text{Br} & \text{CO}_2\text{Bn} \\ \text{Br} & \text{F} & \text{CO}_2\text{Bn} \\ \text{Br} & \text{H} & \text{CO}_2\text{Bn} \\ \text{F} & \text{H} & \text{CO}_2\text{Bn} \\ \text{Br} & \text{Br} & \text{CO}_2\text{Bn} \end{array}$	123
	DMD, CH ₂ Cl ₂ , acetone, rt		I (45)		143
			II (21)		
	DMD, acetone, H ₂ O, rt		(70)		143
	DMD, acetone, CH ₂ Cl ₂ , EtOH, rt		(45)		143
	DMD (1 eq), acetone, 0°, 2 h		(88)		153
	DMD (2 eq), acetone, 0°, 12 h		(71)		153
	DMD, acetone, CH ₂ Cl ₂ , MgSO ₄ , rt		(75)		142

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		DMD, acetone, N ₂ , -78°, 1 h		350
		DMD, acetone, N ₂ , -78°		
	R = Me, Et, n-Pr	DMD, acetone, 0°		353
	$\begin{array}{ccc} \text{R}^1 & \text{R}^2 & \text{R}^3 \\ \text{MeO} & \text{MeO} & 1,3,4-\text{Cl}_3\text{C}_6\text{H}_2\text{O} \\ \text{MeO} & \text{MeO} & 3\text{-Me-4-O}_2\text{NC}_6\text{H}_3\text{O} \\ \text{EtO} & \text{EtO} & 1,4\text{-Cl}_2\text{-4-BrC}_6\text{H}_2\text{O} \\ \text{EtO} & \text{EtO} & 4\text{-O}_2\text{NC}_6\text{H}_4\text{O} \\ n\text{-Bu} & n\text{-Bu} & n\text{-Bu} \\ \text{Ph} & \text{Ph} & \text{Ph} \end{array}$	DMD, acetone, CH ₂ Cl ₂ , rt, 5 min		150
		DMD (2 eq), acetone, 1-38 h		154
			$\xrightarrow[\text{0° to rt}]{\text{Temp}} \begin{array}{cc} \text{R} & \text{R} \\ \text{CO}_2\text{Me} & \text{Bz} \end{array}$	
		DMD, acetone, 0°		353

	DMD (x eq), acetone, CH_2Cl_2 , 0–5°		354
$\begin{array}{c} \text{R}^1 \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R}^2 \\ \\ \text{H} \end{array}$	x	
H	H	1.42	
H	H	3.25	
Cl	Me	2.25	
Cl	Me	3.17	
H	Me	2.01	
H	Me	3.00	
Me	Me	1.80	
Me	Me	3.50	
H	Ph	2.12	
H	Ph	4.10	
		% Conv.	
		I	cis:trans I
		II	(4.8)
		86	(93)
		100	(—)
		98	(86)
		100	(0)
		91	(81)
		100	(—)
		100	(88)
		100	(—)
		100	(77)
		100	(—)
		70:30	(92)

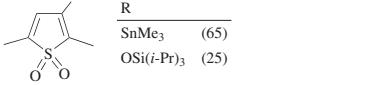
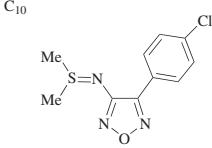
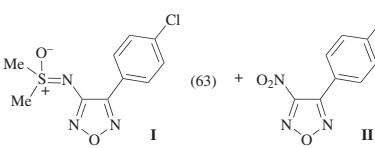
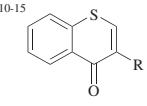
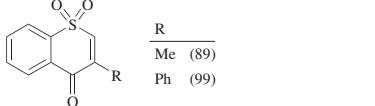
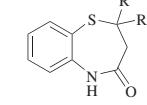
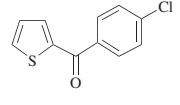
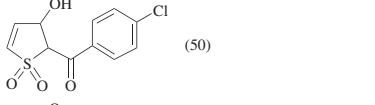
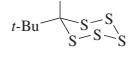
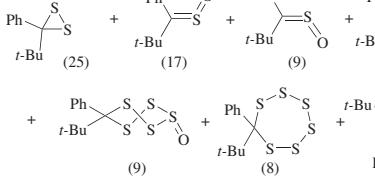
	DMD, acetone, CH_2Cl_2 , 5°, 3 h		139
		$\frac{\text{R}}{\text{SnMe}_3 \text{ (65)}} \text{ OSi}(i\text{-Pr})_3 \text{ (25)}$	
	DMD, acetone, rt, 16 h		149
	Wet DMD, acetone, rt	I (36) + II (64)	149
	DMD, acetone, CH_2Cl_2		355

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)			
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, cyclohexanone, –20°, 10 min		356
	DMD (x eq), acetone, CH_2Cl_2 , 0 to 5°	I + II + III + IV	357
$\begin{array}{c} \text{R}^1 \\ \\ \text{Me} \end{array}$	$\begin{array}{c} \text{R}^2 \\ \\ \text{H} \end{array}$	x	
Me	H	1.41	
Me	Me	1.80	
2-furyl	H	2.40	
2-furyl	H	2.85	
Ph	H	2.08	
Ph	H	3.73	
		% Conv.	
		I	(71)
		II	(3)
		III	23:77
		IV	50:50
	DMD, acetone, H_2O , rt		358
	DMD, CH_2Cl_2 , acetone, –20° to rt		359

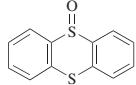
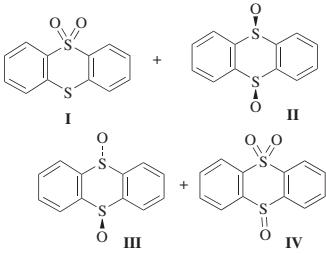
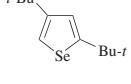
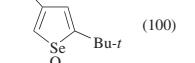
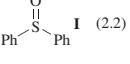
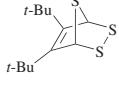
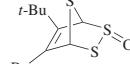
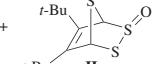
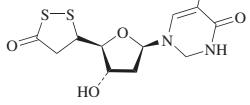
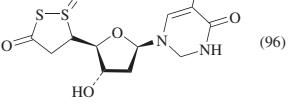
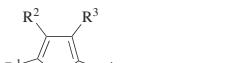
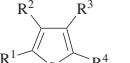
C ₁₂		Dioxirane, acetone, CH ₂ Cl ₂ , additive, 1 h		360, 361
		Dioxirane	Additive Temp % Conv. I II III IV	
	TFD	— —78°	21 (0.8) (3.1) (96) (0.2)	
	TFD	— 0°	20 (2.8) (3.9) (85) (8.1)	
	DMD	— —50°	52 (6.8) (3.1) (90) (0.1)	
	DMD	— 0°	56 (12) (3.9) (84) (0.3)	
	DMD	MeOH 0°	35 (8.8) (160) (75) (—)	
	DMD	AcOH 0°	35 (6.5) (130) (80) (—)	
	DMD	CF ₃ CO ₂ H 0°	53 (1.6) (5.7) (93) (—)	
	Methyl(isopropyl)dioxirane	— —40°	44 (4.3) (1.2) (94) (—)	
	Methyl(isopropyl)dioxirane	— 0°	44 (13) (2.50) (84) (—)	
	Methyl(isopropyl)dioxirane	CF ₃ CO ₂ H 0°	42 (—) (2.5) (98) (—)	
	Cyclohexanone dioxirane	— —70°	46 (5.8) (11) (82) (1.9)	
	Cyclohexanone dioxirane	— 0°	46 (12) (12) (76) (0.9)	
	Cyclohexanone dioxirane	CF ₃ CO ₂ H 0°	45 (1.0) (13) (86) (—)	
		Phenyl(trifluoromethyl)-dioxirane, MeCN, 20°, 30 min		362
		Diphenyldioxirane, 20°, 1.5 h	I (19)	363
		Bis(4-methoxyphenyl)dioxirane, 20°, 1.5 h	I (42)	363

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)					
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₁₂	Ph—S—S—Ph	DMD, acetone, CH ₂ Cl ₂ , N ₂ , 30°		5	
		DMD, CH ₂ Cl ₂ , acetone, —50°		(100)	155
	Ph—S—Ph	Diphenyldioxirane, 20°, 1.5 h		I (2.2)	363
		Bis(4-methoxyphenyl)dioxirane, 20°, 1.5 h	I (37)	363	
		DMD, acetone, —18°	 + 	I + II (100), I:II = 7:1	364
		DMD, acetone, rt, 2h		(96)	365
C ₁₂₋₃₂		DMD (2 eq), acetone, 0° to rt, 1–38 h		(96)	153

	R ¹	R ²	R ³	R ⁴		
C ₁₃	t-Bu	H	t-Bu	H	(97)	5
	Me	Ph	Ph	Me	(97)	
	4-ClC ₆ H ₄	4-ClC ₆ H ₄	4-ClC ₆ H ₄	4-ClC ₆ H ₄	(69)	
	Ph	Ph	Ph	Ph	(97)	
	4-MeC ₆ H ₄	4-MeC ₆ H ₄	4-MeC ₆ H ₄	4-MeC ₆ H ₄	(89)	
	4-MeOC ₆ H ₄	4-MeOC ₆ H ₄	4-MeOC ₆ H ₄	4-MeOC ₆ H ₄	(99)	
173			DMD, acetone, cyclohexanone, -20°, 10 min		(—)	
			DMD, acetone, CH ₂ Cl ₂ , EtOH, rt		(91)	143
			DMD (2 eq), acetone, 20°, 30 min		(95)	366
C ₁₃₋₁₄			DMD, acetone, CH ₂ Cl ₂ , N ₂ , rt, 10 min		(100)	123
C ₁₃₋₁₅			DMD, acetone, CH ₂ Cl ₂ , N ₂ , -30°, 2-4 h		(—)	367

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₁₃₋₁₅		DMD, acetone, CH ₂ Cl ₂ , N ₂ , 30°		(100) 367	
C ₁₄	PhS—≡—SPh	DMD, acetone, 20°, 1 h		(—) 133	
		DMD, acetone, cyclohexanone, -20°, 10 min		(—) 368	
174	PMP—S—S—PMP	DMD, acetone		(—) 135	
	PMP—S—S—S—PMP	DMD, acetone-d ₆ , -20°		I (—) + II (—) + III (—) +	135
				IV I (—) + II (—) + III (—) +	
	PMP—S—S—S—PMP	DMD, acetone-d ₆ , -20°			135
	PMP—S—S—PMP	DMD, acetone, CH ₂ Cl ₂ , rt		I (—) + II (—) I (—) +	135

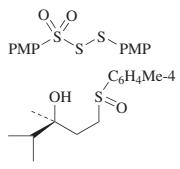
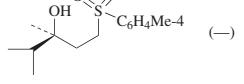
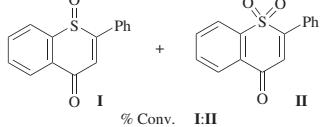
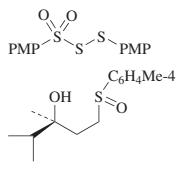
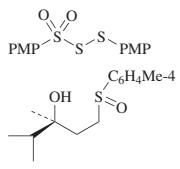
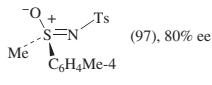
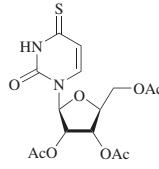
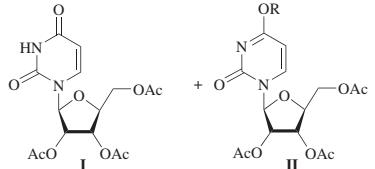
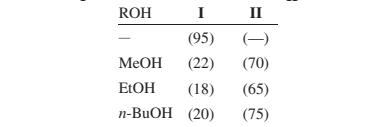
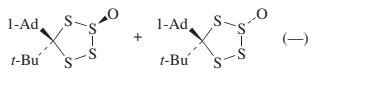
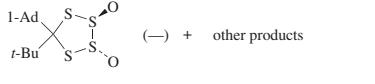
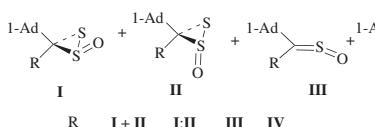
	TFD, acetone, TFP or CH ₂ Cl ₂ , TFP, rt	I (—) + II (—)	135
	TFD, acetone, TFP, -80°	I (—)	135
	DMD, acetone- <i>d</i> ₆ , -20°	III (—) + other products	135
	DMD, acetone, rt, 5 h		369
	DMD (1.2 eq), solvent, 0°, 24 h		354
	Solvent	% Conv. I:II	
	CCl ₄	29 7:93	
	CCl ₄ /acetone (9:1)	25 12:88	
	acetone	15 35:65	
	CCl ₄ /MeOH (1:1)	29 48:52	
	CHCl ₃	21 60:40	
	CCl ₄ /AcOH (1:1)	25 66:34	
	DMD, acetone, 0° to rt		148
		(97), 80% ee	

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (<i>Continued</i>)				Refs.
Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
	DMD, acetone, CH ₂ Cl ₂ , ROH, rt			117
				
		ROH I (95) (—) MeOH (22) (70) EtOH (18) (65) <i>n</i> -BuOH (20) (75)		
	DMD (4 eq), CH ₂ Cl ₂ , acetone, -78°, 1 h; rt, 4 h		(28) (24)	370
	DMD, CH ₂ Cl ₂ , acetone, -20°		(—)	370
	DMD (4 eq), CH ₂ Cl ₂ , acetone, -20°		(—) + other products	370
	DMD, acetone, rt, 3 h		I (31) II 50:50 III (4) (52) I-Ad (38) II 50:50 III (12) (25)	136

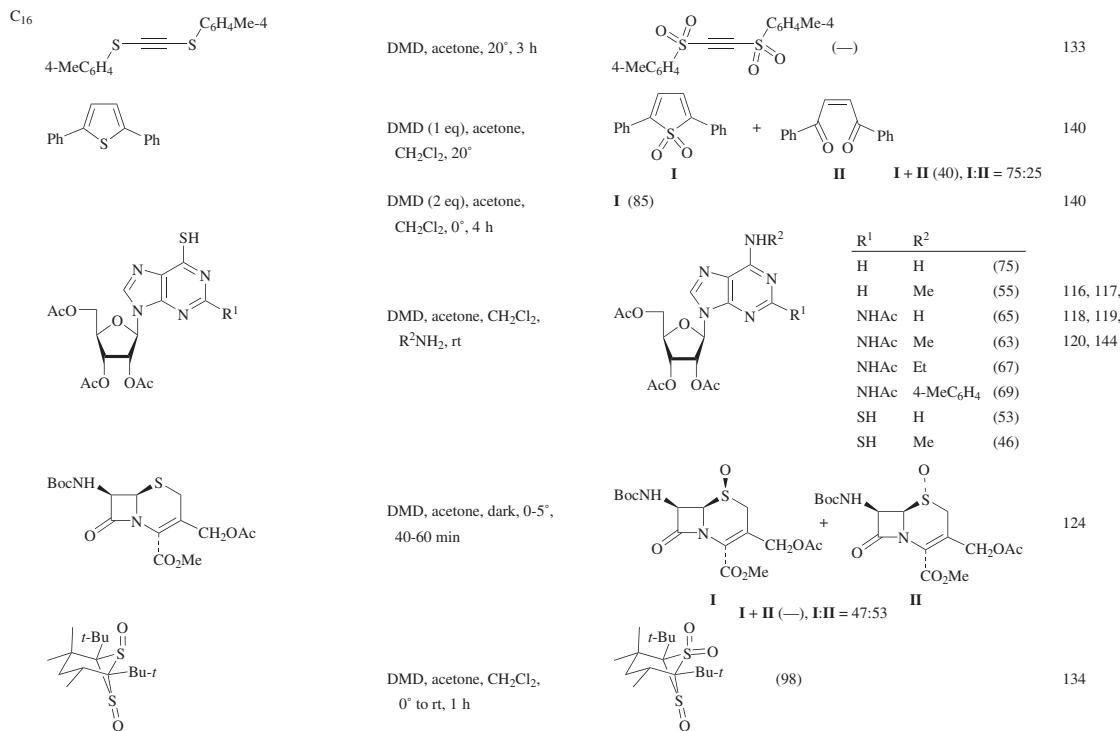


TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (<i>Continued</i>)				Refs.
	Substrate	Conditions	Product(s) and Yield(s) (%)	
C₁₆₋₁₇		DMD (2-4 eq), acetone, rt, 30 min		Ar 4-ClC ₆ H ₄ (74) 4-MeOC ₆ H ₄ (75)
		DMD (5-8 eq), acetone, rt, 30 min		Ar 4-ClC ₆ H ₅ (90) 4-MeOC ₆ H ₅ (91)
C₁₆₋₁₈		DMD, acetone, CH ₂ Cl ₂ , rt		138
		DMD, acetone, 0-5°; dark, 40-60 min		(100)
C₁₆₋₁₂		DMD, acetone, 0-5°; dark, 40-60 min		124
		DMD, acetone, 0-5°; dark, 40-60 min		(100)
C₁₇		1. DMD, acetone, CH ₂ Cl ₂ , 0° 2. rt, 1 h		(98)
		1. DMD, acetone, CH ₂ Cl ₂ , 0° 2. rt, 1 h		(98)

<p>C₁₈₋₁₉ C₁₈</p> <p>DMD, acetone, 0 to 5°; dark, 40-60 min</p> <p>C₁₉</p> <p>DMD, acetone, CH₂Cl₂; ROH, rt</p>	<p>R CH=CH₂ (95) CH₂CO₂Me (100)</p> <p>124</p>															
<p>DMD, acetone, CH₂Cl₂</p> <p>DMD, acetone, -78° to rt, overnight</p> <p>DMD, acetone</p>	<p>I + II (95) (—) Me (22) (70) Et (18) (65) <i>n</i>-Bu (20) (75)</p> <p>I II</p> <p>Y Temp Time</p> <p>S 0° 1 h (89)</p> <p>Se 0° to rt 30 min (100)</p> <p>(9) + t-Bu-SO₂-phenyl (29)</p> <p>I + II (100) II</p> <p>Temp I:II</p> <p>20° 20:1</p> <p>-78° 100:0</p> <p>134</p> <p>147</p> <p>147</p>															
<p>C₂₀</p> <p>1. DMD (1 eq), CH₂Cl₂, -78° to rt, 6 h</p> <p>2. KOAc, AcOH, -78° to rt</p> <p>3. KOH, EtOH, H₂O, rt</p> <p>C₂₀₋₂₉</p> <p>DMD, acetone, 0 to 5°; dark, 4 days</p> <table border="1" style="margin-left: 20px;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> </tr> </thead> <tbody> <tr> <td>BnCONH</td> <td>Me</td> <td>AcOCH₂</td> </tr> <tr> <td>PhOCH₂CONH</td> <td>Cl</td> <td>Ph₂CH</td> </tr> <tr> <td>BnCONH</td> <td>Me</td> <td>AcOCH₂</td> </tr> <tr> <td>PhOCH₂CONH</td> <td>Cl</td> <td>Ph₂CH</td> </tr> </tbody> </table> <p>C₂₁₋₃₁</p> <p>1. DMD, acetone, rt</p> <p>2. Toluene, heating</p>	R ¹	R ²	R ³	BnCONH	Me	AcOCH ₂	PhOCH ₂ CONH	Cl	Ph ₂ CH	BnCONH	Me	AcOCH ₂	PhOCH ₂ CONH	Cl	Ph ₂ CH	<p>(52) + t-Bu-SO₂-phenyl (40)</p> <p>I II</p> <p>dr</p> <p>(85) 83:17 (95) — (85) 83:17 (95) —</p> <p>I I II</p> <p>(38) (35) (65) (—) (52) (—) (85) (—) (67) (15) (82) (—) (61) (—)</p> <p>124</p> <p>373</p> <p>374</p>
R ¹	R ²	R ³														
BnCONH	Me	AcOCH ₂														
PhOCH ₂ CONH	Cl	Ph ₂ CH														
BnCONH	Me	AcOCH ₂														
PhOCH ₂ CONH	Cl	Ph ₂ CH														

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C₂₀			
	1. DMD (1 eq), CH ₂ Cl ₂ , -78° to rt, 6 h 2. KOAc, AcOH, -78° to rt 3. KOH, EtOH, H ₂ O, rt	(52) + t -Bu-SO ₂ -phenyl (40)	373
C₂₀₋₂₉	DMD, acetone, 0 to 5°; dark, 4 days	dr (85) 83:17 (95) — (85) 83:17 (95) —	124
C₂₁₋₃₁	1. DMD, acetone, rt 2. Toluene, heating	I I II (38) (35) (65) (—) (52) (—) (85) (—) (67) (15) (82) (—) (61) (—)	374

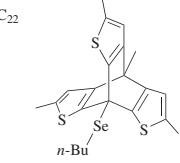
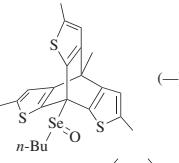
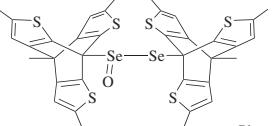
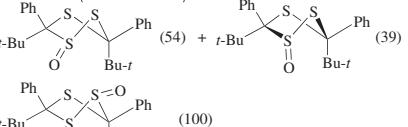
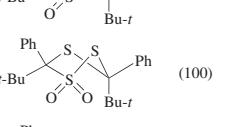
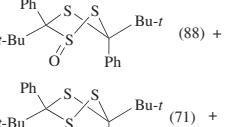
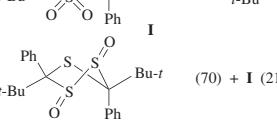
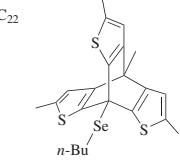
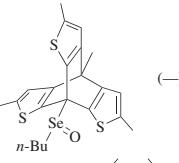
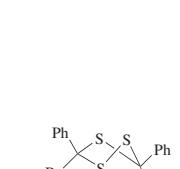
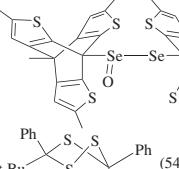
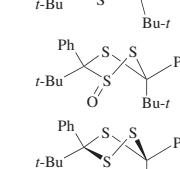
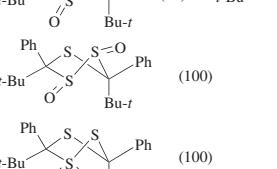
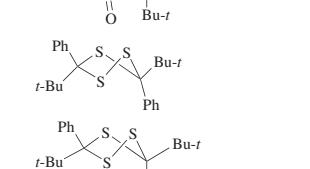
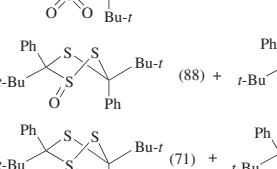
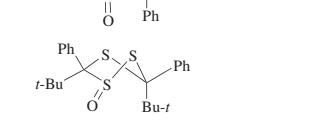
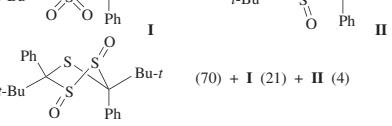
	DMD, acetone, -78°		(—)	152
	1. DMD, acetone, -78° 2. rt		(70)	152
	DMD (1.2 eq), acetone, CH ₂ Cl ₂ , -20°		(54) + (39)	375
	DMD (2 eq), acetone, CH ₂ Cl ₂ , -20°, 1.5 h		(100)	375
	DMD (4 eq), acetone, CH ₂ Cl ₂ , -20°, 2.5 h		(100)	375
	DMD (1.2 eq), acetone, CH ₂ Cl ₂ , -20°, 1 h		(88) + (4)	376
	DMD (4 eq), acetone, CH ₂ Cl ₂ , -20°, 7 h		(71) + (20)	376
	DMD (2 eq), acetone, CH ₂ Cl ₂ , -20°, 2 h		(70) + I (21) + II (4)	376

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD (1 eq), acetone, CH ₂ Cl ₂ , 0°, 10 min	 (100)	376
	DMD, acetone, -78° to rt	 (87)	377
	DMD (4 eq), acetone, CH ₂ Cl ₂ , -20°, 1 h	 R t-Bu (42) 1-Ad (60)	267
	DMD, acetone, 0-5°, dark, 40-60 min	 (95)	124
	DMD, acetone, CH ₂ Cl ₂ , rt, 16 h	 Ar ¹ Ph Ph Ph Ph 4-(i-Pr)C ₆ H ₄ 3-ClC ₆ H ₄ 4-ClC ₆ H ₄ 2,4-Cl ₂ C ₆ H ₃ 3,4-Cl ₂ C ₆ H ₃ 4-ClC ₆ H ₄ 2,4-Cl ₂ C ₆ H ₃ Ar ² Ph 2-AcOC ₆ H ₄ 4-AcOC ₆ H ₄ 4-AcOC ₆ H ₄ 2-AcOC ₆ H ₄ 2-AcOC ₆ H ₄ 2-AcOC ₆ H ₄ 2-AcOC ₆ H ₄ 4-AcOC ₆ H ₄ 2-MeC ₆ H ₄	378

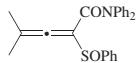
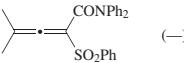
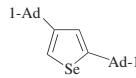
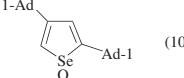
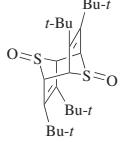
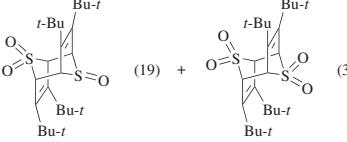
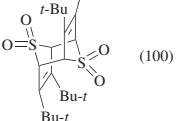
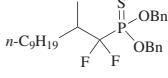
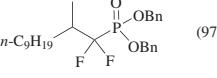
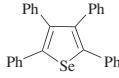
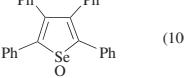
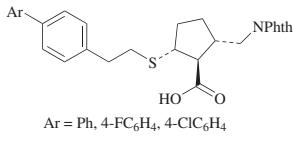
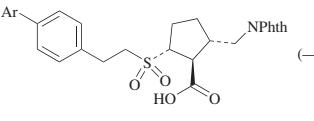
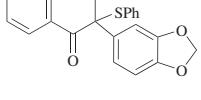
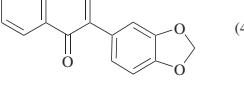
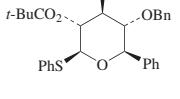
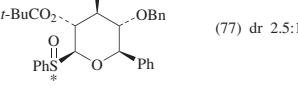
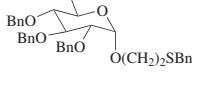
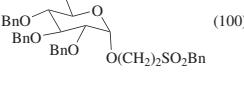
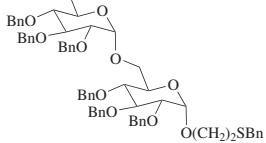
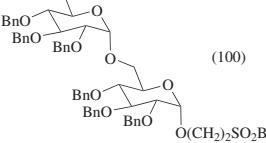
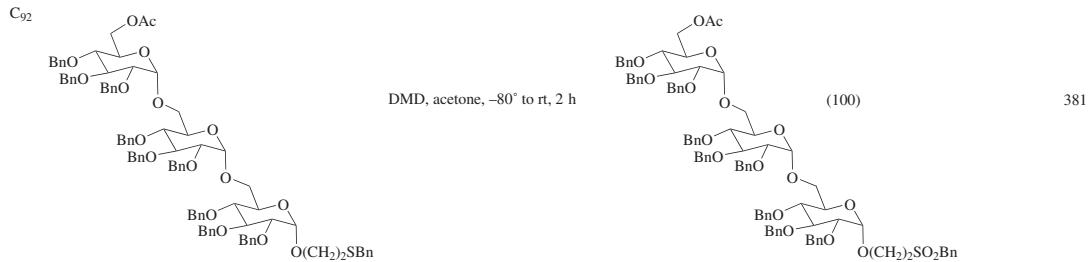
C ₂₄		DMD, acetone, cyclohexanone, -20°, 10 min		379
		DMD, CH ₂ Cl ₂ , acetone, -50°		155
		DMD (1.0 eq), acetone, 0°		380
183		DMD (2.8 eq), acetone, 0°		380
C ₂₆		DMD, acetone, rt, 3 h		151
C ₂₈		DMD, CH ₂ Cl ₂ , acetone, -50°		155

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₉		DMD, acetone, 0° to rt		371
C ₃₆		1. DMD, acetone, rt 2. Toluene, heating		374
184		DMD, acetone, CH ₂ Cl ₂ , 0°, 30 min		125
C ₃₈		DMD, acetone, -80° to rt, 2 h		381
C ₆₅		DMD, acetone, -80° to rt, 2 h		381



^a Methyl(trifluoromethyl)dioxirane (TFD) was added dropwise.

^b The percent isotopic oxygen labeling for these compounds was as follows : CF₃C(¹⁸OH)₂CH₃; 49%; H₂¹⁸O; 98%; CF₃C¹⁸O₂H; 49%.

TABLE 3C. PHOSPHORUS OXIDATION BY ISOLATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
^{C₁₈} Ph ₃ P		DMD, acetone	Ph ₃ P=O I (100)	121
		DMD, acetone, -70 to -50°	I (-)	156
		DMD, CDCl ₃	I (-)	157
^{C₃₄} 			(100)	158
		DMD, acetone, CH ₂ Cl ₂ , 0°, 10 min	(100)	158
^{C₃₈₋₄₄} 		DMD, acetone, CH ₂ Cl ₂ , rt, 10 min	R NHAc (98) OAc (100) NHCbz (99)	158
			R NHAc (98) OAc (100) NHCbz (99)	158
			R NHAc (98) OAc (100) NHCbz (99)	158
^{C₃₉} 		1. Methyl glycolate, tetrazole, MeCN, 0° 2. DMD, acetone, CH ₂ Cl ₂ , rt	(78)	382
		2-Ethyl-2-methylidioxirane, CH ₂ Cl ₂ , rt, 2 h	(78)	383
^{C₅₃} 		DMD, acetone, -40°	(80)	384
			(80)	384

TABLE 3D. OXYGEN OXIDATION BY ISOLATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₀	HSO ₅ ⁻	DMD, acetone/H ₂ O, NaHCO ₃ , 20°	O ₂ (—) + HSO ₄ ⁻ (—)	160
C ₁		F ₂ C^O _~ O, CsF, -50°, 20 h	(—) n = 1, 2, 3	385
	* = ¹³ C			
		F ₂ C^O _~ O, CsF, -50°, 16 h	(—) + (—) n = 1, 2, 3	385
C ₃		TFD, CH ₂ Cl ₂ , <i>n</i> -Bu ₄ NiI, 0°, 5 min	O ₂ (96)	164
		DMD, acetone, dark, rt, 5-10 d		121
C ₅₋₈		BF ₃ , acetone, ether, 0°	MeCO ₂ Me (—)	121
	R ¹ R ² R ³ R ⁴ R ⁵	DMD, CDCl ₃ , 20°	¹ O ₂ I R ¹ R ² R ³ R ⁴ R ⁵	165
	H H H H H (—)		Me H H H Me (—)	
	Me H H H H (—)		H Me Me H H (—)	
	H Me Me H H Me (—)		Me H Me H H Me (—)	
	H H Me ₂ N H H (30)		H H Me ₂ N H H (30)	
C ₅₋₁₂		TFD, TFA, 20°	I R ¹ R ² R ³ R ⁴ R ⁵	165
	H H H H H (4.8)		Me H H H Me (1.3)	
	Me H H H H (0.2)		H Me Me H H (0.6)	
	H H Me ₂ N H H (5)		Me O (0.08-0.60)	
			PhCH ₂ CH ₂ (0.04-0.09)	
C ₆		DMD, CDCl ₃ , 20°	I R Y	165
TMS ¹⁸ O ¹⁸ OSO ₃ TMS	Cyclohexanone, CH ₂ Cl ₂ , He, -80 to -10°, 10 h	³² O ₂ (—) + ³⁴ O ₂ (—) + ³⁶ O ₂ (—) I:II:III = 92.7:6.4:0.9	I II III	386
C ₇		DMD, acetone, 0°	¹ O ₂ (—) + (—) + (—) I:II = 16:84	26
C ₈		DMD, acetone	¹ O ₂ (—) + (—)	26
PhMe ₂ N ⁺ —O ⁻	DMD, CDCl ₃ , 20°	¹ O ₂ (0.33)		165
C ₉		TFD, TFA, 20°	¹ O ₂ (0.02)	165

TABLE 3D. OXYGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉		DMD, acetone, air or N ₂ , 20°, 2-4 h	 I II	166
C ₁₂		TFD, TFA, 0°, 2-4 h	¹ O ₂ (> 96%)	166
		TFD, CH ₂ Cl ₂ , 0°, 2 h	 I	23
		TFD, hν, CH ₂ Cl ₂ , -10°	I (39) + II	23
C ₁₅		TFD, TFA, 20°	I (0.12-0.88)	165
		Dioxirane, acetone, 0°	 I II III IV	166
		Dioxirane Time	I II III IV	
	DMD 3 h	(16) (8.5) (18) (12)		
	TFD 30 min	(12) (14) (19) (21)		
C ₁₆		DMD, acetone, 20°, 3 h	¹ O ₂ (—) + I	26
		DMD, acetone, CH ₂ Cl ₂	¹ O ₂ (—) + I (—) + II I:II = 62:38	26
C ₂₁		DMD, CDCl ₃ , 20°	¹ O ₂ (0.65-1.18)	165

TABLE 3E. HALOGEN OXIDATION BY ISOLATED DIOXIRANES

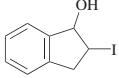
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₀	LiI	TFD, TMSCl, CH ₂ Cl ₂ , 0°, 20 min	TMS-O-TMS (—)	164
C ₁ 192	CH ₃ I	Alkene (0.5 equiv)	1. DMD (1 eq), acetone, -70°, 1 h 2. Alkene, -70° to rt, 20 h	
			 (78)	170
			 (85)	170
			 (0)	170
			 (72)	170
			 (82)  (85)  (44)  (75)  (60)	170
			 (82)	170
			 I +  II I + II (85), I:II = 65:35	170
C ₆ 193				
C ₆₋₇				

TABLE 3E. HALOGEN OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇₋₈		DMD, acetone, CH ₂ Cl ₂ , 0°, 8 h	 R OMe (89) OEt (84)	387
C ₈		DMD, acetone, ether, rt, 1 h	 (58)	169
C ₉₋₁₃		DMD, acetone, rt, 8 h	 (76-90)	388
C ₁₀		DMD, acetone, ether, 0°	 (77)	169
		DMD, acetone, ether, rt, 1 h	 (80)	169
C ₁₀₋₁₆		DMD, acetone, rt, 8 h	 R (S)-NHCH(Me)CO ₂ Me (96) (S)-NHCH(Bn)CO ₂ Me (68) (S)-NHCH(<i>i</i> -Pr)CO ₂ Me (84) (S)-NHCH(<i>i</i> -Bu)CO ₂ Me (63) (R)-NHCH(Ph)Me (67)	387, 389
C ₁₀₋₁₇		DMD, acetone, rt	 (45-73) R (S)-CH(Me)CO ₂ Me (R)-CH(Me)CO ₂ Me (S)-CH(Bn)CO ₂ Me (S)-CH(<i>i</i> -Bu)CO ₂ Me CH ₂ CH ₂ CO ₂ H CH(Me)CH ₂ CO ₂ H (R)-CH(Ph)CH ₃	390
161	C ₁₁ Ph-CH ₂ -CH ₂ -CH ₂ -SO ₂ CF ₃	DMD, acetone, ether, rt, 1 h	 (93)	169
C ₁₆	(<i>n</i> -Bu) ₄ NI	TFD, CH ₂ Cl ₂ , 0°	I ₂ (—)	164
		TFD, PhCOCl, CH ₂ Cl ₂ , 0°, 10 min	 (—)	164

TABLE 3F. NITROGEN OXIDATION BY IN SITU GENERATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.	
C ₄₋₁₁		Oxone®, acetone, H ₂ O, NaHCO ₃ , rt					114	
	R ¹	R ²	x	Solvent	I	II	III	IV
	n-Pr	H	4.5	CH ₂ Cl ₂	(24)	(30)	6 ^a	27 ^a
	n-Pr	H	4.5	—	(40)	(40)	12 ^a	(—)
	—(CH ₂) ₅ —		4.5	CH ₂ Cl ₂	(10)	(43)	(10)	(10)
	—(CH ₂) ₅ —		8	CH ₂ Cl ₂	12 ^a	60 ^a	14 ^a	14 ^a
	—(CH ₂) ₅ —		16	CH ₂ Cl ₂	12 ^a	50 ^a	18 ^a	20 ^a
	—(CH ₂) ₅ —		8	—	2 ^a	26 ^a	72 ^a	(—)
	—(CH ₂) ₅ —		16	—	(—)	14 ^a	86 ^a	(—)
	—(CH ₂) ₅ —		20	—	(—)	(11)	(65)	(—)
	Ph	H	6	CH ₂ Cl ₂	(55)	(—)	(—)	38 ^a
	Ph	H	6	—	(52)	(—)	(—)	(trace)
	n-C ₉ H ₁₉	H	4.5	CH ₂ Cl ₂	(15)	(35)	5 ^a	(37)
	n-C ₉ H ₁₉	H	4.5	—	(—)	(64)	(9)	13 ^a
C ₅		Oxone®, acetone, H ₂ O (pH 7.5-8.0), 2 h		I (93)				121
		Oxone®, acetone, 50°, 16 h		I (63) +	(4)			121
		Oxone®, acetone		I (70-80)				121
C ₆		Oxone®, cyclohexanone, buffer (pH)		I	pH			391
					7.0 (72)			
					7.5 (85)			
					8.0 (94)			
					8.5 (96)			
					9.0 (95)			
					9.5 (86)			
		Oxone®, acetone, CH ₂ Cl ₂ , phosphate buffer (pH 7.5-8.5), aq. KOH, (n-Bu) ₄ NHSO ₄ , 0°, 45 min		I (17.5) +	(17.5) (17.5)			267
		Oxone®, THF, acetone, CH ₂ Cl ₂ , phosphate buffer (pH 7.5-8.5), aq. KOH, (n-Bu) ₄ NHSO ₄ , 0°, 15 min		I (78)				267
		Oxone®, , acetone, CH ₂ Cl ₂ , phosphate buffer (pH 7.5-8.5), aq. KOH, (n-Bu) ₄ NHSO ₄ , 0°, 45 min		I (98)				267
197		Oxone®, acetone, phosphate buffer (pH 8.0), KOH, 5°, 7 h				(34)		112
		Oxone®, acetone, phosphate buffer (pH 8.0), KOH, 5°, 7 h				(57)		112

TABLE 3F. NITROGEN OXIDATION BY IN SITU GENERATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																						
C ₇		Oxone®, acetone, H ₂ O, NaOH, NaHCO ₃ , EDTA, 2–18°, 4 h	 (73)	392																																																																						
		Oxone®, acetone, H ₂ O, NaOH, NaHCO ₃ , EDTA, 2–18°, 4 h	 (74)	392																																																																						
198		Oxone®, acetone, phosphate buffer (pH 8.0), KOH, 5°, 7 h	 I + II (88), I : II = 3:1	112																																																																						
		Oxone®, acetone, phosphate buffer (pH 8.0), KOH, 5°, 7 h	 (56)	112																																																																						
C _{7,9}		Oxone®, acetone, CH ₂ Cl ₂ , phosphate buffer (pH 7.5–8.5), aq. KOH, (n-Bu) ₄ NHSO ₄ , 0°, 45 min		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> </tr> </thead> <tbody> <tr> <td>MeO</td> <td>H</td> <td>H</td> <td>H (100)</td> </tr> <tr> <td>H</td> <td>MeO</td> <td>H</td> <td>(73)</td> </tr> <tr> <td>H</td> <td>—OCH₂O—</td> <td></td> <td>H (57)</td> </tr> <tr> <td>MeO</td> <td>H</td> <td>MeO</td> <td>H (85)</td> </tr> <tr> <td>MeO</td> <td>H</td> <td>H</td> <td>MeO (51)</td> </tr> <tr> <td>H</td> <td>MeO</td> <td>MeO</td> <td>MeO (52)</td> </tr> <tr> <td>H</td> <td>MeO</td> <td>CO₂Me</td> <td>H (78)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	MeO	H	H	H (100)	H	MeO	H	(73)	H	—OCH ₂ O—		H (57)	MeO	H	MeO	H (85)	MeO	H	H	MeO (51)	H	MeO	MeO	MeO (52)	H	MeO	CO ₂ Me	H (78)	267																																					
R ¹	R ²	R ³	R ⁴																																																																							
MeO	H	H	H (100)																																																																							
H	MeO	H	(73)																																																																							
H	—OCH ₂ O—		H (57)																																																																							
MeO	H	MeO	H (85)																																																																							
MeO	H	H	MeO (51)																																																																							
H	MeO	MeO	MeO (52)																																																																							
H	MeO	CO ₂ Me	H (78)																																																																							
199		Oxone® (1–2 eq), CH ₂ Cl ₂ , H ₂ O		393																																																																						
	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>CO₂Me</td> <td>H</td> <td>0.5 h</td> <td>(100)</td> </tr> <tr> <td>H</td> <td>CO₂Me</td> <td>H</td> <td>1 h</td> <td>(100)</td> </tr> <tr> <td>CO₂Me</td> <td>H</td> <td>H</td> <td>3 h</td> <td>(100)</td> </tr> <tr> <td>CO₂H</td> <td>H</td> <td>H</td> <td>3.5 h</td> <td>(96)</td> </tr> <tr> <td>CN</td> <td>H</td> <td>H</td> <td>3 h</td> <td>(96)</td> </tr> <tr> <td>H</td> <td>Br</td> <td>H</td> <td>3.5 h</td> <td>(70)</td> </tr> <tr> <td>H</td> <td>Et</td> <td>H</td> <td>12 h</td> <td>(65)</td> </tr> <tr> <td>H</td> <td>SO₃H</td> <td>H</td> <td>4 h</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>SO₃NBu₄</td> <td>H</td> <td>0.5 h</td> <td>(97)</td> </tr> <tr> <td>H</td> <td>CH₂OH</td> <td>H</td> <td>1 h</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>CH₂CO₂H</td> <td>H</td> <td>4 h</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>CH₂NHBoc</td> <td>H</td> <td>9.5 h</td> <td>(60)</td> </tr> <tr> <td>CO₂Me</td> <td>H</td> <td>Me</td> <td>3.5 h</td> <td>(96)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Time		H	CO ₂ Me	H	0.5 h	(100)	H	CO ₂ Me	H	1 h	(100)	CO ₂ Me	H	H	3 h	(100)	CO ₂ H	H	H	3.5 h	(96)	CN	H	H	3 h	(96)	H	Br	H	3.5 h	(70)	H	Et	H	12 h	(65)	H	SO ₃ H	H	4 h	(—)	H	SO ₃ NBu ₄	H	0.5 h	(97)	H	CH ₂ OH	H	1 h	(—)	H	CH ₂ CO ₂ H	H	4 h	(—)	H	CH ₂ NHBoc	H	9.5 h	(60)	CO ₂ Me	H	Me	3.5 h	(96)			
R ¹	R ²	R ³	Time																																																																							
H	CO ₂ Me	H	0.5 h	(100)																																																																						
H	CO ₂ Me	H	1 h	(100)																																																																						
CO ₂ Me	H	H	3 h	(100)																																																																						
CO ₂ H	H	H	3.5 h	(96)																																																																						
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H	Br	H	3.5 h	(70)																																																																						
H	Et	H	12 h	(65)																																																																						
H	SO ₃ H	H	4 h	(—)																																																																						
H	SO ₃ NBu ₄	H	0.5 h	(97)																																																																						
H	CH ₂ OH	H	1 h	(—)																																																																						
H	CH ₂ CO ₂ H	H	4 h	(—)																																																																						
H	CH ₂ NHBoc	H	9.5 h	(60)																																																																						
CO ₂ Me	H	Me	3.5 h	(96)																																																																						
C ₈		Oxone®, acetone, CH ₂ Cl ₂ , phosphate buffer (pH 7.5–8.5), aq. KOH, (n-Bu) ₄ NHSO ₄ , 0°, 45 min	 (40) + (18)	267																																																																						
		Oxone®, TFP, CH ₂ Cl ₂ , H ₂ O, NaHCO ₃ , 0°, 80 min	 (47)	311																																																																						
		Oxone®, acetone, phosphate buffer (pH 8.0), KOH, 5°, 7 h	 I = Ph=NHOH + II = PhCO ₂ H I + II (74), I : II = 3:1	112																																																																						

TABLE 3F. NITROGEN OXIDATION BY IN SITU GENERATED DIOXIRANES (*Continued*)

TABLE 3F. NITROGEN OXIDATION BY IN SITU GENERATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄		Oxone®, acetone, CH ₂ Cl ₂ , Na ₂ HPO ₄ buffer (pH 7.5-8.0), aq. KOH, (n-Bu) ₄ NHSO ₄ , 0°		(89)
		Oxone®, acetone, CH ₂ Cl ₂ , Na ₂ HPO ₄ buffer (pH 7.5-8.0), aq. KOH, (n-Bu) ₄ NHSO ₄ , 0°		(90)
C ₁₅		Oxone® (2.3 eq), acetone, H ₂ O, CH ₂ Cl ₂ , buffer salt (x eq)		396
		Buffer salt x	I II	
	NaHCO ₃ 6.4		(76) (4)	
	Na ₂ HPO ₄ 6.4		(79) (2)	
	Na ₂ HPO ₄ 8.0		(86) (3)	
	Na ₂ HPO ₄ 9.2		(84) (3)	
	K ₂ HPO ₄ 6.4		(79) (2)	
		Oxone®, acetone, H ₂ O, NaHCO ₃ , Ar, rt, 30 min		(67)
				327

^aThis value is the ratio of the products in the crude mixture.

TABLE 3G. SULFUR OXIDATION BY IN SITU GENERATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.	
C ₄		Oxone®, acetone, H ₂ O, 0-5°, 75 min		(67)		397	
C ₇₋₁₃	R ¹ -S-R ²	Oxone®, acetone, bovine serum albumin, NaHCO ₃ , Na ₂ EDTA, buffer (pH 7.2-7.8), 4°		I + II	III	I:II	130, 131
	R ¹ R ²	Time					
	Ph Me	180 min		(98)	(—)	53.5:46.5	
	Bz Me	180 min		(85)	(—)	62:38	
	Ph Et	60 min		(51)	(—)	49.5:50.5	
	4-MeC ₆ H ₄ Me	60 min		(77)	(—)	66:34	
	4-MeC ₆ H ₄ Et	105 min		(68)	(—)	82:18	
	Ph i-Pr	120 min		(56)	(5)	10.5:89.5	
	Ph t-Bu	120 min		(70)	(—)	13.5:86.5	
	4-MeC ₆ H ₄ i-Pr	120 min		(50)	(11)	64.5:35.5	
	4-MeC ₆ H ₄ t-Bu	85 min		(40)	(14)	45.5:54.5	
	Ph c-C ₆ H ₁₁	25 min		(45)	(5)	24:76	
	Ph Bz	180 min		(30)	(14)	84:16	
C ₈₋₁₃	R ¹ -S-R ²	Oxone®, PhCOCF ₃ , bovine serum albumin, NaHCO ₃ , Na ₂ EDTA, buffer (pH 7.2-7.8), 4°	I + II + III				130, 131
	R ¹ R ²	Time					
	4-MeC ₆ H ₄ Me	135 min		(80)	(—)	45.5:54.5	
	4-MeC ₆ H ₄ Et	180 min		(78)	(5)	52:48	
	Ph i-Pr	120 min		(96)	(—)	18:82	
	Ph t-Bu	90 min		(37)	(10)	14.5:85.5	
	Ph Bz	150 min		(22)	(3)	86.5:13.5	

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TABLE 3G. SULFUR OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
C ₈₋₉		Oxone® (x eq), acetone, buffer (pH 7.5-8.0), NaHCO ₃ , EDTA		I	II	398
	R ¹ R ²	x Time Temp				
	H CH ₂ CO ₂ H	0.65 5 min 0-2°		(98.6)	(—)	
	H CH ₂ CO ₂ H	1.35 1-2 h rt		(—)	(96.7)	
	CO ₂ H Me	0.65 5 min 0-2°		(76.8)	(—)	
	CO ₂ H Me	1.35 1-2 h rt		(—)	(92.6)	
	H (CH ₂) ₂ OH	0.65 5 min 0-2°		(81.5)	(—)	
	H (CH ₂) ₂ OH	1.35 1-2 h rt		(—)	(92.8)	
	CH ₂ OH Me	0.65 5 min 0-2°		(46.6)	(—)	
	CH ₂ OH Me	1.35 1-2 h rt		(—)	(83.4)	
	H Z-CH=CHCO ₂ H	0.65 5 min 0-2°		(95.0)	(—)	
	H Z-CH=CHCO ₂ H	1.35 1-2 h rt		(—)	(35)	
	R ¹ -S-R ²	Oxone®, cyclohexanone, bovine serum albumin, NaHCO ₃ , Na ₂ EDTA, buffer (pH 7.2-7.8), 4°		I	II	130, 131
	R ¹ R ²	Time				
	4-MeC ₆ H ₄ Me	240 min		(60)	53:47	
	Ph i-Pr	120 min		(46)	42:58	
C ₈₋₁₄	R ¹ -S-R ²	Oxone®, TFP, bovine serum albumin, NaHCO ₃ , Na ₂ EDTA, buffer (pH 7.2-7.8), 4°		I + II	III	130, 131

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	R ¹	R ²	Time	I + II	III	I:II		
	4-MeC ₆ H ₄	Me	10 min	(78)	(5)	52:48		
	4-MeC ₆ H ₄	Et	60 min	(66)	(12)	80.5:19.5		
	Ph	i-Pr	5 min	(67)	(—)	5.5:94.5		
	Ph	t-Bu	5 min	(55)	(—)	16.5:83.5		
	Ph	Bz	5 min	(20)	(21)	86:14		
	4-MeC ₆ H ₄	Bz	5 min	(95)	(—)	69:31		
C ₉			Oxone®, acetone, benzene, H ₂ O, 18-crown-6, KHCO ₃ , N ₂ , rt, 4 h		(33)		146	
C ₉₋₁₅			Oxone®, bovine serum albumin, NaHCO ₃ , Na ₂ EDTA, buffer (pH 7.2-7.8), 4°				130, 131	
	R ¹	R ²	Time	I	% ee	II		
	H	Me	40 min	(100)	6	(—)		
	Me	Me	30 min	(100)	72	(—)		
	H	i-Pr	10 min	(84)	35	(—)		
	Me	i-Pr	10 min	(94)	82	(—)		
	Me	t-Bu	30 min	(83)	79	(—)		
	Me	Ph	20 min	(59)	9	(10)		
C ₁₀			Oxone®, acetone, benzene, H ₂ O, 18-crown-6, KHCO ₃ , N ₂ , rt, 4 h		(20)		(29)	146
C ₁₁			Oxone®, acetone, H ₂ O, 0°, 40 min		(94)		(6)	122

TABLE 3G. SULFUR OXIDATION BY IN SITU GENERATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.			
C ₁₂		Oxone®, acetone, phosphate buffer (pH 7.5), 18-crown-6, EDTA, 0° to rt, 24 h		(4) +	(16) +	(6)	399
		Oxone®, carbonyl compound, 18-crown-6, CH ₂ Cl ₂ , H ₂ O, 0°	I + II + III				400
		Ketone or aldehyde	I + II + III	I:II:III			
	acetone		(10.1)	59:15:26			
	t-BuCOMe		(5.33)	61:31:8			
	cyclohexanone		(1.88)	58:30:12			
	t-BuCHO		(5.04)	49:3:48			
C ₁₃		Oxone®, bovine serum albumin, NaHCO ₃ , Na ₂ EDTA, buffer (pH 7.2-7.8), 4°, 140 min		(63)	84% ee		130, 131
		Oxone®, CHCl ₃ , MeOH, H ₂ O, 0°, 30 min		(68)			401

C ₁₅		Oxone®, acetone, benzene, H ₂ O, 18-crown-6, KHCO ₃ , N ₂ , rt, 4 h			I Ar = 4-MeC ₆ H ₄ (79) II Ar = 4-MeOC ₆ H ₄ (97) (0)	146
C ₁₇		Oxone®, acetone, NaHCO ₃ , 2 h			(41)	402
C ₁₉		Oxone®, acetone, H ₂ O, 60°, 12 h			(91)	403
207						
C ₂₀₋₂₆		Oxone®, acetone, H ₂ O, CH ₂ Cl ₂ , NaHCO ₃ , rt, 2-7 h			R Et (98) 93 i-Pr (98) 99 t-Bu (97) 91 n-Bu (98) 93 Ph (96) 95 4-MeOC ₆ H ₄ (88) 88 PhCH ₂ CH ₂ (98) 95	404

TABLE 3G. SULFUR OXIDATION BY IN SITU GENERATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₇		Oxone®, acetone, MeCN, H ₂ O, NaHCO ₃ , 5°, 20 h		(51) dr 58:42 405
208				
C ₂₉		Oxone® (1.2 eq), MeOH, -20°, 2-5 min		(—) 406
		Oxone® (3 eq), MeOH, rt		(—) 406
C ₃₁		Oxone®, acetone, buffer (pH 7.5-8.0), NaHCO ₃ , EDTA, rt		(96) 398

TABLE 3H. OXIDATION OF OTHER HETEROATOMS BY IN SITU GENERATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₀				
Cl ⁻	Oxone®, ketone, buffer (pH 9.0)		OCl ⁻ (—)	161
		Ketone	<i>k</i> _{rel}	
	—	—	< 0.1	
	acetone	—	1.0	
	cyclohexanone	—	6.1	
	<i>N,N</i> -dimethyl-4-oxopiperidinium nitrate	—	1300	
ONO ₂ ⁻	AcCO ₂ Me, phosphate buffer (pH 7.4)		NO ₂ ⁻ (—) + NO ₃ ⁻ (—) I (—) + II (—)	163
	AcCOMe, phosphate buffer (pH 7.4)		I (—) + II (—)	163
	Oxone®, ketone, buffer (pH = 9.0)		SO ₄ ²⁻ (—) + O ₂ (—)	161
		Ketone	<i>k</i> _{rel}	
	—	—	< 0.1	
	acetone	—	1.0	
	cyclohexanone	—	9.4	
	<i>N,N</i> -dimethyl-4-oxopiperidinium nitrate	—	1400	
C ₁₈	Ph ₃ P	Oxone®, acetone, phosphate buffer, KOH, < 0°, 10 min	Ph ₃ P=O (—)	121

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C _{3,9}		1. <i>t</i> -BuOK, THF, 20°, 5 min 2. DMD, H ₂ O, acetone, 20°, 5 min		407
C ₅		DMD, acetone, rt, min		103
		DMD, acetone, rt		408
C _{5,9}	R-N≡•=S	1. DMD, acetone, N ₂ , rt, 15 min 2. Isopropylamine, 0°, 1.5 h		409
210		1. <i>t</i> -BuOK, THF, 20°, 5 min 2. DMD, H ₂ O, acetone, 20°, 5 min		107
C _{5,23}		DMD, acetone, rt		105

R ₁	R ₂	Time	Product	
Me	Me	16 h	II (95)	
Me	EtO	10 h	I (100)	
—(CH ₂) ₃ —		26 h	I (93)	
EtO	EtO	29 h	II (100)	
—CH ₂ C(Me) ₂ CH ₂ —		20 h	II (89)	
—(1,2-C ₆ H ₄)—		20 h	II (100)	
Me	Ph	24 h	II (98)	
OEt	Ph	35 h	I (94)	
Ph	Ph	(—)-menthO =	II (100)	
(—)-menthO	(—)-menthO	30 h	II (100)	
		10 h	II (100)	
C ₆		DMD, acetone, rt, 2 h		106
211		DMD, acetone, rt, min		103
		1. BuLi, THF, Ar, -70°, 5 min 2. DMD, acetone, H ₂ O, THF, Ar, -70°, 6 min		407
		DMD, H ₂ O, -70°, 15 min		410

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.																																																																																																														
C ₇		DMD, acetone, rt, min		103																																																																																																														
		DMD, acetone, rt, min		103																																																																																																														
212		1. <i>n</i> -BuLi, THF, Ar, -70°, 5 min 2. DMD, acetone, H ₂ O, -70°, 5 min		111																																																																																																														
		DMD, acetone, rt, 1 h		411																																																																																																														
		DMD, acetone, 0°, 30 min		411																																																																																																														
		DMD, H ₂ O, -70°, 15 min		410																																																																																																														
		DMD, H ₂ O, -70°, 15 min		410																																																																																																														
C ₇₋₂₃		DMD, H ₂ O, -70°, 15 min		410																																																																																																														
213		DMD, acetone, THF, Ar, 20°, 5 min		413																																																																																																														
	<table border="1"> <thead> <tr> <th>R¹</th><th>R²</th><th>Z</th><th>I</th><th>II</th><th>III</th><th>IV</th></tr> </thead> <tbody> <tr> <td>Me</td><td>Me</td><td>H</td><td>(—)</td><td>(85)</td><td>(—)</td><td>(—)</td></tr> <tr> <td>H</td><td>SO₂Ph</td><td>H</td><td>(—)</td><td>(—)</td><td>(—)</td><td>(60)</td></tr> <tr> <td>Me</td><td>SO₂Ph</td><td>H</td><td>(—)</td><td>(—)</td><td>(—)</td><td>(33)</td></tr> <tr> <td>Ph</td><td>CO₂Me</td><td>H</td><td>(—)</td><td>(63)</td><td>(—)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>Ph</td><td>2-Cl</td><td>(58)</td><td>(30)</td><td>(—)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>Ph</td><td>3-Cl</td><td>(61)</td><td>(10)</td><td>(—)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>Ph</td><td>2-I</td><td>(33)</td><td>(38)</td><td>(—)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>Ph</td><td>H</td><td>(51)</td><td>(28)</td><td>(18)</td><td>(—)</td></tr> <tr> <td>—(9-fluorenyl)—</td><td>H</td><td></td><td>(—)</td><td>(99)</td><td>(—)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>Ph</td><td>3-CN</td><td>(64)</td><td>(—)</td><td>(—)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>Ph</td><td>2-MeO</td><td>(58)</td><td>(36)</td><td>(—)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>Ph</td><td>3-MeO</td><td>(44)</td><td>(13)</td><td>(30)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>4-ClC₆H₄</td><td>3-MeO</td><td>(40)</td><td>(26)</td><td>(33)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>1-Naph</td><td>H</td><td>(75)</td><td>(20)</td><td>(—)</td><td>(—)</td></tr> <tr> <td>Ph</td><td>Ph</td><td>(CH)₄</td><td>(91)</td><td>(—)</td><td>(—)</td><td>(—)</td></tr> </tbody> </table>	R ¹	R ²	Z	I	II	III	IV	Me	Me	H	(—)	(85)	(—)	(—)	H	SO ₂ Ph	H	(—)	(—)	(—)	(60)	Me	SO ₂ Ph	H	(—)	(—)	(—)	(33)	Ph	CO ₂ Me	H	(—)	(63)	(—)	(—)	Ph	Ph	2-Cl	(58)	(30)	(—)	(—)	Ph	Ph	3-Cl	(61)	(10)	(—)	(—)	Ph	Ph	2-I	(33)	(38)	(—)	(—)	Ph	Ph	H	(51)	(28)	(18)	(—)	—(9-fluorenyl)—	H		(—)	(99)	(—)	(—)	Ph	Ph	3-CN	(64)	(—)	(—)	(—)	Ph	Ph	2-MeO	(58)	(36)	(—)	(—)	Ph	Ph	3-MeO	(44)	(13)	(30)	(—)	Ph	4-ClC ₆ H ₄	3-MeO	(40)	(26)	(33)	(—)	Ph	1-Naph	H	(75)	(20)	(—)	(—)	Ph	Ph	(CH) ₄	(91)	(—)	(—)	(—)	
R ¹	R ²	Z	I	II	III	IV																																																																																																												
Me	Me	H	(—)	(85)	(—)	(—)																																																																																																												
H	SO ₂ Ph	H	(—)	(—)	(—)	(60)																																																																																																												
Me	SO ₂ Ph	H	(—)	(—)	(—)	(33)																																																																																																												
Ph	CO ₂ Me	H	(—)	(63)	(—)	(—)																																																																																																												
Ph	Ph	2-Cl	(58)	(30)	(—)	(—)																																																																																																												
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Ph	Ph	H	(51)	(28)	(18)	(—)																																																																																																												
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Ph	Ph	2-MeO	(58)	(36)	(—)	(—)																																																																																																												
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Ph	4-ClC ₆ H ₄	3-MeO	(40)	(26)	(33)	(—)																																																																																																												
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Ph	Ph	(CH) ₄	(91)	(—)	(—)	(—)																																																																																																												

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇₋₁₇		DMD, acetone, -35°, 15-30 min		412
	R = Et, i-Bu, c-C ₅ H ₉ , n-C ₆ H ₁₃ , Ph, 3-BrC ₆ H ₄ , 4-FC ₆ H ₄ , 2-MeOC ₆ H ₄ , 4-MeOC ₆ H ₄ , 3-CF ₃ C ₆ H ₄ , 4-PhC ₆ H ₄			
C ₈		DMD, H ₂ O, -70°, 15 min		410
			(22) + (4) + (23)	
		DMD, H ₂ O, -70°, 15 min		410
		DMD, acetone, rt, min		103
214		DMD, acetone, rt, 24 h		411
		DMD, acetone, CH ₂ Cl ₂ , 0°, 1 min		106
		DMD, acetone, rt, min		103
C ₉		DMD, acetone, CH ₂ Cl ₂ , 20°, 3 min		414
		DMD, acetone, 0°, 2-3 min		113
		1. DMD (3 eq), acetone, CH ₂ Cl ₂ , -25° 2. rt, 12-15 h		315
		1. DMD (6 eq), acetone, CH ₂ Cl ₂ , -25° 2. rt, 12-15 h		315
		DMD, acetone, 0°, 2-3 min		113
		1. t-BuOK, THF, rt, 5 min 2. DMD, acetone, H ₂ O, -70°, 7 min		407
		DMD, acetone		104
215		DMD, acetone, 0°, 2-3 min		113
				407
				104
C ₉₋₁₀		DMD, acetone, 0°, 2-3 min		113
C ₉₋₁₄		DMD, acetone		104

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

TABLE II. C=O OXIDATION BY ISOLATED DIOXIRINES (continued)				Refs.
	Substrate	Conditions	Product(s) and Yield(s) (%)	
C ₁₀		DMD, acetone, rt, 2 h	 I + II (—), I:II = 70:30	106
		DMD, acetone, rt, 2 h	 I + II + III (—), I:(II+III) = 30:70	106
		DMD, acetone, rt, 24 h	 (97)	411
		DMD, acetone, 0°, 5 min	 (100)	411
		DMD, acetone, rt, 0.5 h	 (31)	22
		DMD, acetone, 0°, 30 min	 (98)	411
		DMD, acetone, 0°, 10 min	 (94)	411
C ₁₀₋₁₂		1. t-BuOK, THF, Ar, -70°, 15 min 2. DMD, acetone, H ₂ O, THF, Ar, -70°, 15 min	 I : II :	415
C ₁₁		DMD, acetone, 0°, 2-3 min	 (92)	113
		DMD, acetone, CH ₂ Cl ₂ , 0°, 1 h	 (—)	102
		DMD, acetone, 0°, 2-3 min	 (97)	113
C ₁₂		DMD, acetone, H ₂ O, 0°, 1.5 h, rt, overnight	 (45)	416
		DMD, acetone	 (—)	104

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂		DMD, acetone, rt	(100)	103
		DMD, acetone (or TFD, TFP), CH ₂ Cl ₂		414
218		DMD, acetone	(—)	104
		DMD, acetone, rt, 1 h	(100)	411
		DMD, acetone, 0°, 2-3 min	(92) 98% ee	113
C ₁₂₋₁₅		DMD, acetone	(—) R CO ₂ Bu- <i>t</i> or CO ₂ Bn	104
C ₁₃		DMD, acetone, rt	(100)	106
		DMD, acetone, rt	(100)	106
		DMD, acetone, CH ₂ Cl ₂ , 0°, 5 min	(85) 92% ee + I (30)	414
		1. <i>t</i> -BuOK, THF, 20°, 5 min 2. DMD, acetone, 20°, 5 min	I (76)	111
219		DMD, acetone, rt, 48 h	(—)	411
		DMD, acetone	(—)	104
C ₁₃₋₁₅		DMD, acetone, CH ₂ Cl ₂ , R ³ NH ₂ , rt	 R ¹ R ² R ³ H H H (81) H H Me (58) H H Et (78) H H 4-MeC ₆ H ₄ (79) Me H H (77) Me H Me (73) Me H Et (61) Me H 4-MeC ₆ H ₄ (68) H OAc H (90) H OAc Me (72) H OAc Et (72) H OAc 4-MeC ₆ H ₄ (76) H OAc 2,6-(Me) ₂ C ₆ H ₃ (81)	144

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

220

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₁₄		DMD, acetone, rt		(100)	106
		DMD, acetone, rt		(100)	106
C ₁₅		DMD, acetone, CH ₂ Cl ₂ , 20°		$\frac{R}{NO_2}$ 2 h (82) H 30 min (92)	414
		DMD, H ₂ O		(81)	417
221		DMD, H ₂ O, DMF, THF, acetone, Ar, -70°, 5 min		(72)	110
		DMD, H ₂ O, DMF, THF, acetone, Ar, -70°, 5 min		(69-77)	110
221		DMD, H ₂ O, DMF, THF, acetone, Ar, -70°, 5 min		(87) + (3)	110
		DMD, H ₂ O, DMF, THF, acetone, Ar, -70°, 5 min		(81) + (7)	110
		DMD, acetone, THF, Ar, -70°, 5 min		(25) I	407
		DMD, acetone, H ₂ O, THF, Ar, -70°, 5 min	I (—)	—	407
221		DMD, H ₂ O (x eq), DMF, THF, acetone, Ar, -70°, 5 min		I	110
				II	—
			$\frac{x}{0}$ 0 0.5 1.0	$\frac{I}{(47)} \quad \frac{II}{(6)}$ $\frac{(71)}{(5)}$ $\frac{(77-83)}{(4-6)}$	—

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C ₁₅		Dioxirane, THF, Ar, -70°, 5 min			111
		Dioxirane Solvent	I	II	
	DMD acetone —	(trace)	(trace)		
	DMD acetone H ₂ O	(77-83)	(4-6)		
	DMD acetone MeOH	(33-63)	(4-5)		
	TFD TFP —	(38)	(10)		
	TFD TFP H ₂ O	(32)	(9)		
222		DMD, acetone, THF, Ar, -70°, 5 min		(—) K _H /K _D = 1.01 ± 0.01	111
	DMD, acetone, CH ₂ Cl ₂ , additive, rt				144
	Additive	R	I	II	
	—	H	I + II (95)	I:II = 1:1	
	MeOH	Me	(22)	(70)	
	EtOH	Et	(18)	(65)	
	n-PrOH	n-Pr	(15)	(70)	
	n-BuOH	n-Bu	(20)	(75)	
C ₁₅₋₁₈		1. DMD, acetone, CH ₂ Cl ₂ , rt 2. RNH ₂ , MeOH, rt		R	144
				H (73) Me (64) Et (75) n-Pr (55) n-Bu (58) 4-MeC ₆ H ₄ (69)	
	DMD, acetone			(—)	104
223	C ₁₆ 	DMD, acetone, H ₂ O, THF, Ar, -70°, 5 min		(76)	407
		DMD, acetone, H ₂ O, THF, Ar, -70°, 5 min		(73)	407
		DMD, acetone, H ₂ O, THF, Ar, -70°, 5 min		(28)	407

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₁₇		DMD, acetone		(—)	104
C ₁₈		DMD, acetone, rt, 2 h		(97)	418
224		DMD, acetone, CH ₂ Cl ₂ , MeNH ₂ , rt		(83)	116, 117, 118, 119, 120, 144
C ₁₉		DMD, acetone, H ₂ O, THF, Ar, -70°, 5 min		(65)	407
		DMD, acetone, solvent, Ar, 20°, 5 min		I II III	27
C ₂₁₋₂₂		Solvent	% Conv. I:II:III		
	THF	83 17:63:16			
	THF	88 33:47:16			
	THF	95 48:26:17			
	THF	96 0:80:3			
	THF	97 0:95:0			
	DMF	93 29:60:8			
	THF/DMF (3:1)	91 37:45:14			
	toluene	90 51:33:15			
225		DMD, acetone, CH ₂ Cl ₂ , TsOH, rt, 10 min		Z I II	417
C ₂₂		1. N,N,N',N'-Tetramethylguanidine, CH ₂ Cl ₂ , 0° 2. DMD, acetone		(78)	419
C ₂₃		DMD, acetone		(—)	104

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₂₄		1. <i>t</i> -BuOK, THF, H ₂ O 2. DMD, acetone		109
C ₂₆		DMD, MeOH, acetone, rt		420
226		DMD, MeOH, acetone, rt		420
		DMD, MeOH, acetone, rt		420
C ₂₆₋₂₈		DMD, acetone, CH ₂ Cl ₂ , rt, 1 h		159
C ₂₇		DMD, acetone, CH ₂ Cl ₂ , 20°, 15 min		414
227		DMD, MeOH, acetone, rt		420
		DMD, BnNH ₂ , CH ₂ Cl ₂ , acetone, -78°		420
		DMD, H ₂ N- <i>i</i> -CO ₂ Me, CH ₂ Cl ₂ , acetone, -78°		420
C ₂₈		DMD, acetone, CH ₂ Cl ₂ , 20°, 1 h		414
C ₂₈₋₃₂		DMD, MeOH, acetone, rt		420
C ₃₀		DMD, acetone, CH ₂ Cl ₂ , additive, rt		144
		Additive	I (43) II (20) III (—)	
		—	(37) (26) (—)	
		ROH	(24) (15) (—)	
		RNH ₂	(38) (22) (8)	
		—		

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃₀		DMD (2.4 eq), MeOH, acetone, 0°		420
		DMD, MeOH, acetone, rt		420
C ₃₆		DMD, acetone, MeOH		159
228				
C ₃₈		DMD, MeOH, acetone, 0°		420

TABLE 4B. C=Y OXIDATION BY IN SITU GENERATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																	
C ₄₋₁₃		Oxone®, wet alumina, microwave	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>n-Pr</td> <td>(84)</td> </tr> <tr> <td>—(CH₂)₅—</td> <td></td> <td>(87)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(95)</td> </tr> <tr> <td>2-O₂NC₆H₄</td> <td>H</td> <td>(99)</td> </tr> <tr> <td>4-O₂NC₆H₄</td> <td>H</td> <td>(98)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>(89)</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>H</td> <td>(94)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>H</td> <td>(90)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>Me</td> <td>(82)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(86)</td> </tr> </tbody> </table>	R ¹	R ²		Me	n-Pr	(84)	—(CH ₂) ₅ —		(87)	Ph	H	(95)	2-O ₂ NC ₆ H ₄	H	(99)	4-O ₂ NC ₆ H ₄	H	(98)	Ph	Me	(89)	4-MeC ₆ H ₄	H	(94)	4-MeOC ₆ H ₄	H	(90)	4-MeOC ₆ H ₄	Me	(82)	Ph	Ph	(86)	421
R ¹	R ²																																				
Me	n-Pr	(84)																																			
—(CH ₂) ₅ —		(87)																																			
Ph	H	(95)																																			
2-O ₂ NC ₆ H ₄	H	(99)																																			
4-O ₂ NC ₆ H ₄	H	(98)																																			
Ph	Me	(89)																																			
4-MeC ₆ H ₄	H	(94)																																			
4-MeOC ₆ H ₄	H	(90)																																			
4-MeOC ₆ H ₄	Me	(82)																																			
Ph	Ph	(86)																																			
C ₅₋₁₁		Oxone® (3 eq), dioxane, H ₂ O, 12 h	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>(98)</td> <td>(95)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(83)</td> <td>(78)</td> </tr> <tr> <td>H</td> <td>CH₂CO₂Et</td> <td>(78)</td> <td>(65)</td> </tr> <tr> <td>H</td> <td>Bn</td> <td>(85)</td> <td>(70)</td> </tr> </tbody> </table>	R ¹	R ²	I	II	H	Me	(98)	(95)	Me	Me	(83)	(78)	H	CH ₂ CO ₂ Et	(78)	(65)	H	Bn	(85)	(70)	422													
R ¹	R ²	I	II																																		
H	Me	(98)	(95)																																		
Me	Me	(83)	(78)																																		
H	CH ₂ CO ₂ Et	(78)	(65)																																		
H	Bn	(85)	(70)																																		
		Merrifield resin																																			
		Oxone® (3 eq), MeOH, 12 h	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>(95)</td> <td>(96)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(72)</td> <td>(70)</td> </tr> <tr> <td>H</td> <td>CH₂CO₂Et</td> <td>(67)</td> <td>(56)</td> </tr> <tr> <td>H</td> <td>Bn</td> <td>(77)</td> <td>(73)</td> </tr> </tbody> </table>	R ¹	R ²	I	II	H	Me	(95)	(96)	Me	Me	(72)	(70)	H	CH ₂ CO ₂ Et	(67)	(56)	H	Bn	(77)	(73)	422													
R ¹	R ²	I	II																																		
H	Me	(95)	(96)																																		
Me	Me	(72)	(70)																																		
H	CH ₂ CO ₂ Et	(67)	(56)																																		
H	Bn	(77)	(73)																																		

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	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄		Oxone®, acetone, NaHCO ₃ , H ₂ O, 0°, 1 h		423
C ₃₀		Oxone®, dioxane, H ₂ O, 12 h		422
		Merrifield resin		

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TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2		DMD, acetone, rt, 2 h		121
		DMD, 2-Me-quinoline, CF_3CO_2H , 0° , 8 h		35
C_3		DMD, acetone, rt, 2 h		121
		TFD, TFP, CH_2Cl_2 , -20° , 8 min		29
C_{3-11}		DMD, acetone, 20°		424
	R^1	R^2	n	$k \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$
	H	H	1	4.83 ± 0.35
	<i>n</i> -Pr	H	1	33.0
	<i>i</i> -Pr	H	1	24.8 ± 1.2
	H	Me	2	0.61 ± 0.06
	<i>i</i> -Pr	H	2	0.74 ± 0.01
	<i>i</i> -Pr	Me	2	1.36 ± 0.09
	Ph	H	1	45.0 ± 2.2
	Ph	H	2	3.2 ± 0.05
	Ph	Me	2	9.25 ± 0.42

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TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4		DMD, 2-Me-quinoline, CF_3CO_2H , acetone, 0° , 8 h		35
		DMD, acetone, CH_2Cl_2 , 0° , 70 h		191
		TFD, TFP, CH_2Cl_2 , 0° , 10 min		191
		TFD, TFP, CH_2Cl_2 , -20° , 10 min		29
		TFD, TFP, CH_2Cl_2 , -20° , 20 min		29
		TFD, TFP, CH_2Cl_2 , -20° , 4 min		29
		TFD, TFP, CH_2Cl_2 , -20° , 12 min		29
		TFD, TFP, CH_2Cl_2 , -20° , 12 min		29

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	DMD, 2-Me-quinoline, CF ₃ CO ₂ H, acetone, 0°, 8 h		(12) + (1.2) + (3.2)	35
	TFD, TFP, -20°, 30 min		EtOH + CH ₃ CHO + CH ₃ CO ₂ H + AcOEt + AcOMe + CF ₃ CO ₂ H + CF ₃ CO ₂ Me + CF ₃ CO ₂ Et + AcOCF ₃	(—) 187
	TFD, TFP, CH ₂ Cl ₂ , -20°, 10 min	n-PrCO ₂ H (89) +	(8)	29
	DMD, acetone, rt, overnight		(85) + (5)	269
	DMD, CH ₂ Cl ₂ , acetone, 0°, 4 h		(92) > 98% ee	184

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.
	DMD, acetone; or TFD, TFP		I	II		425
x	Dioxirane (M)	Temp	Time	% Conv.	I	II
0.181	DMD (0.018)	20°	60 min	40	(89)	(11)
0.181	DMD (0.018)	20°	150 min	75	(70)	(30)
0.181	DMD (0.002)	20°	15 min	60	(> 99)	(—)
0.181	DMD (0.002)	20°	27 min	82	(> 99)	(—)
0.028	DMD (0.024)	20°	150 min	70	(> 99)	(—)
0.028	DMD (0.002)	20°	120 min	25	(> 99)	(—)
0.033	DMD (0.002)	20°	90 min ^a	35	(> 99)	(—)
0.209	TFD (0.002)	0°	5 min	95	(79)	(21)
0.002	TFD (0.001)	0°	30 min	35	(92)	(8)
	1. aq. HBF ₄ , MeCN, (pH 2-3), 0° 2. TFD, CH ₂ Cl ₂ , rt, 3 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h			(90)		192
	1. aq. HBF ₄ , MeCN, (pH 2-3), 0° 2. TFD, CH ₂ Cl ₂ , rt, 10 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h			(93)		192
	TFD, TFP, Et ₂ O, -20°		(—) + other products			187
	TFD, CCl ₄ , 0°, 10 min			(90)		191
	DMD, acetone, rt, overnight			(95)		269

	TFD, TFP, CH ₂ Cl ₂ , 0°, 15 min		(77) + (8)	191
	DMD, 4-Me-quinoline, CF ₃ CO ₂ H, 0°, 8 h		(60) + (26) + (0.4) + (1.1)	35
	TFD, TFP, CH ₂ Cl ₂ , -20°, 15 min		(94)	29
	TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 15 min		(90)	426
	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , 0°, 6 h		(86)	426
	TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 15 min		(I) (92)	426
	TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 20 min		(I) (88)	426

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₅		DMD (1.5 eq), acetone, CH ₂ Cl ₂ , 0°, 3 h		426
		TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 20 min		426
C ₅₋₈		DMD, acetone, rt, 1-2 d		427
236		DMD, acetone, 20°		424
	R ¹ Me Me H 1 Me Me CH ₂ OH 1 Me Me Me 2 —(CH ₂) ₅ — H 1		$k \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ 0.38 ± 0.05 0.54 ± 0.04 0.42 ± 0.01 9.25 ± 0.42	
C ₅₋₁₃	1-C(=O)-C(OH)-C(=O)-R ³)"/>	194		

R ₁	R ²	R ³	Catalyst	Time	% Conv.	
OMe	H	OMe	—	24 h	15	
OMe	H	OMe	Ni(OAc) ₂	16 h	>95	
—O(CH ₂) ₂ —	Me	—	—	3.5 h	90	
—O(CH ₂) ₂ —	Me	—	Ni(acac) ₂	3.5 h	>95	
Me	H	OEt	—	24 h	35	
Me	H	OEt	Ni(OAc) ₂	24 h	>95	
—O(CH ₂) ₂ —	OEt	—	—	5 h	46	
—O(CH ₂) ₂ —	OEt	—	Ni(OAc) ₂	5 h	84	
—(CH ₂) ₃ —	OEt	—	—	3.5 h	75	
—(CH ₂) ₃ —	OEt	—	Ni(acac) ₂	3.5 h	>95	
OEt	Me	OEt	—	120 h	—	
OEt	Me	OEt	Ni(OAc) ₂	12 h	47	
—(CH ₂) ₄ —	Et	—	—	3 h	88	
—(CH ₂) ₄ —	Et	—	Ni(OAc) ₂	3 h	90	
Me	Bn	OEt	—	4.25 h	11	
Me	Bn	OEt	Ni(acac) ₂	4.25 h	78	

C ₆	Substrate	Reagents	Product(s)	Yield (%)	Ref.
		TFD, TFP, CH ₂ Cl ₂ , -12.5°		(—) $k_H/k_D = 1.6 \pm 0.15$	29
		DMD (3.0 eq), acetone, 20°, 72 h		(98)	193
	$\xrightarrow[\text{N}_3]{\text{R}^1}$ $\xrightarrow[\text{OH}]{\text{R}^2}$	DMD, acetone, rt, 24 h		(>95)	428

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆		TFP, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 10 min	(>99)	172
		DMD, CCl ₃ Br, acetone, (O ₂)	(+) + I (—)	429
		TFD, TFP, CH ₂ Cl ₂ , -22°, 18 min	I (98)	30, 173
		TFD, TFP, -20°, 30 min	I (95)	173
		DMD, acetone, rt	(30-50)	429
		TFD, TFP, CH ₂ Cl ₂ , -20°, 20 min	I (97)	29
		DMD, acetone, O ₂ , 22°, 6 h	I (—)	35
		DMD, acetone, Ar, 22°, 6 h	I (45) + AcOME (27.2) + MeOH (13.5) + AcOCH ₂ Ac (12.1) + CH ₄ (—)	34, 35
		DMD, acetone, CH ₂ Cl ₂ , 18°, 96 h	I (9) + II (17)	191
		TFD, TFP, CH ₂ Cl ₂ , -10°, 15 min	I (32) + II (49)	191

	DMD (3.0 eq), acetone, 20°, 72 h		(-)	430
	TFD, TFP, CH ₂ Cl ₂ , 0°, 30 min		(62)	191
	DMD, CH ₂ Cl ₂ , acetone, 0°, 8 h		(> 96) 94% ee	184
	DMD, acetone, rt, overnight		(80-90)	269
	DMD, acetone, rt, overnight		(92)	269
	DMD, acetone, rt, overnight		(53) +	269
	1. aq. HBF ₄ , MeCN, (pH 2-3), 0° 2. TFD, CH ₂ Cl ₂ , rt, 15 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h		(54)	192
	TFD, TFP, CH ₂ Cl ₂ , -22°, 3 min		(98)	30

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₆ 	TFP, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 40 min		(58) +	(42) 172
i-PrO-Pr-i	DMD, acetone, Ar, 22°, 6 h	CH ₄ (-) +	(38.4) + MeOH (12.1)	34, 35
	DMD, acetone, DEK, Ar, 22°, 6 h		(2.1) +	(9.6) 35
	DMD, acetone, rt, overnight		(50) +	(25) 269
	1. aq. HBF ₄ , MeCN (pH 2.0-3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 8 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h		(88) 192	
	DMD (1.6 eq), acetone, CH ₂ Cl ₂ , 0°, 6 h		(83) II 426	
	TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 20 min	II (88)	426	
	TFD (3.0 eq), acetone, 0°, 3 h		(67) 426	

C ₆₋₈		DMD, acetone, rt		428
	$\begin{array}{c} \text{R} \\ \\ \text{OH} \\ \\ \text{OMe} \\ \\ \text{OAc} \end{array}$	Time 24 h	$\begin{array}{c} \text{I} \\ \text{II} \\ \text{III} \end{array}$ (50) (0) (0) (0) (0) (0) (0) (50) (50)	
C ₆₋₁₆		Dioxirane (x eq), 0°		431
	$\begin{array}{c} \text{R} \\ \\ \text{OH} \\ \\ \text{R} \\ \\ \text{OH} \end{array}$	Time 24 h	$\begin{array}{c} \text{I} \\ \text{II} \\ \text{III} \end{array}$ (50) (0) (0) (0) (0) (0) (0) (50) (50)	
241		Dioxirane x Solvent Time % Conv. I II		
	$\begin{array}{c} \text{R} \\ \\ \text{Me} \\ \\ \text{Me} \\ \\ \text{Me} \\ \\ \text{Ph} \\ \\ \text{Me} \\ \\ \text{Me} \\ \\ \text{Ph} \end{array}$	DMD 1 CH ₂ Cl ₂ , acetone 3 h 60 (—) (98)		
C ₇		DMD 3 CH ₂ Cl ₂ , acetone 6 h 95 (3) (95)		
		DMD 3 acetone 6 h 95 (65) (20)		
		DMD 3 acetone 6 h 95 (70) (30)		
		TFD 3 CH ₂ Cl ₂ , TFP 0.5 h 95 (74) (—)		
		TFD 3 acetone 0.3 h 95 (90) (—)		
		TFD 3 acetone 0.3 h 95 (96) (—)		
		TFD, TFP, CH ₂ Cl ₂ , -20°		29
		Time I II		
		30 min (43) (2)		
		60 min (48) (11)		
		90 min (5) (83)		
		DMD, acetone, 0°		432
		% Conv. k _H /k _D		
		8 4.5 ± 0.2		
		23 4.6 ± 0.2		

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇		DMD, acetone, 0°		432
		Time I II		
		7 4.4 ± 0.2		
		18 4.5 ± 0.2		
		TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 20 min		433
		(40) + (4)		
		1. aq. HBF ₄ , MeCN, (pH 2.0-3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 3 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h		192
		(97)		
		1. aq. HBF ₄ , MeCN, (pH 2.0-3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 10 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h		192
		(96)		
		1. aq. HBF ₄ , MeCN, (pH 2.0-3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 8 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h		192
		(94)		
		DMD, acetone, rt, overnight		434
		(75)		
		TFD, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 40 min		172
		(5) + (95)		

	TFD, TFP, CH ₂ Cl ₂ , -22°, 90 min		(14)	30
	DMD, acetone		(23)	435
	TFD, TFP, CH ₂ Cl ₂ , -20°, 2 min		(95)	29
	DMD (3.0 eq), acetone, 20°, 72 h		(37)	436
	1. aq. HBF ₄ , MeCN, (pH 2.0-3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 5 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h		(96)	192
	TFD, TFP, -20°, 45 min		I (6) + II (12) + III (12)	173
	TFD, TFP, CH ₂ Cl ₂ , -22°, 70 min		I (18) + II (40) + III (40)	30, 173
	DMD, acetone, CH ₂ Cl ₂ , 0°, 2 h		> 95%	191

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<i>C</i> ₇		DMD, acetone, rt, 4 d		437
		TFD, TFP, CH ₂ Cl ₂ , -22°, 8 min		30
		TFD, TFP, CH ₂ Cl ₂ , 0°, 40 min		190
		TFD, TFP, CH ₂ Cl ₂ , 0°, 20 min		190
<i>C</i> ₇₋₈		DMD, acetone, rt, dark, 18 h R = Br, NO ₂ , H, CN, Me, MeO		438
		DMD, acetone, rt, dark, N ₂ or Ar R = Br, NO ₂ , H, MeO		438
<i>C</i> ₇₋₁₀		1. TFD, CH ₂ Cl ₂ , -40° 2. (CF ₃ CO) ₂ O		439

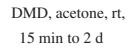
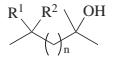
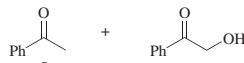
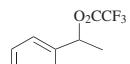
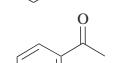
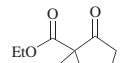
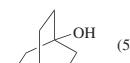
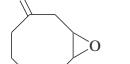
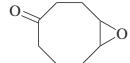
				(—)	427	
	BnCHO	DMD, acetone, O ₂ , 20°, 6 h		(0.75)	35	
		DMD, acetone, Ar, 20°, 6 h	I (1.98) + BnOAc II (4.02) + AcOMe (2.52) + MeOH (0.546) + AcOCH ₂ Ac (0.504) + CH ₄ (—)		35	
		DMD, acetone, Ar, 60°, 6 h	I + II (—), I:II = 13:87		35	
		DMD, acetone, 20°	I (—)		168	
		DMD, acetone, N ₂ (Ar), 20°	I (2) + II (4)		168	
		DMD, acetone, N ₂ , 60°	I (2) + II (14)		168	
		DMD, acetone, rt, 30 min		(80)	176	
		DMD, acetone, rt			175	
	R ¹ R ² k _H /k _D					
	H H —		 (73)	 (2)	2.24±0.06	
	D H 3.55				(70) (3.5)	0.63±0.02
	H D 1.09				(70) (2)	2.05±0.06

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFD, TFP, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 20 min		172
	TFD, TFP, CH ₂ Cl ₂ , 0°, 80 min		30
	TFD, TFP, CH ₂ Cl ₂ , -20°, 20 min	I (97)	29
	DMD (3.0 eq), acetone, 20°, 72 h		193
	TFP, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 2 min		172
	TFD, TFP, CH ₂ Cl ₂ , -22°, 2 min		30
	DMD (2.1 eq), acetone, CH ₂ Cl ₂ , 20°, 24 h		440
	DMD (2.2 eq), acetone, CH ₂ Cl ₂ , 20°, 24 h		440

	DMD, acetone, CH ₂ Cl ₂ , 0°, 24 h	 I (33)	191
	TFD, TFP, CH ₂ Cl ₂ , 0°, 2 h	 I (98)	191
	TFD, TFP, CH ₂ Cl ₂ , 0°, 15 min	 I (96)	182
	DMD, acetone, CH ₂ Cl ₂ , 0°, 4 h	 I (65)	182
	DMD, acetone, 22°, dark, 18 h	 I (45)	174
	TFD, TFP, CH ₂ Cl ₂ , -22°, 10 min	 I (90) + (5) + (4)	30
	DMD, acetone, 22°, dark, 18 h	 I (100)	174
	TFD, TFP, CH ₂ Cl ₂ , -22°, 4 min	 I (95)	30
	DMD, acetone/solvent (v/v = 1:1), rt	 (→) Solvent k ₂ (x 10 ⁻³ M ⁻¹ s ⁻¹) acetone 1.37±0.03 2-butanol 1.29±0.01 EtOAc 1.02±0.02 CH ₂ Cl ₂ 3.08±0.06 CHCl ₃ 4.44±0.13 CDCl ₃ 4.05±0.04	441

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₈		TFP, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 60 h	 (> 99)	172	
		TFD, TFP, CH ₂ Cl ₂ , -20°, 20 min	 (99)	29	
		1. aq. HBF ₄ , MeCN, (pH 2.0–3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 8 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h	 (88)	192	
248		DMD, acetone, 0°	 (—) + (—)	% Conv. k _H / k _D 6 1.00 ± 0.02 11 0.99 ± 0.02 18 1.01 ± 0.02 32 0.98 ± 0.02	432
		TFD (1.2 eq), TFP, CH ₂ Cl ₂ , 0°, 35 min	 (38)	433	
		DMD (1.5 eq), acetone, CH ₂ Cl ₂ , 0°, 6 h	 I (77)	427	
		TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 10 min	 I (86)	427	

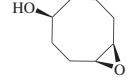
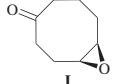
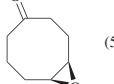
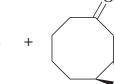
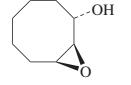
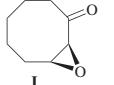
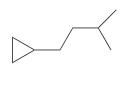
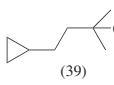
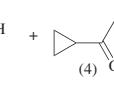
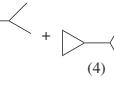
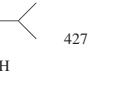
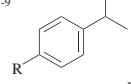
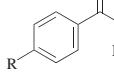
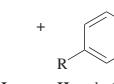
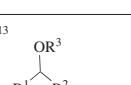
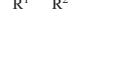
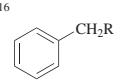
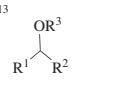
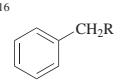
	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , 0°, 6 h TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 10 min	 I (93)	427
	TFD (4.0 eq), acetone, 0°, 2 h	 (57) +  (19)	427
	DMD (1.6 eq), acetone, CH ₂ Cl ₂ , 0°, 3 h TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 10 min	 I (91)	427
	TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 30 min	 I (94) +  (39) +  (4) +  (4)	427
	DMD, acetone, rt, 3 h	 I +  II	175
		I (96) II (3) $k_2 \times 10^{-2} \text{ Mol}^{-1} \text{ s}^{-1}$ (1.51±0.04) (97) (3) 1.59±0.04 (97) (2) 1.85±0.04 (98) (2) 2.24±0.06 (97) (2) 2.89±0.06 (97) (3) 3.56±0.08 (97) (2) 0.76±0.04	
			
			
			
			
			
			
			
			
			
			
			
			
			
			
			

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.	
	DMD, acetone, rt		R ¹	R ²	R ³	175
			Ph	Me	H (98)	
			Ph	Et	H (92)	
			Ph	n-Pr	H (92)	
			Ph	i-Pr	H (90)	
			Ph	t-Bu	H (90)	
			Ph	Ph	H (96)	
			Ph	c-C ₃ H ₅	H (92)	
			Bn	Me	H (85)	
			Ph	Me	Me (90)	
			Ph	Et	Me (81)	
			Ph	n-Pr	Me (86)	
			Ph	i-Pr	Me (48)	
			Ph	t-Bu	Me (24)	
			Ph	Ph	Me (84)	
			Ph	c-C ₃ H ₅	Me (88)	
			Bn	Me	Me (80)	
			Ph	Me	TMS (95)	
			Ph	Me	Ac (96)	
	DMD, acetone, dark, rt, 3 d		R	Me	(6.9)	442
			Et		(22)	
			t-Bu		(2.7)	
			Ph		(3.2)	
			PhCH ₂		(22)	
			Ph(CH ₂) ₂		(28)	
			Ph(CH ₂) ₂		(99)	
			Ph(CH ₂) ₃		(16)	

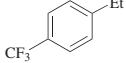
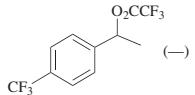
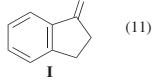
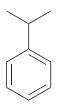
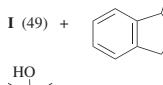
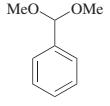
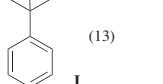
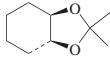
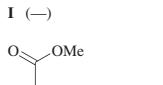
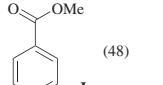
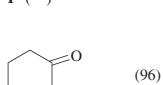
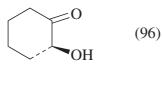
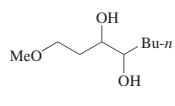
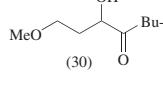
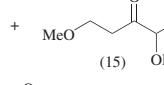
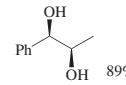
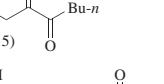
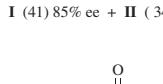
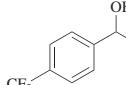
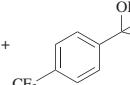
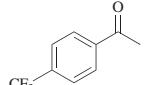
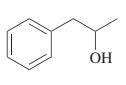
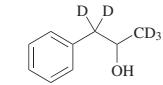
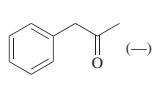
			 (-)	172
	DMD, acetone, dark, rt, 3 d		 (11)	442
	DMD, acetone, 4°, dark, 3 d		 (11)	442
	TFD, CH2Cl2, TFP, 0°, 10 min		 (13)	30
	TFD, TFP, 0°, dark		 (-)	443
	DMD, acetone, CH2Cl2, 18°, 96 h		 (48)	191
	DMD, acetone, CH2Cl2, dark, 0-5°, 24 h		 (-)	189
	TFD, 20 min		 (96) 99% ee	190

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD (6 eq), acetone, rt, 72 h	 (30) +  (15)	428
 89% ee	DMD, CH2Cl2, acetone, 0°, 22 h	 (42) 86% ee +  (34) 82% ee +  (12)	184
	TFD, CH2Cl2, TFP, 0°, 40 min	 (-)	184
 + 	DMD, acetone, 0°	 (-) % Conv. 20 4.8 ± 0.2 31 4.8 ± 0.2	432
 + 	DMD, acetone, 0°	 (-) % Conv. 4 0.98 ± 0.2 8 0.98 ± 0.2 17 1.01 ± 0.2 35 0.98 ± 0.2	432

	DMD, acetone		435
	DMD, acetone	I + II + III (9), EII:III ~ 65:10:25	435
	TFD (1.5 eq), TFP, CH ₂ Cl ₂ , 0°, 10 min	(29) + (12) + (7) + (8)	433
C ₉₋₁₀			186
	R Br Cl F H CF ₃ Me MeO	DMD, acetone, rt	

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉₋₁₅ 	DMD, acetone, rt	(—)	
			444
		R k _{rel}	
		I 0.14±0.01	
		H 1.00±0.00	
		OH 10.17±0.50	
		Me 1.91±0.01	
		MeO 3.58±0.10	
		Ac 0.047±0.002	
		PhO 7.05±0.40	
C ₉₋₁₉ 	DMD, acetone, dark, rt, 3 d	R ¹ R ² Me Me (13.4) Ph Me (1.0) Ph t-Bu (0.5) Ph Ph (17.5)	442
C ₁₀			
	DMD, acetone, CH ₂ Cl ₂ , N ₂ , 0°, 12 h	(38)	89
	DMD, acetone, dark, rt, 3 d	(13)	442
	DMD (2 eq), acetone, rt, 30 min	I + II (100), I:II = 70:30	176
	DMD (3 eq), acetone, rt, 60 min	II (100)	176

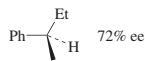
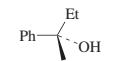
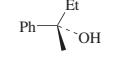
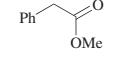
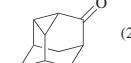
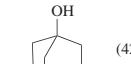
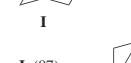
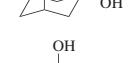
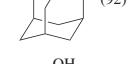
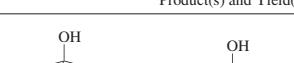
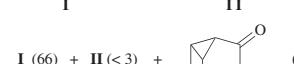
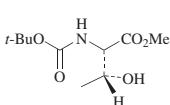
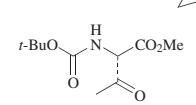
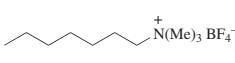
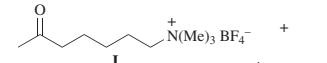
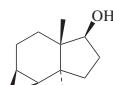
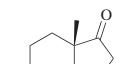
	72% ee		
	TFD, TFP, (CH ₂ Cl ₂), -24°, 1 h		(95) 72% ee
	DMD, acetone, CH ₂ Cl ₂ , rt, 48 h		(30) 72% ee
	DMD, acetone, CH ₂ Cl ₂ , dark, 0-5°, 43 h		(—)
	DMD, acetone, 20°, 2 h		(29)
	Cyclohexanone dioxirane, cyclohexanone, CH ₂ Cl ₂ , 10°, 6 h		(21)
	DMD, acetone, 22°, dark, 18 h		I (42) + II (57)
	DMD, acetone, (CBrCl ₃)		I (87) + II (2.6) + III (2.6)
			(—) + other products
	TFD, TFP, CH ₂ Cl ₂ , -22°, 1 min		I (92) + II (5)
	TFD (2.3 eq), TFP, CH ₂ Cl ₂ , -20°, 40 min		I (91) + II (3)

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
			
	TFD (6 eq), TFP, CH ₂ Cl ₂ , -20°, 2 h		(92) + (8)
	TFD (2 eq), TFP, CH ₂ Cl ₂ , 0°, 1.5 h		(32) + (48)
	TFD (4 eq), TFP, CH ₂ Cl ₂ , 0°, 1.5 h		I (66) + II (<3) + III (25)
	DMD, acetone, CH ₂ Cl ₂ , rt, 3 d		(61)
	TFD, CH ₂ Cl ₂ , MeCN (pH 2.0-3.0), 0°, 15 h		I + II (—), I:II = 60:40
	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , 0°, 2.5 h		(96)
	TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 15 min		I (96)

	TFD, CH ₂ Cl ₂ , TFP, 0°, 15 min	 I (99)	182
	DMD, acetone, CH ₂ Cl ₂ , 0°, 4 h	 I (49)	182
	1. aq. HBF ₄ , MeCN, (pH 2.0-3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 3 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h	 I (97)	192
	TFD, TFP, CH ₂ Cl ₂ , -22°, 11 min	 I (61) + (17) + (15)	30
	DMD, acetone, dark, 22°, 17 h	 I (20)	174
	TFD, TFP, CH ₂ Cl ₂ , -22°, 11 min	 (92) + (4) + (2) + (1)	30

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀		DMD, acetone, 22°, dark, 17 h	 (84)	174
		DMD, acetone, rt, 8 h	 (99)	22
		DMD, acetone/CH ₂ Cl ₂ , 0°, 2 h	 (94)	182
258		TFD, 15 min	 (98)	190
		DMD, acetone, rt	 (-)	444
	R		$k_2 (10^{-3} \text{ M}^{-1} \text{ s}^{-1})$	
	Br		0.290±0.011	
	Cl		0.213±0.007	
	H		2.978±0.099	
	OH		1.430±0.063	
	CO ₂ H		0.957±0.049	
	Ac		0.406±0.006	
	CO ₂ Et		0.557±0.04	

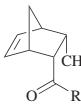
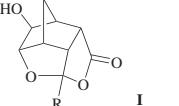
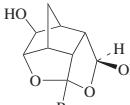
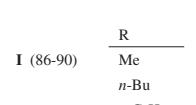
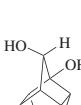
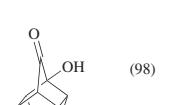
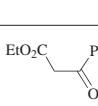
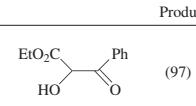
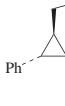
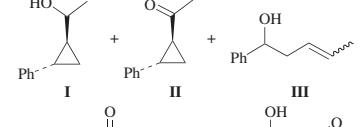
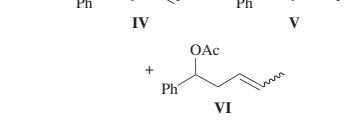
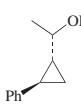
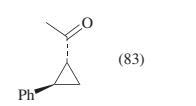
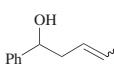
 <p>R</p> <hr/> <p>F ONO₂ NH₃^{+a} OMs OAc NHAc CH₂OAc OTs</p>	<p>TFD, TFP, CH₂Cl₂, -15°, 2 h</p>	 <p>I + II (—)</p>	<p>445</p>	<p>2.572 ± 0.0145 2.030 ± 0.0452 0.914 ± 0.0284 2.534 ± 0.0156 2.504 ± 0.0554 1.538 ± 0.0168 1.006 ± 0.0217 2.365 ± 0.0510</p>
 <p>CHO O= R</p>	<p>1. DMD (3 eq), acetone, -78° to rt, 0.5 h 2. 1 M HCl, 10 min</p>	 <p>I</p>	<p>446</p>	<p>(80) (84) (83)</p>
 <p>C₁₁</p>	<p>DMD (1.5 eq), acetone, -78° to rt, 0.5 h</p>	 <p>I (86-90)</p>	<p>446</p>	<p>Me n-Bu n-C₈H₁₇</p>
 <p>C₁₁</p>	<p>DMD, acetone, CH₂Cl₂, 0°, 70 h</p>	 <p>(98)</p>	<p>182</p>	

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (<i>Continued</i>)						
	Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
C ₁₁		DMD, acetone, CH ₂ Cl ₂ , MgSO ₄	 (97)			206
		DMD, acetone, atmos., rt, 2 h	 <p>I + II + III + IV + V + VI</p>			38
						
		Atmos.	I (0.3) — — O ₂ Ar	II (2.1) (1.7) (0.05) (2.2) (1.7)	III + IV + V (—) (0.05) (0.08) (0.08) (0.05)	VI (—) (0.14) (0.01) (0.01) (0.09)
		DDM	 (83)			38
		DDM	 <p>V (5) + VI (25)</p>			38

	TFD, CH ₂ Cl ₂ , TFP, 0°, 10 min		(96)	182
	DMD, acetone, CH ₂ Cl ₂ , 0°, 2 h		I (84)	182
	DMD, acetone, CH ₂ Cl ₂ , rt, 3 d		(62)	93
	1. DMD, acetone, CH ₂ Cl ₂ , 0°, 24 h 2. TFD, 0°, 45 min		(> 94)	190
	TFD (1.4 eq), TFP, CH ₂ Cl ₂ , cold, 2 h		(78)	447
	+		(-)	447
	DMD, acetone, CH ₂ Cl ₂ , 0°, 32 h		(68) 92% ee	190
	TFD, acetone, CH ₂ Cl ₂ , 0°, 30 min		(54) 92% ee +	190
	DMD, acetone, rt, overnight		(35)	269
			(85)	

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
	DMD, acetone, rt, 3 d		(-)	287
	DMD, CH ₂ Cl ₂ , acetone, rt, 3 d		(42)	93, 448
	DMD (6 eq), acetone, CH ₂ Cl ₂ , 20°, 120 h		(15)	310
	DMD, acetone, 20°		(-)	424
	TFD, TFP, -20°, 30 min		(-)	187
			$k = 4.52 \pm 0.27 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$	
	TFD (1.2 eq), TFP, CH ₂ Cl ₂ , 0°, 20 min		(> 90)	433

C ₁₂₋₁₄		DMD (x eq), acetone, CH ₂ Cl ₂ , rt		I, II > 96% Conv.	449
	R ¹ R ²	x Time		I II	
	H Me	3 12 h		(85) (8)	
	NO ₂ Me	5 24 h		(70) (15)	
	MeO Me	3 12 h		(> 96) (—)	
	MeO CO ₂ Me	5 48 h		(72) (—)	
C ₁₃		DMD, acetone, dark, rt, 3 d		(8.2)	442
263		DMD, acetone, rt, 8 h		(95)	176
	Ph-CH ₂ -Ph	DMD, acetone, rt, 24 h		(92)	176
		DMD (4.0 eq), acetone, 20°, 72 h		(100)	193
		DMD, CH ₂ Cl ₂ , -20°, 4 h		(70)	436

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃		TFD, 0°, 35 min		190
		TFD (1.4 eq), TFP, CH ₂ Cl ₂ , cold, 2 h		447
C ₁₄		DMD, acetone, rt, 24 h		176
264		TFD, TFP, dark, 0°		443
		DMD, acetone, rt, overnight		269
		DMD, CH ₂ Cl ₂ , acetone, 0°, 48 h		184
		TFD, CH ₂ Cl ₂ , TFP, 0°, 100 min		184

	DMD, acetone, ca. 20°, 2 h		(98)	177				
	DMD, acetone, ca. 20°, 2 h		(75)	177				
<i>n</i> -C ₇ H ₁₅ O-C ₇ H ₁₅ - <i>n</i>	DMD, acetone, CH ₂ Cl ₂ , 0°, 3 h	<i>n</i> -C ₆ H ₁₃ CHO (19) + <i>n</i> -C ₆ H ₁₃ COOH (22) + <i>n</i> -C ₇ H ₁₅ OH (9)	191					
	DMD, acetone, dark, rt, 14 h		(39)	450				
	TFD (6 eq), TFP, CH ₂ Cl ₂ , <i>t</i> -BuOH, 0°, 15 min		(33) +	451				
			(39) + (5)					
C ₁₄₋₁₉		DMD, acetone, dark, rt, 3 d		I		II	R I II	442
							Me (4.2) (—)	
							Bu- <i>t</i> (6.8) (11)	
							Ph (21) (—)	

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.		
C ₁₅		DMD, acetone, CH ₂ Cl ₂ , rt		(27) +	452	
				(14) + (10)		
		DMD (4.0 eq), acetone, N ₂ , 20°, 96 h		(15) +	(85)	193
		DMD, acetone, CH ₂ Cl ₂ , dark, 48 h		(93)		188
		DMD, acetone, CH ₂ Cl ₂ , rt, 3 d		(58)		93
		DMD, acetone, CH ₂ Cl ₂ , rt, 3 d		(35)		93, 448

	DMD (xs), acetone, CH ₂ Cl ₂ , rt	(100)	449
	DMD (x eq), acetone, CH ₂ Cl ₂ , rt	+ (II)	449
		(III)	
R	x	Time	% Conv. I II III
3'-F	1	8 h	60 (46) (14) (—)
3'-F	3	8 h	>95 (—) (45) (34)
4'-F	1	12 h	60 (52) (8) (—)
4'-F	3	8 h	>95 (—) (58) (25)
4'-NO ₂	1	12 h	63 (38) (25) (—)
4'-NO ₂	3	18 h	>95 (—) (68) (17)
H	1	6 h	75 (59) ^c (16) (—)
H	3	12 h	>95 (—) (56) (34)
3'-OMe	3	5 h	90 (—) (56) (34)
3'-OMe	5	12 h	>95 (—) (—) (70)
4'-OMe	1	4 h	65 (—) (32) ^d (—)
4'-OMe	3	10 h	>95 (19) ^d (30) (65)

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, rt	(40)	68
	DMD, acetone, rt, 11 h	(100)	453
	DMD, CH ₂ Cl ₂ , acetone, dark, 20°, 45 h	(35)	189
	DMD, acetone, CH ₂ Cl ₂ , dark, rt, 48 h	(89)	188
	DMD, acetone, CH ₂ Cl ₂ , dark, rt, 48 h	(90)	188
	DMD, acetone, CH ₂ Cl ₂ , rt, 3 d	(38)	93, 448
	TFD, 50 min	(92) 97% ee	190

C₁₇₋₂₁ DMD, acetone, CH ₂ Cl ₂ , rt	 R ¹ R ² H OAc (63) OAc H (57)	452
C₁₈ DMD, acetone, CH ₂ Cl ₂ , rt, 3 d	 (33) + (1)	93, 448
 DMD, CH ₂ Cl ₂ , acetone, 20°, 40 h	 (69)	179
C₁₉ DMD, acetone, CH ₂ Cl ₂ , 0°	 (47) + (20)	454
 DMD, acetone, 60 h	 I II III I II III (76) (20) (—) (46) (7) (11)	455
Temp 20° 30°		

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C₁₉₋₂₃ 		R 4-BrC ₆ H ₄ CH ₂ (85) Bn (87) 4-CNC ₆ H ₄ CH ₂ (87) 2-naphthyl-CH ₂ (90)		188
C₂₀ 1. DMD, acetone, -20°, 2 d 2. Ac ₂ O, pyridine	 I (80)		456	
 1. DMD, acetone, -20°, 2 d 2. Ac ₂ O, pyridine	 I (75)		456	
 DMD, acetone, 20°, 22 h	 (74)		457	
 DMD, acetone, 20°, 22 h	 (80)		457	

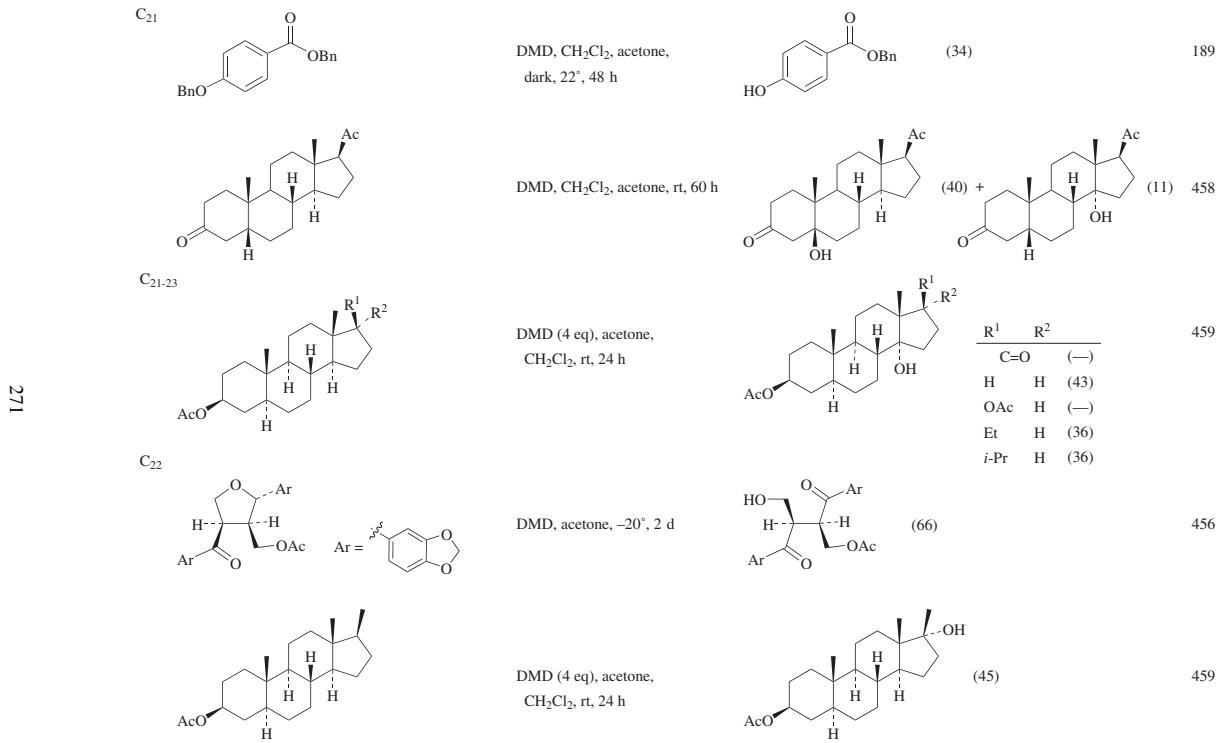
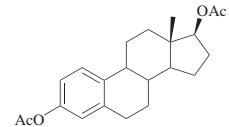
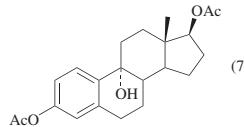
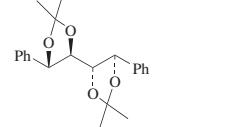
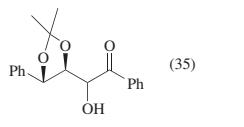
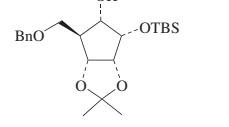
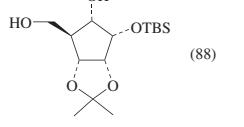
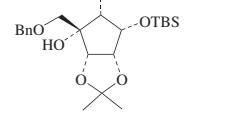
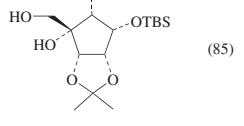
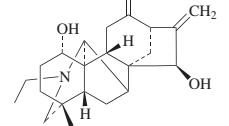
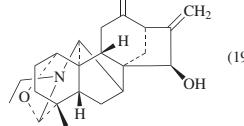
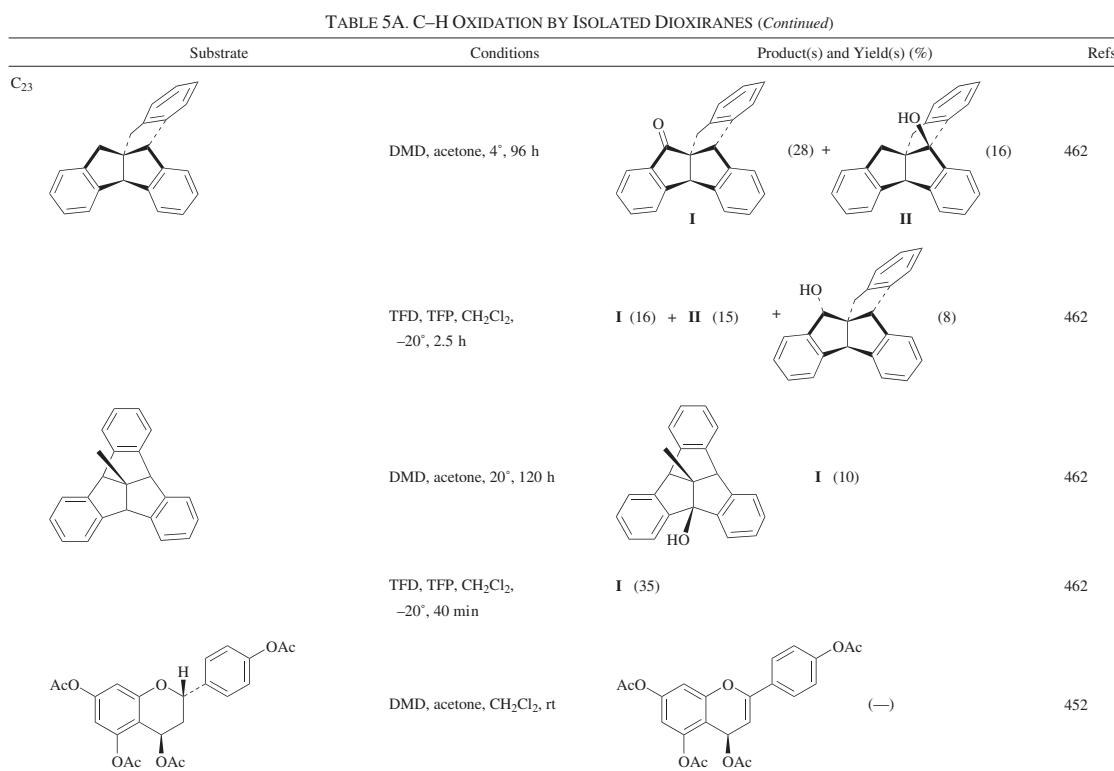
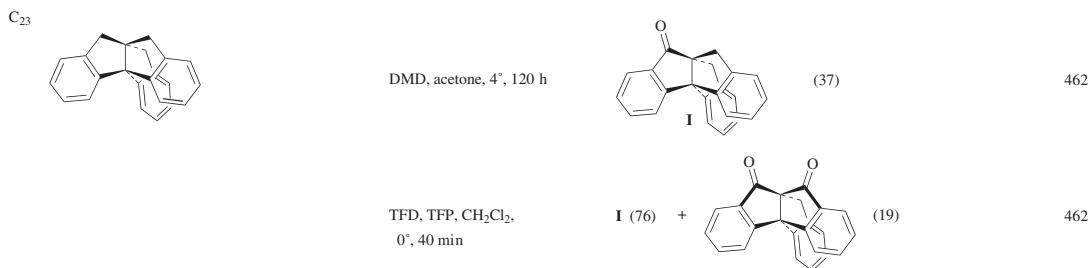
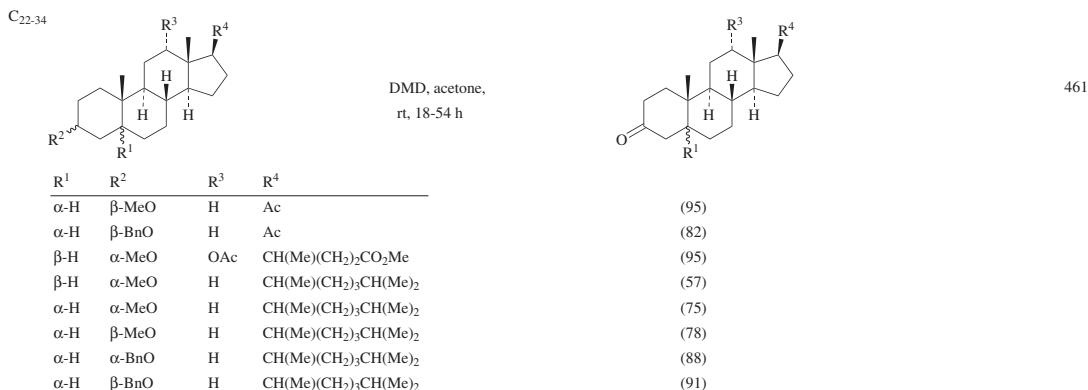
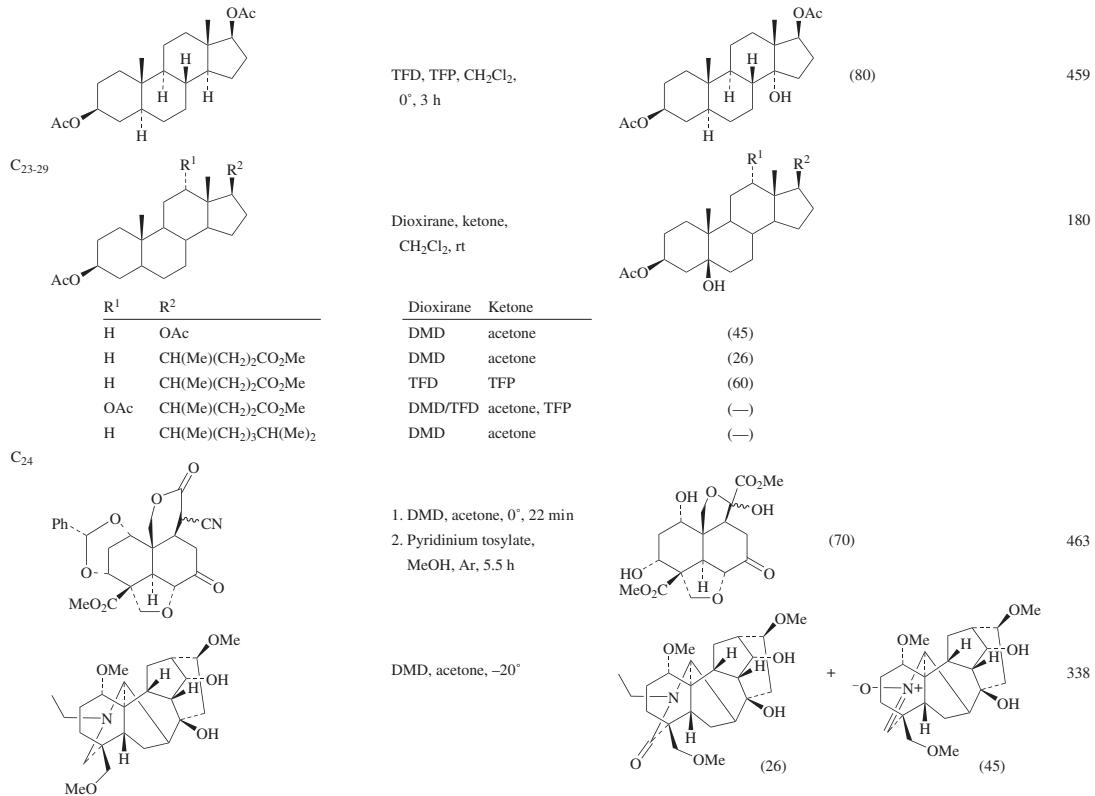


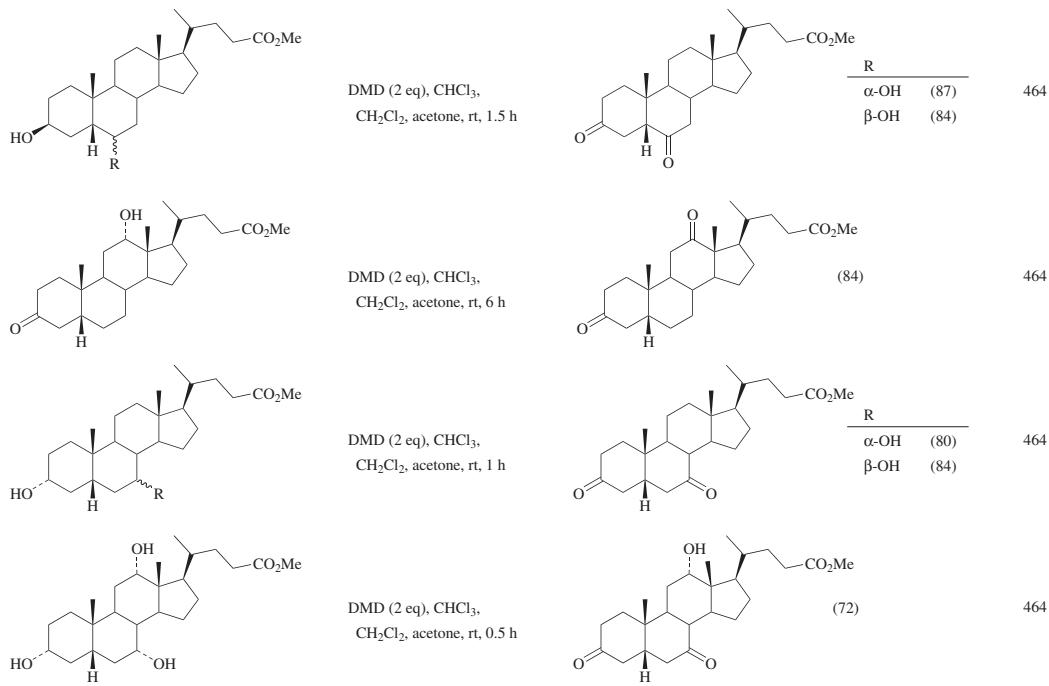
TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C₂₂</p>	DMD, acetone	 <p>(75)</p>	460
	TFD, TFP, CH ₂ Cl ₂ , 0°, 2.5 h	 <p>(35)</p>	190
	DMD, acetone, CH ₂ Cl ₂ , dark, rt, 48 h	 <p>(88)</p>	188
	DMD, acetone, CH ₂ Cl ₂ , dark, rt, 48 h	 <p>(85)</p>	188
	DMD, acetone, <i>t</i> -BuOH, -20°	 <p>(19)</p>	338



TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, rt, 3 d	 (40) + (13)	93
	DMD (2 eq), CHCl ₃ , CH ₂ Cl ₂ , acetone, rt, 0.5 h	 R α-OH (90) β-OH (83)	464
	DMD (2 eq), CHCl ₃ , CH ₂ Cl ₂ , acetone, rt, 1.5 h	 (69)	464



Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₅	DMD (2 eq), CHCl ₃ , CH ₂ Cl ₂ , acetone, rt, 1.5 h	 (83)	464
	DMD (2 eq), CHCl ₃ , CH ₂ Cl ₂ , acetone, rt, 0.5 h	 (87)	464
	DMD (2 eq), CHCl ₃ , CH ₂ Cl ₂ , acetone, rt, 1 h	 (55)	464
	DMD (2 eq), CHCl ₃ , CH ₂ Cl ₂ , acetone, rt, 1 h	 I + II (83), I:II = 3:1	464

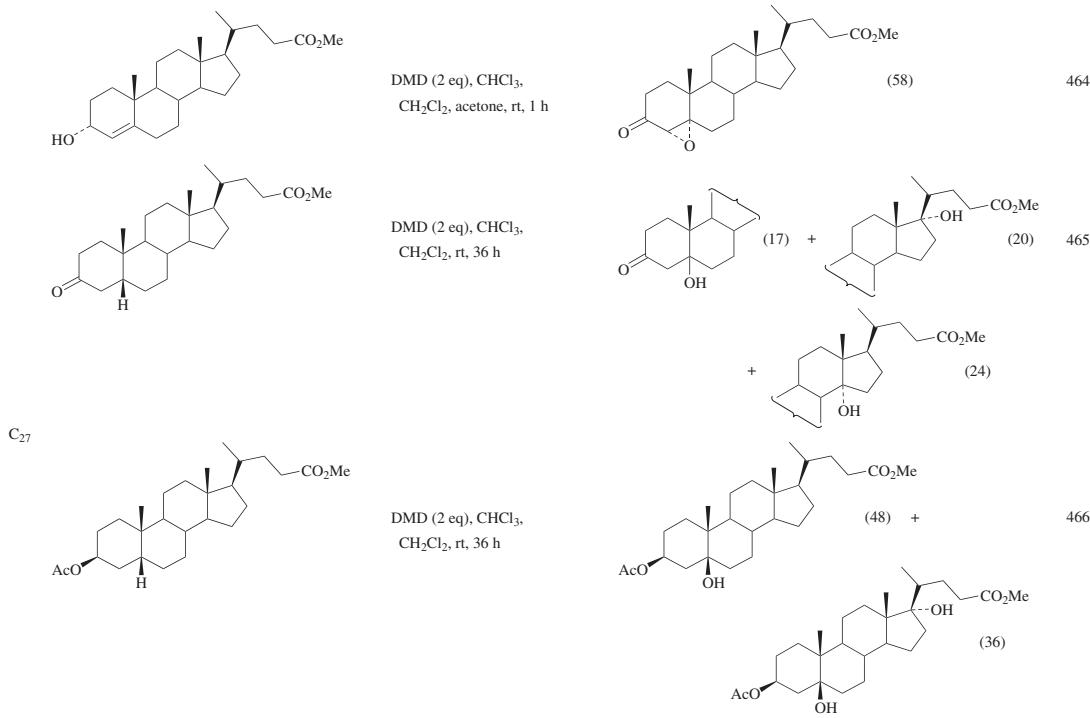
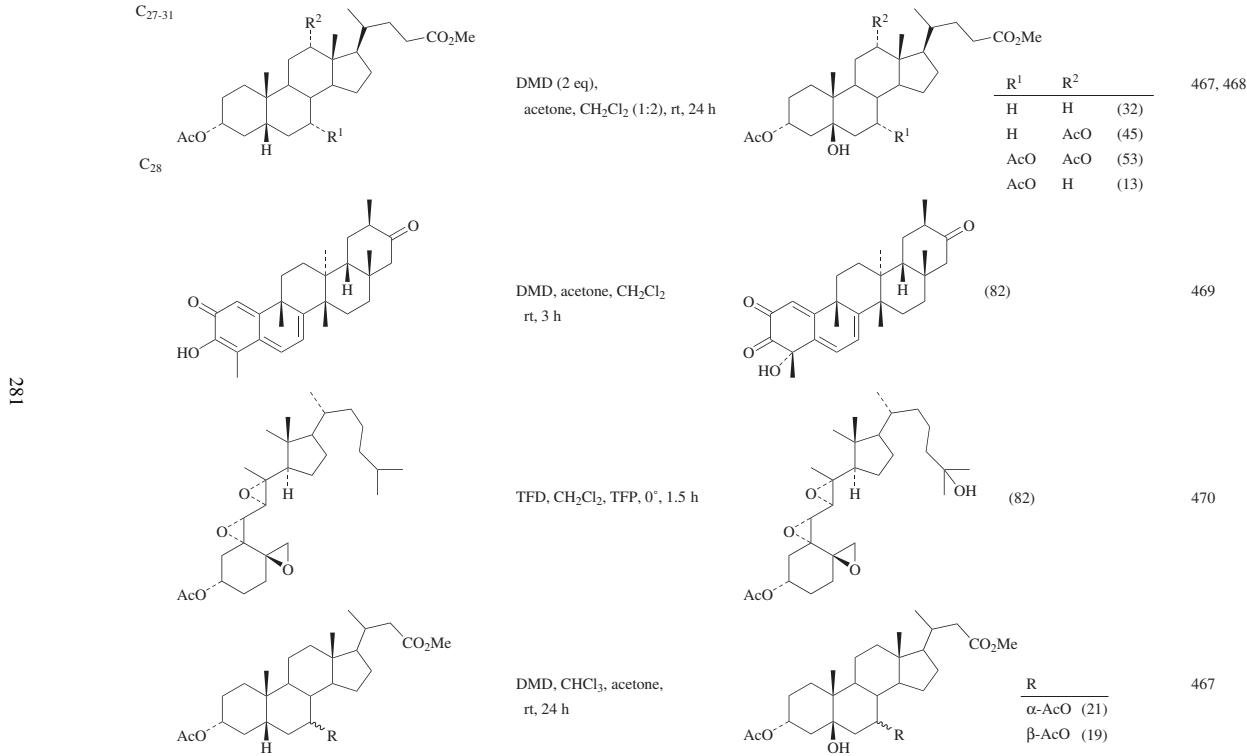
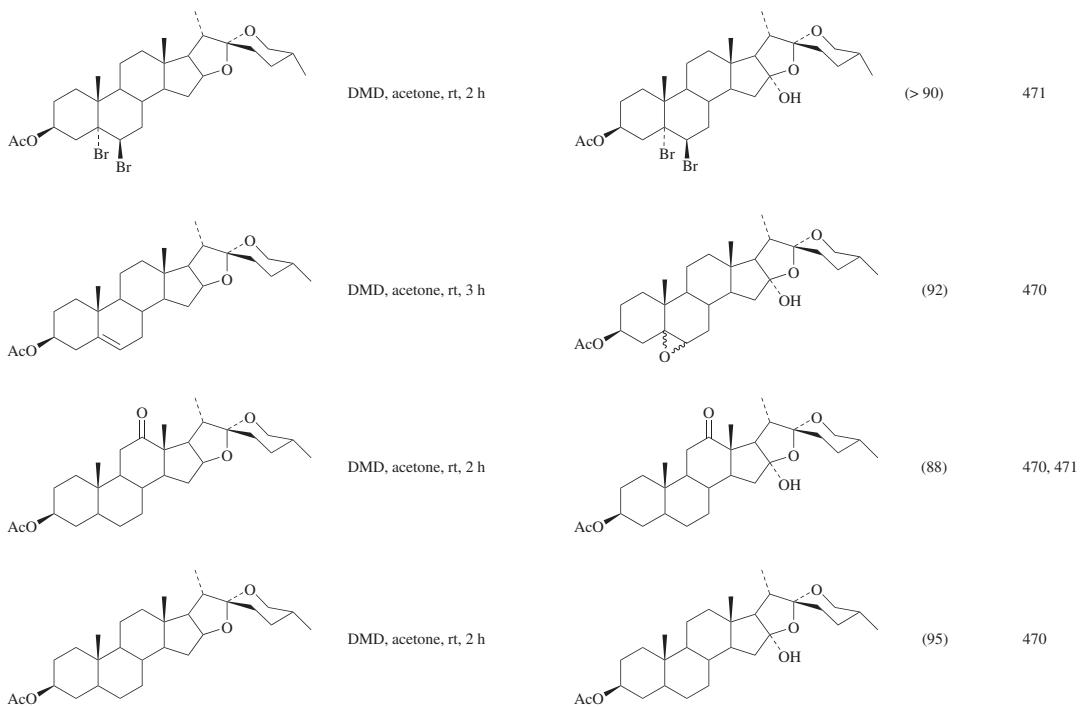


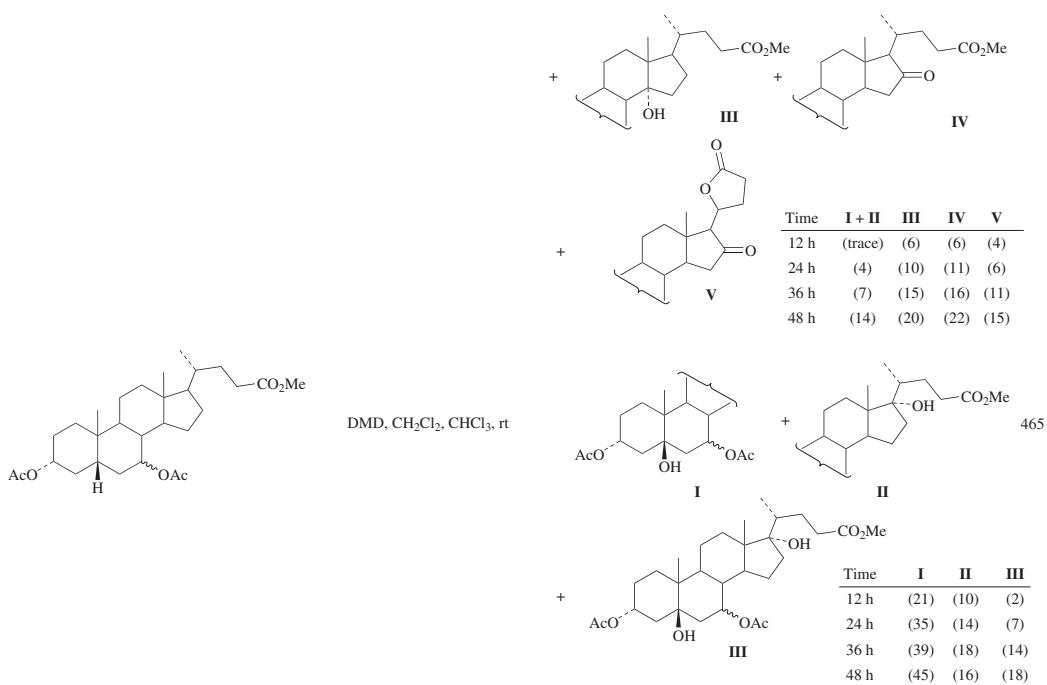
TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (<i>Continued</i>)																															
	Substrate	Conditions	Product(s) and Yield(s) (%)																												
C ₂₇		DMD, acetone, rt, 3 d	 (43)																												
		DMD, acetone, rt, 3 d	 (41)																												
		DMD, acetone, rt, 3 d	 (38)																												
C ₂₇₋₂₉		DMD, CH ₂ Cl ₂ , acetone, 20°, 24 h	 I																												
		TFD, CH ₂ Cl ₂ , TFP, –40 to 0°, 3 h	<table style="margin-left: auto; margin-right: auto;"> <tr> <td>R¹</td> <td>R²</td> <td>R³</td> </tr> <tr> <td>C=O</td> <td>H</td> <td>(29)</td> </tr> <tr> <td>H</td> <td>OAc</td> <td>Br (44)</td> </tr> <tr> <td>H</td> <td>OAc</td> <td>H (24)</td> </tr> </table> <table style="margin-left: auto; margin-right: auto;"> <tr> <td>I</td> <td>R¹</td> <td>R²</td> <td>R³</td> </tr> <tr> <td></td> <td>C=O</td> <td>H</td> <td>(74)</td> </tr> <tr> <td></td> <td>H</td> <td>OAc</td> <td>Br (62)</td> </tr> <tr> <td></td> <td>H</td> <td>OAc</td> <td>Br (66)</td> </tr> </table>	R ¹	R ²	R ³	C=O	H	(29)	H	OAc	Br (44)	H	OAc	H (24)	I	R ¹	R ²	R ³		C=O	H	(74)		H	OAc	Br (62)		H	OAc	Br (66)
R ¹	R ²	R ³																													
C=O	H	(29)																													
H	OAc	Br (44)																													
H	OAc	H (24)																													
I	R ¹	R ²	R ³																												
	C=O	H	(74)																												
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TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

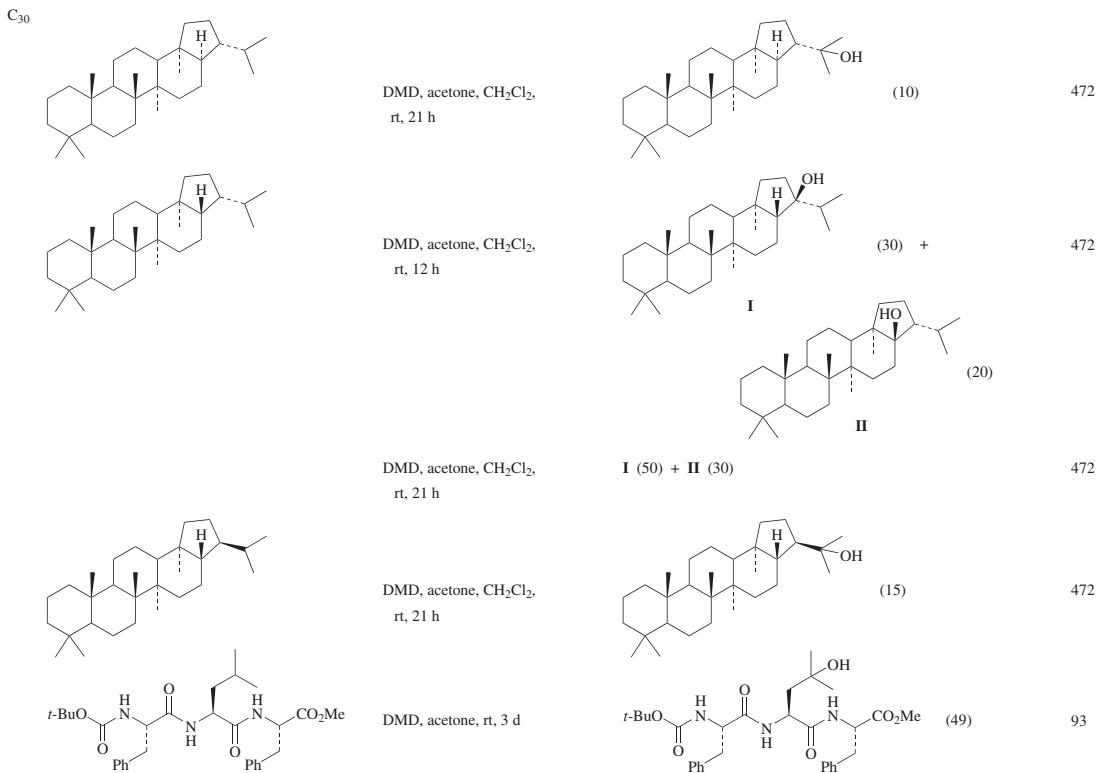
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₉		DMD, CH ₂ Cl ₂ , acetone, rt, 48 h		(35) 458
		TFD, CH ₂ Cl ₂ , TFP, <i>t</i> -BuOH, -10°, 25 min		(56) 462
282		TFD, CH ₂ Cl ₂ , TFP, 0°, 20 min		I (44) 443
		TFD, CH ₂ Cl ₂ , TFP, <i>t</i> -BuOH, -10°, 25 min		(54) 462
		TFD, CH ₂ Cl ₂ , TFP, 0°, 15 min		(53) 443

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.	
	TFD (3 eq), CH ₂ Cl ₂ , TFP (9:1), 0°, 1.5 h		(82)	469
	DMD, CHCl ₃ , acetone, rt, 24 h	 (12) +	(12) + 467	467
	DMD, CHCl ₃ , acetone, rt, 24 h	 (22) +	(22) + (12)	467
	DMD, CH ₂ Cl ₂ , CHCl ₃ , rt	 I +	I + II	465

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₉		DMD, CH ₂ Cl ₂ , CHCl ₃ , rt	 I + II + III + IV 12 h: (37), (3), (5) 24 h: (45), (8), (12) 36 h: (39), (19), (29)	465
286		DMD (2.2 eq), CH ₂ Cl ₂ , rt, 7 d		471
		DMD, CH ₂ Cl ₂ , -50°, 30 min		471

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C₃₀			
	DMD, CH_2Cl_2 , CHCl_3 , rt, 24 h	I (31) + II (40)	465
	DMD, CH_2Cl_2 , CHCl_3 , rt, 36 h	I (33) + II (30)	465
C₃₁			
	DMD, CH_2Cl_2 , CHCl_3 , rt, 12 h	I (5) + II (10) + III (22)	465
	DMD, CH_2Cl_2 , CHCl_3 , rt, 24 h	I (5) + II (8) + III (18) + IV (22)	465

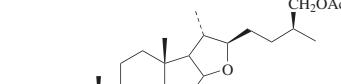
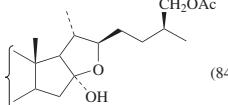
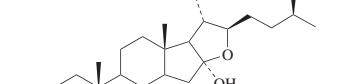
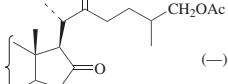
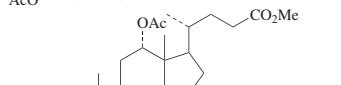
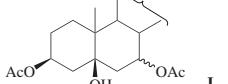
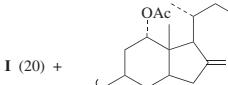
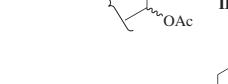
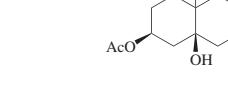
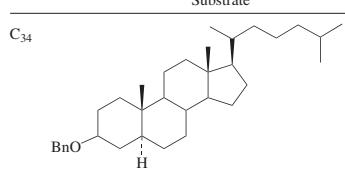
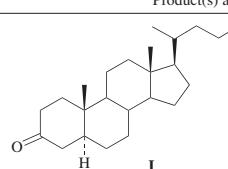
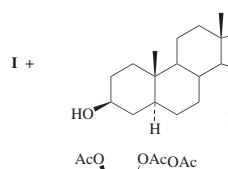
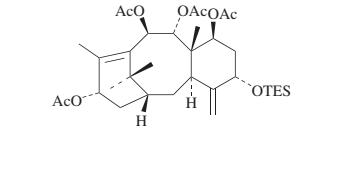
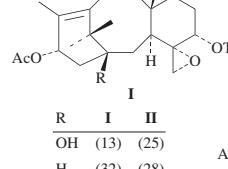
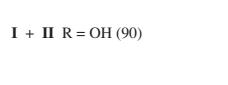
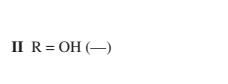
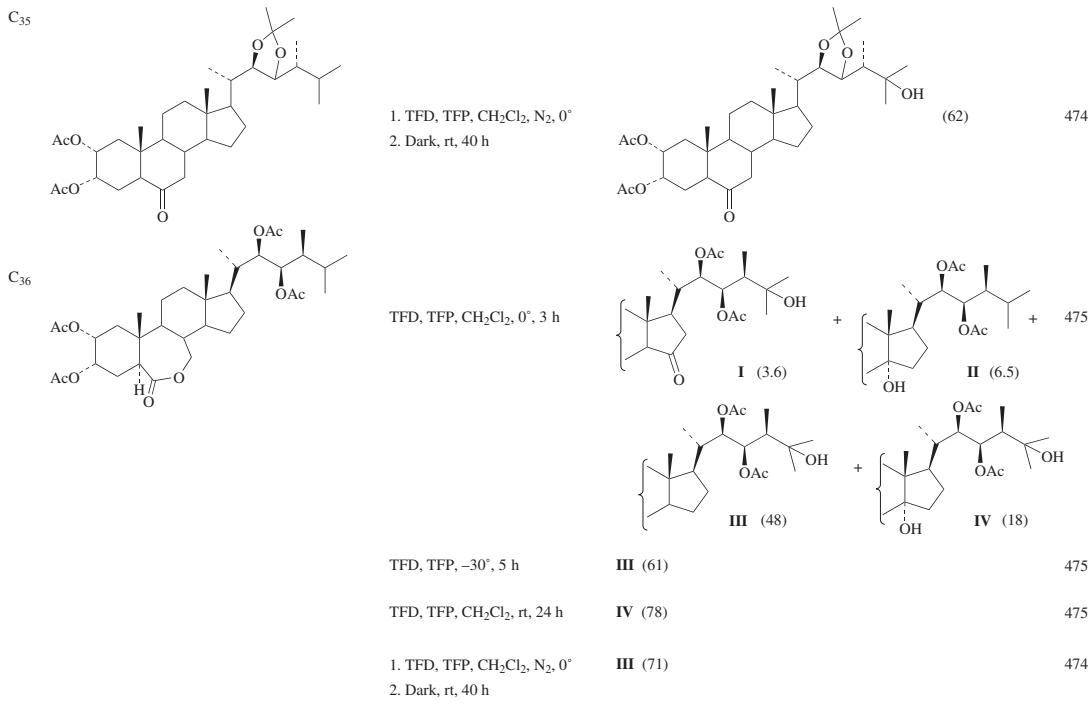
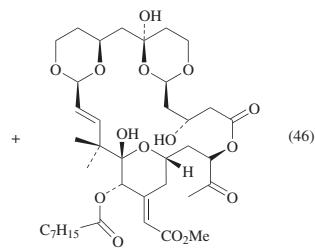
	DMD, acetone, 0°, 4 h		(84)	470												
	DMD, acetone		(—)	470												
	DMD, CH ₂ Cl ₂ , CHCl ₃ , rt, 12 h		I (11)	465												
	DMD, CH ₂ Cl ₂ , CHCl ₃ , rt, 24 h		II (2)	465												
	DMD, CH ₂ Cl ₂ , CHCl ₃ , rt, 36 h		III (3)	465												
	DMD, CH ₂ Cl ₂ , CHCl ₃ , rt		I + II + III	465												
		<table border="1" style="margin-left: auto; margin-right: auto;"><tr><td>Time</td><td>I</td><td>II</td><td>III</td></tr><tr><td>48 h</td><td>(40)</td><td>(2)</td><td>(4)</td></tr><tr><td>60 h</td><td>(44)</td><td>(4)</td><td>(6)</td></tr></table>	Time	I	II	III	48 h	(40)	(2)	(4)	60 h	(44)	(4)	(6)		
Time	I	II	III													
48 h	(40)	(2)	(4)													
60 h	(44)	(4)	(6)													

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD (2 eq), CH ₂ Cl ₂ , acetone, dark, 22°, 15 h	 I (60)	189
	DMD (1 eq), CH ₂ Cl ₂ , acetone, dark, 22°, 14 h	 II I + II (—), I:II = 3:1	189
	DMD (15 eq), acetone, rt, 48 h	 I R OH (13) (25) H (32) (28)	473
I R = H	DMD (30 eq), acetone, rt, 48 h	 I + II R = OH (90)	473
II R = H	DMD (25-30 eq), acetone, rt, 48 h	 I R = OH (—)	473
	DMD (25-30 eq), acetone, rt, 48 h	 II R = OH (—)	473

TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C₃₇		DMD, acetone, rt, 48 h	 (70)	476
C₃₈		DMD, acetone, rt, 48 h	 (9)	476



^a Reaction was run using solutions purged with pure, oxygen-free nitrogen gas.

^b The reaction was carried out under N₂.

^c The diastereomer ratio was 10:1.

^d The value includes 14% of an oxo aldehyde byproduct.

TABLE 5B. REGIOSELECTIVE C–H OXIDATION BY ISOLATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.				
C ₄		DMD, acetone, rt, 18–22 h		(90)		183				
C ₅		DMD, acetone, rt, 18–22 h		(100)		183				
		DMD, acetone, rt, 18–22 h		(60)		183				
C _{5–11}		DMD, acetone, CH ₂ Cl ₂ , rt		+		428				
			R ¹	R ²	R ³	Time	I	II		
			OH	Me	Me	—	(—)	(—)		
			MeO	Me	Me	—	(—)	(—)		
			AcO	Me	Me	24 h	(90)	(—)		
			Br	n-Pr	Me	48 h	(95)	(—)		
			MeO	H	n-Pr	48 h	(76)	(14)		
			AcO	H	n-Pr	36 h	(83)	(—)		
			N ₃	H	n-C ₅ H ₁₁	48 h	(95)	(—)		
			OH	H	n-C ₅ H ₁₁	24 h	(59)	(—)		
			CH ₂ OH	H	n-Bu	48 h	(38)	(38)		
			OH	Me	n-C ₅ H ₁₁	—	(—)	(—)		
			CH ₂ OMe	H	n-Bu	24 h	(30)	(15)		
			CH ₂ OAc	H	n-Bu	24 h	(60)	(—)		
			OMe	Me	n-C ₅ H ₁₁	36 h	(60)	(—)		
			OAc	Me	n-C ₅ H ₁₁	48 h	(70)	(—)		
C _{5–13}		DMD, acetone, CH ₂ Cl ₂ , rt, 72 h				R ¹	R ²			449
			c-C ₆ H ₁₁	Et	(57)					
			n-C ₉ H ₁₉	Me	(< 10)					
C ₆		DMD, acetone, rt, 18–22 h	mixture							183
		DMD, acetone, rt, 18–22 h		(85)						183
		DMD, acetone, rt, 18–22 h		(82)						434
295		DMD, acetone, rt, overnight		(—)						434
		DMD, acetone, rt, 18–22 h		(60)						183

TABLE 5B. REGIOSELECTIVE C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

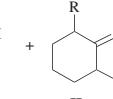
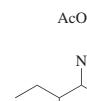
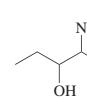
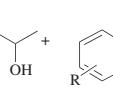
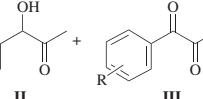
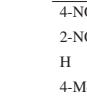
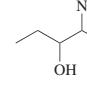
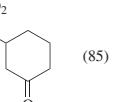
Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
C ₆₋₈	DMD, acetone, rt				428
		R	Time	I	II
	Br	24 h	(> 95)	(—)	
	N ₃	48 h	(> 95)	(—)	
	OH	48 h	(> 95)	(—)	
	OMe	48 h	(74)	(16)	
	AcO (syn, syn)	24 h	(> 95)	(—)	
	AcO (anti, syn)	24 h	(> 95)	(—)	
C ₇	DMD, acetone, rt, overnight			(80)	434
C ₈	DMD, acetone, rt, overnight			(55)	434
C ₉	DMD, acetone, rt, overnight			(> 96)	434
C ₉₋₁₀	DMD, CH ₂ Cl ₂ , acetone, rt				449
C ₁₀	DMD, acetone, dark, rt, 3 d				
C ₁₀₋₁₁	DMD, CH ₂ Cl ₂ , acetone, rt				449
C ₁₁	TFD, CH ₂ Cl ₂ , -20°, 48 h			(> 98)	477
C ₁₂	DMD, acetone, rt, overnight			(85)	434
	TFD, CH ₂ Cl ₂ , -20°, 48 h			(—)	477
				(80)	
				I:II = 12:88	

TABLE 5B. REGIOSELECTIVE C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

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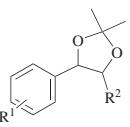
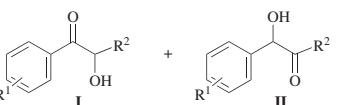
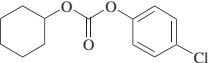
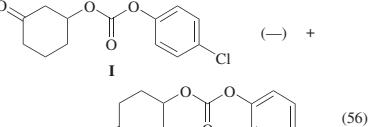
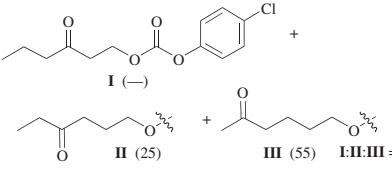
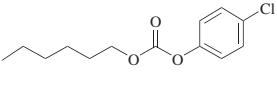
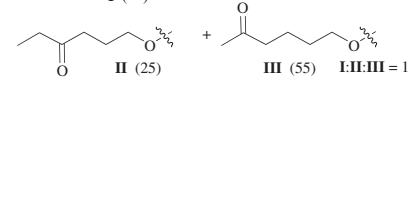
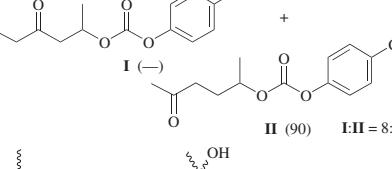
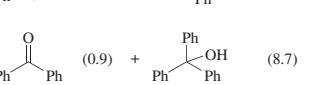
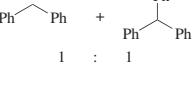
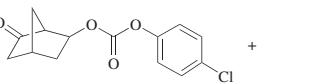
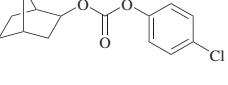
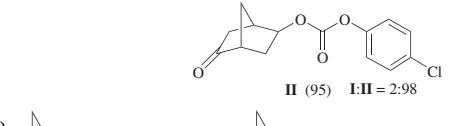
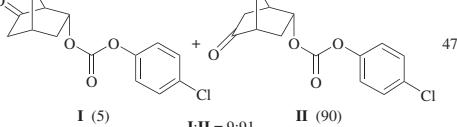
	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.s.
C ₁₂		TFD, CH ₂ Cl ₂ , -20°, 48 h	 (97)	477
C ₁₂₋₁₄		DMD, acetone, rt	 I + II	449
			$\begin{array}{ccccc} R^1 & R^2 & \text{Time} & \text{I} & \text{II} \\ 4\text{-NO}_2 & \text{Me} & 24 \text{ h} & (70) & (15) \\ \text{H} & \text{Me} & 12 \text{ h} & (85) & (8) \\ \text{H} & \text{CO}_2\text{Me} & — & (—) & (—) \\ 4\text{-MeO} & \text{Me} & 12 \text{ h} & (> 96) & (—) \\ 4\text{-MeO} & \text{CO}_2\text{Me} & 48 \text{ h} & (72) & (—) \end{array}$	
C ₁₃		TFD, CH ₂ Cl ₂ , -20°, 48 h	 I + II I:II = 40:60	477
			 I (-) II (25) III (55) I:II:III = 14:29:57	477
C ₁₃		TFD, CH ₂ Cl ₂ , -20°, 48 h	 I (-) II (90) I:II = 8:92	477
			 I (-) II (33) III (20)	442
		DMD, acetone, dark, rt, 3 d	 I (-) II (90) I:II = 8:92	442
		DMD, acetone, dark, rt, 3 d	 I (-) II (0.9) III (8.7)	442
C ₁₄		TFD, CH ₂ Cl ₂ , -20°, 48 h	 I (-) II (95) I:II = 2:98	477
			 I (5) II (90) I:II = 9:91	477

TABLE 5B. REGIOSELECTIVE C–H OXIDATION BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄		TFD, CH ₂ Cl ₂ , -20°, 48 h	 I (9) + II (83) I:II = 15:85	477
C ₁₉		DMD, acetone, dark, rt, 3 d		442

TABLE 5C. C–H OXIDATION BY IN SITU GENERATED DIOXIRANES

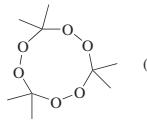
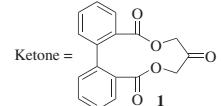
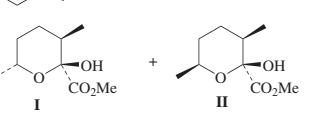
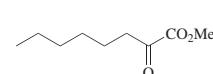
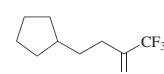
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂	CH ₃ CHO	Oxone [®] , acetone, rt, 5 h	CH ₃ CO ₂ H (—) + 	(2) 121
C ₆		Oxone [®] , acetone, phosphate buffer (pH 7.3–7.5), CH ₂ Cl ₂ , KF, 20°, 1 h	 (85)	193
		Oxone [®] , acetone, H ₂ O, NaHCO ₃	 (14)	478
C ₇		Oxone [®] , ketone 1 , NaHCO ₃ , MeCN, H ₂ O, EDTA, rt, 3.5 h Ketone = 	 (91)	52
C ₈		Oxone [®] , ketone 1 , NaHCO ₃ , MeCN, H ₂ O, EDTA, rt, 3.5 h	 (80)	52
		Oxone [®] , acetone, phosphate buffer (pH 7.3–7.5), CH ₂ Cl ₂ , KF, 20°, 1 h	 (85)	193

TABLE 5C. C–H OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈		Oxone [®] , acetone, H ₂ O, NaHCO ₃	 (96)	478
		Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , rt, 24 h	 (86)	195
		Oxone [®] , ketone 1 , NaHCO ₃ , MeCN, H ₂ O, EDTA, rt, 4 h	 (95)	52
C ₉		Oxone [®] , ketone 1 , NaHCO ₃ , MeCN, H ₂ O, EDTA, rt, 5 h	 (94)	52
		Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt	 I II	479
		Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 24 h	 (70)	195
		Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 24 h	 (74)	480

C ₁₀		Oxone®, MeCN, H ₂ O, NaHCO ₃ , rt, 24 h		(72) + (15)	195
		Oxone®, MeCN, H ₂ O, NaHCO ₃ , rt, 120 h		(31) + (7)	195
		Oxone®, ketone, CH ₃ CN, H ₂ O, NaHCO ₃ , rt, 2 h ketone = TFP, AcCO ₂ Me, AcCH ₂ Cl or AcCH ₂ F		I (—)	195
303		Bu ₄ NHSO ₅ , acetone, NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , 20°, 23.5 h	I (100)	x y Time % Conv.	481
		Bu ₄ NHSO ₅ (x eq), acetone (y eq), CH ₂ Cl ₂ , NaHCO ₃ , H ₂ O, rt	I	10 0 21 h (—)	
				4 6 4 d 30	481
				4 208 4 d 34	
				10 150 21 h 55	
				10 520 21 h 100	
				20 1040 21 h 100	
		Oxone®, ketone I, NaHCO ₃ , MeCN, H ₂ O, EDTA, rt, 4 h		(75)	52
		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 24 h		(67)	480

TABLE 5C. C-H OXIDATION BY IN SITU GENERATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 24 h	 I I:II = 1:15 II	(85) 479
		Oxone®, ketone I, NaHCO ₃ , MeCN, H ₂ O, EDTA, rt, 12 h		(77) 52
		Oxone®, MeCN, H ₂ O, NaHCO ₃ , rt, 24 h		(78) 195
		Oxone®, MeCN, H ₂ O, NaHCO ₃ , rt, 24 h		(66) + (17) 195
		Oxone®, MeCN, H ₂ O, NaHCO ₃ , rt, 72 h	 I X I II Cl (56) (21) F (41) (14)	(93) 195
		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 120 h		(93) 480

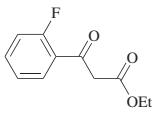
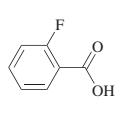
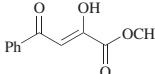
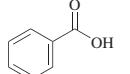
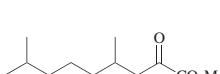
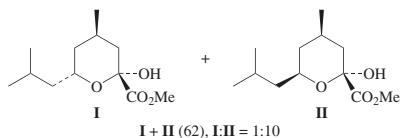
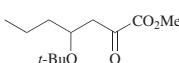
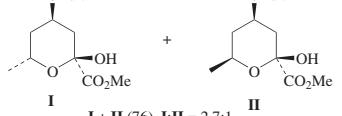
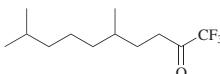
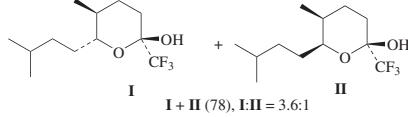
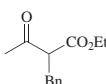
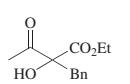
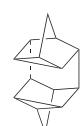
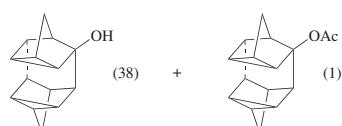
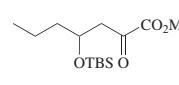
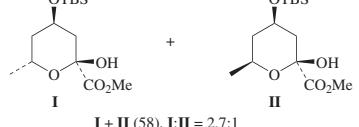
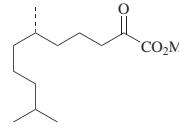
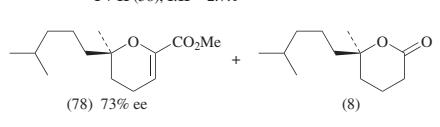
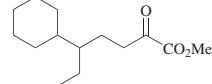
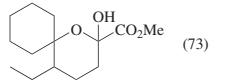
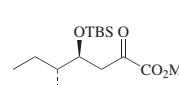
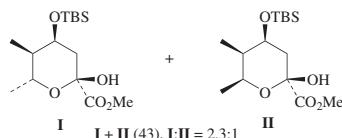
		Oxone®, acetone, H ₂ O, NaHCO ₃		(90)	478
		Oxone®, acetone, H ₂ O, NaHCO ₃		(96)	478
C ₁₂		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 4.5 h		I + II (62), I:II = 1:10	479
305		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 5 h		I + II (76), I:II = 2.7:1	479
		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 24 h		I + II (78), I:II = 3.6:1	479
C ₁₃		Oxone®, acetone, phosphate buffer (pH 7.3–7.5), CH ₂ Cl ₂ , Bu ₄ NF, 20°, 1 h		(75)	193

TABLE 5C. C–H OXIDATION BY IN SITU GENERATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄		1. Oxone®, acetone, CH ₂ Cl ₂ , H ₂ O, NaHCO ₃ , 0°, 2 h 2. rt, 12 h		(38) + (1) (450)
		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 27 h		I + II (58), I:II = 2.7:1 (479)
306		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 6 h		(78) 73% ee + (8) (480)
		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 24 h		(73) (480)
C ₁₅		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 20 h		I + II (43), I:II = 2.3:1 (479)

		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 20 h		I + II (59), I:II = 3.1:1	479
C ₁₆		Oxone®, acetone, H ₂ O, NaHCO ₃		(97)	478
C ₂₀₋₂₁		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 48 h		(45)	479
307		Oxone®, acetone, phosphate buffer (pH 7.5), CH ₂ Cl ₂ , Na ₂ EDTA, Bu ₄ NHSO ₄ , 2°, 7 h		R ¹ R ² (79) OAc H (75)	460
C ₂₂		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 120 h		(16) (39) (15)	480

TABLE 5C. C–H OXIDATION BY IN SITU GENERATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₂		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 120 h		(I) (70) (II) (18) 480
C ₂₄		Oxone®, acetone, H ₂ O, NaHCO ₃ , 0° to rt, 15 min		(87) 478
308		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 120 h		II (69) III (34) 480 II (15) III (42)
	Conc. 1.5 mM 10 mM			

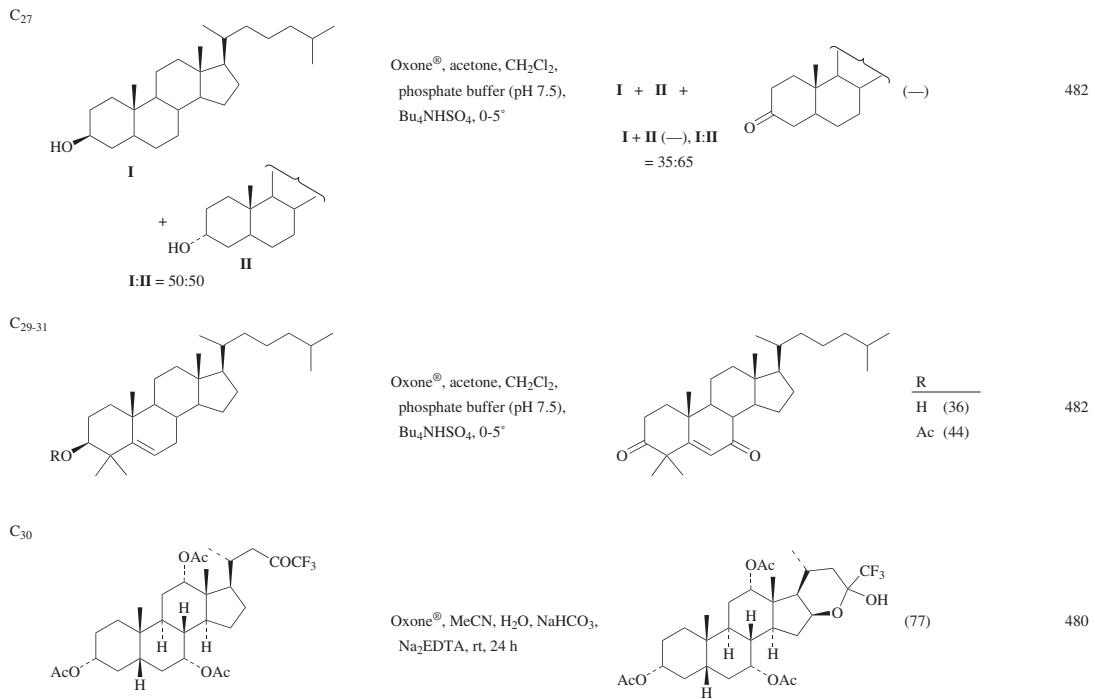
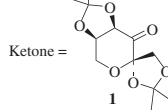
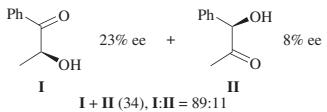
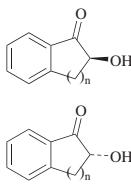
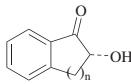


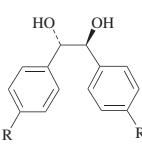
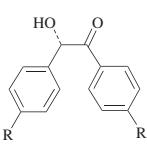
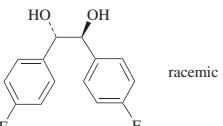
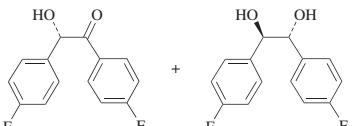
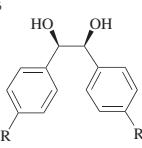
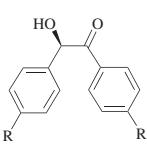
TABLE 5C. C-H OXIDATION BY IN SITU GENERATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃₁		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 24 h		(58) 195, 480
310		Oxone®, MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 41 d		(3) (4) (10) (17) (6) 480

TABLE 5D. ASYMMETRIC C–H OXIDATION BY IN SITU GENERATED OPTICALLY ACTIVE DIOXIRANES

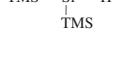
	Substrate	Conditions	Product(s) and Conversions(s) (%)	Refs.													
C ₉		racemic	Oxone®, K ₂ CO ₃ , ketone, buffer (pH 10.5), MeCN, 0°, 2 h 	 I: 23% ee, II: 8% ee I + II (34), I:II = 89:11	197												
		racemic	Oxone®, K ₂ CO ₃ , ketone 1, buffer (pH 10.5), MeCN, 0°, 2 h	I + II (20), I: 71% ee, II: 11% ee, I:II = 84:16	197												
C ₉₋₁₀		racemic	Oxone®, K ₂ CO ₃ , ketone 1, buffer (pH 10.5), MeCN, 0°, 2 h	 <table border="1"><tr><td>n</td><td>% ee</td></tr><tr><td>1 (30)</td><td>9</td></tr><tr><td>2 (18)</td><td>14</td></tr></table>	n	% ee	1 (30)	9	2 (18)	14	197						
n	% ee																
1 (30)	9																
2 (18)	14																
		racemic	Oxone®, K ₂ CO ₃ , ketone 1, buffer (pH 10.5), MeCN, 0°, 2 h	 <table border="1"><tr><td>n</td><td>% ee</td></tr><tr><td>1 (26)</td><td>20</td></tr><tr><td>2 (8)</td><td>5</td></tr></table>	n	% ee	1 (26)	20	2 (8)	5	197						
n	% ee																
1 (26)	20																
2 (8)	5																
C ₁₂			Oxone®, K ₂ CO ₃ , ketone 1, buffer (pH 10.5), MeCN, DMM, 0°, 5 h	 (< 5), 11% ee	196, 197												
C ₁₂₋₁₉		meso or rac	Oxone®, K ₂ CO ₃ , ketone 1, buffer (pH 10.5), MeCN, DMM, 0°, 5 h	 <table border="1"><tr><td>R¹</td><td>R²</td><td>% ee</td></tr><tr><td>Ph</td><td>Me</td><td>(6) 44</td></tr><tr><td>Ph</td><td>Ph</td><td>(10) 63</td></tr><tr><td>4-MeC₆H₄</td><td>4-MeC₆H₄</td><td>(10) 65</td></tr></table>	R ¹	R ²	% ee	Ph	Me	(6) 44	Ph	Ph	(10) 63	4-MeC ₆ H ₄	4-MeC ₆ H ₄	(10) 65	197
R ¹	R ²	% ee															
Ph	Me	(6) 44															
Ph	Ph	(10) 63															
4-MeC ₆ H ₄	4-MeC ₆ H ₄	(10) 65															

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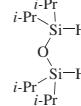
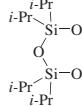
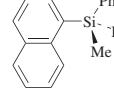
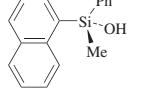
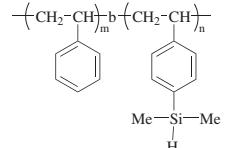
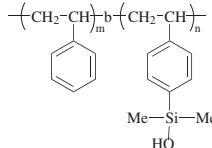
	Substrate	Conditions	Product(s) and Conversions(s) (%)	Refs.																								
C ₁₄₋₁₆		Oxone®, ketone 1, K ₂ CO ₃ , buffer (pH 10.5), MeCN, 0°	 <table border="1"><tr><td>R</td><td>Time</td><td>% ee</td></tr><tr><td>Br</td><td>2 h (10)</td><td>74</td></tr><tr><td>Cl</td><td>2 h (11)</td><td>70</td></tr><tr><td>H</td><td>3 h (51)</td><td>65</td></tr><tr><td>CN</td><td>2.5 h (6)</td><td>75</td></tr><tr><td>Me</td><td>3 h (12)</td><td>61</td></tr></table>	R	Time	% ee	Br	2 h (10)	74	Cl	2 h (11)	70	H	3 h (51)	65	CN	2.5 h (6)	75	Me	3 h (12)	61	197						
R	Time	% ee																										
Br	2 h (10)	74																										
Cl	2 h (11)	70																										
H	3 h (51)	65																										
CN	2.5 h (6)	75																										
Me	3 h (12)	61																										
C ₁₄		racemic	Oxone® (0.75 eq), ketone 1, K ₂ CO ₃ , buffer (pH 10.5), MeCN, 0°, 1.5 h	 I + II (10), I: 71% ee, II: 11% ee	197																							
			Oxone® (1.5 eq), ketone 1, K ₂ CO ₃ , buffer (pH 10.5), MeCN, 0°, 3 h	I + II (31), I: 69% ee, II: 28% ee	197																							
C ₁₄₋₁₆		Oxone®, ketone 1, K ₂ CO ₃ , buffer (pH 10.5), MeCN, 0°	 <table border="1"><tr><td>R</td><td>Time</td><td>% ee</td></tr><tr><td>Br</td><td>2 h (61)</td><td>58</td></tr><tr><td>Cl</td><td>3 h (56)</td><td>54</td></tr><tr><td>F</td><td>3 h (89)</td><td>58</td></tr><tr><td>H</td><td>3 h (95)</td><td>45</td></tr><tr><td>CN</td><td>3 h (<5)</td><td>60</td></tr><tr><td>Me</td><td>3 h (92)</td><td>30</td></tr><tr><td>MeO</td><td>3 h (95)</td><td>24</td></tr></table>	R	Time	% ee	Br	2 h (61)	58	Cl	3 h (56)	54	F	3 h (89)	58	H	3 h (95)	45	CN	3 h (<5)	60	Me	3 h (92)	30	MeO	3 h (95)	24	197
R	Time	% ee																										
Br	2 h (61)	58																										
Cl	3 h (56)	54																										
F	3 h (89)	58																										
H	3 h (95)	45																										
CN	3 h (<5)	60																										
Me	3 h (92)	30																										
MeO	3 h (95)	24																										

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TABLE 5E. Si-H OXIDATION BY ISOLATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.		
C ₅₋₁₈		DMD, acetone, (CCl ₄), rt		(> 99)	R ¹ TMSO	R ² Me	R ³ Me	15 min	483
					Et Et	Et Et		< 5 min	
					t-Bu Ph	Me Me	H	< 5 min 30 min	
					TMSO Ph	TMSO Me	30 min < 5 min		
					TMSO Ph	TMSO Me	TMSO TMS	3 h < 1 min	
					Ph Ph	Ph Ph	Ph	10 min	
C ₆		TFD, TFP, CH ₂ Cl ₂ , -20°, < 1 min		(> 98)					39
C ₈		TFD, TFP, CH ₂ Cl ₂ , -20°, < 1 min		(> 98)					39
C ₉		DMD, acetone, Ar		I	+ TMS-Si-OAc	TMS	II		483
	Additive Temp Time			I	II				
	— 20° < 1 min			(79)	(16)				
	O ₂ 20° < 1 min			(> 99)	(—)				
	— -70° 10 min			(> 99)	(—)				
	hν -70° 10 min			(88)	(5)				
	DMD, (CF ₃ CO) ₂ O, acetone, CCl ₄ , Ar, 20°, < 1 min			(90)	+ TMS-Si-Cl	TMS	(10)		483

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	Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.	
C ₁₂		DMD, acetone, CCl ₄ , rt		(> 99)				483
C ₁₇		96.5% ee (+) TFD, TFP, CH ₂ Cl ₂ , -20°, < 1 min; or, DMD, acetone, CH ₂ Cl ₂ , 0°, 18 min			(> 98), 97% ee			39
C _x		DMD, acetone, 0°			(—)			484

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TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇₋₁₂		DMD, acetone, toluene, -78° to rt, 50 min		227
C ₉₋₁₉		1. DMD, THF, acetone, -78°, 1 min 2. NH ₄ F, H ₂ O, rt, 1-12 h		212
C ₉₋₂₂		1. DMD, THF, acetone, -78°, 1 min 2. NH ₄ F, H ₂ O, rt, 1-12 h		212
C ₉₋₃₈		DMD, acetone; or acetone, CH ₂ Cl ₂		220
C ₁₀		DMD, acetone, -78°, 1 h; rt, 1 h		485

TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀		DMD (1.0 eq), acetone, CH ₂ Cl ₂ , -65°, 10 min		486
		DMD (2.0 eq), acetone, CH ₂ Cl ₂ , -65°, 10 min		486
C ₁₀₋₁₁		DMD (1.0 eq), acetone, CH ₂ Cl ₂ , -65°, 10 min		486
C ₁₀₋₁₂		DMD, acetone, toluene, -78°, 2 h		221
C ₁₀₋₁₃		R ¹ = H, 2-CH ₂ OH, 3-CH ₂ OH, 4-CH ₂ OH, -OCH ₂ CH=CH-	DMD, acetone, 20° 	487
C ₁₀₋₁₄		1. DMD, acetone, N ₂ , -78°, 15 min 2. rt, 1 h		128, 129

	R^1	R^2	R^3	I	II	I:II
C ₁₁	Me	H	H	I + II (93)		1:1
	Me	Me	H	(—)	(78)	10:90
	Me	H	MeO	(33)	(33)	50:50
	Me	MeO	H	(—)	(80)	7:93
	Et	MeO	H	(—)	(39)	15:85
	<i>i</i> -Pr	MeO	H	(56)	(—)	70:30
	<i>t</i> -Bu	Me	H	(92)	(—)	98:2
	Me	<i>t</i> -Bu	H	(—)	(45)	6:94
	<i>t</i> -Bu	MeO	H	(77)	(—)	98:2
C ₁₂	DMD, acetone, 20°			487		
	DMD, acetone, -28°, 1 min			488		
C ₁₃₋₂₅	1. DMD (0.95 eq), acetone, N ₂ , -78°, 15 min 2. -78° to rt, 2 h			217		
C ₁₃	1. DMD, acetone, N ₂ , -78°, 15 min 2. -78° to rt, 2 h			217		

TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (*Continued*)

TABLE 6. CATALYSIS OF ORGANOMETALLICS BY ISOLATED DIORGANETNES (Continued)					
	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs
C ₁₃		DMD, acetone, 0°		(74)	210
C ₁₃₋₁₄		DMD, acetone, Ar, 1 min		R H (—) Me (39)	214
C ₁₃₋₂₈		DMD, acetone		(—)	489
C ₁₄		DMD, acetone, 20°, 3 h		(97)	204
		DMD, acetone, toluene, -78° to rt, 60 min		(68)	226
		1. DMD (1.2 eq), acetone, N ₂ , -78°, 15 min 2. -78° to rt, 2 h		(63)	217
		1. DMD (2.4 eq), acetone, N ₂ , -78°, 15 min 2. -78° to rt, 2 h		(80)	217

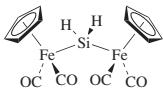
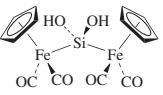
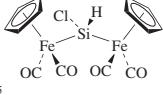
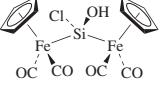
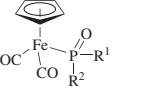
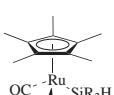
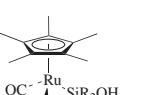
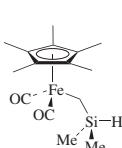
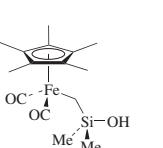
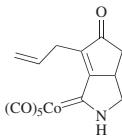
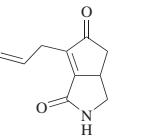
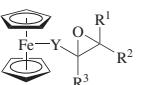
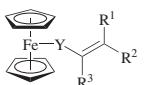
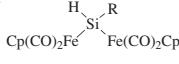
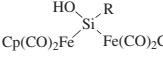
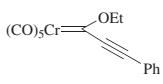
	DMD, acetone, -78°, 45 min		(83)	490
	DMD, acetone, -78°, 1 h		(57)	490
	DMD, acetone, N2, -78°		$\begin{array}{c} \text{R}^1 \\ \\ \text{i-Pr} \end{array}$ $\begin{array}{c} \text{R}^2 \\ \\ t\text{-Bu} \end{array}$ (84) $\begin{array}{c} \text{R}^1 \\ \\ t\text{-Bu} \end{array}$ $\begin{array}{c} \text{R}^2 \\ \\ t\text{-Bu} \end{array}$ (76)	216
C14-26				
	DMD, acetone, toluene, -78° to rt, 45-60 min		$\begin{array}{c} \text{R} \\ \\ \text{Me} \end{array}$ (37) $\begin{array}{c} \text{R} \\ \\ o\text{-MeC}_6\text{H}_4 \end{array}$ (56)	226
C15				
	DMD, acetone		(36)	485
C15-19				
	DMD, acetone		(—)	207
C15-19				

TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions				Product(s) and Yield(s) (%)	Refs.	
C15-19	DMD (x eq), acetone, CH ₂ Cl ₂ , gas					213	
	x	Time	Temp	Gas			
Y	R ¹	R ²	R ³				
CO	Me	Me	H	6.0	5 h	20° Ar	(24)
CO	Me	Me	H	9.0	9 h	20° Ar	(44)
CO	Me	Me	H	12.0	14 h	20° Ar	(58)
CO	H	Me	Me	6.0	6 h	20° Ar	(59)
CO	H	Me	Me	6.0	24 h	20° O ₂	(38)
CH ₂	Me	Me	H	3.0	40 min	0° Ar	(66)
CH ₂	Me	Me	H	3.0	10 min	20° Ar	(75)
CH ₂	Me	Me	H	3.0	1 min	56° Ar	(63)
CH ₂	Me	Me	H	4.0	1 min	56° Ar	(76)
CH ₂	Me	Me	H	3.0	25 min	20° O ₂	(28)
CH ₂	H	Me	Me	3.0	15 min	20° Ar	(67)
CH ₂	H	Me	Me	3.0	30 min	20° O ₂	(53)
CO	H	Ph	H	6.0	8 h	20° Ar	(30)
CH ₂	H	Ph	H	6.0	45 min	20° Ar	(38)
C15-21		DMD, acetone, -78° to rt, 25 min		$\begin{array}{c} \text{HO} \\ \\ \text{Si}-\text{R} \\ \\ \text{Cp}(\text{CO})_2\text{Fe} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{Me} \end{array}$ (89) $\begin{array}{c} \text{R} \\ \\ 4\text{-MeC}_6\text{H}_4 \end{array}$ (95)	223	
C16		DMD, O ₂ , acetone, -20°, 4 h	Ph-C≡C-CO ₂ Et	I (90)	204, 205		
	TFD, O ₂ , TFP, -20°, 4 h		I (91)		205		

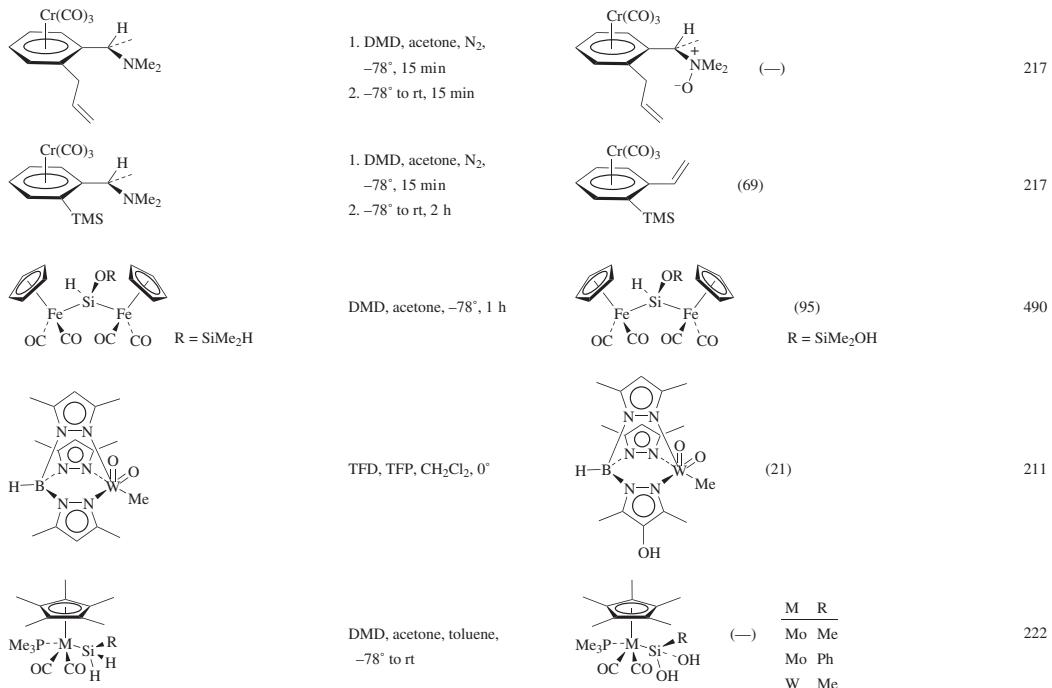


TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)					
	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C ₁₆₋₂₂		DMD, acetone, solvent, $\text{N}_2, -78^\circ$		(—)	216
	$\begin{array}{c} \text{L} \quad \text{R}^1 \quad \text{R}^2 \\ \hline \text{CO} \quad t\text{-Bu} \quad t\text{-Bu} \\ \text{CO} \quad \text{H} \quad 2,4,6\text{-Me}_3\text{C}_6\text{H}_2 \\ \text{CO} \quad \text{Me} \quad 2,4,6\text{-Me}_3\text{C}_6\text{H}_2 \\ \text{CO} \quad 2\text{-MeC}_6\text{H}_4 \quad 2\text{-MeC}_6\text{H}_4 \\ \text{PMe}_3 \quad \text{Ph} \quad \text{Ph} \end{array}$	$\begin{array}{c} \text{Solvent} \\ \text{toluene} \end{array}$	(88) (80) (69) (67)		
C ₁₇		DMD, O ₂ , acetone, -20° , 4 h		(94)	204
	$\text{Et}_4\text{N}^+ \text{TpMo}(\text{CO})_5^-$	DMD, acetone, Ar, rt, 15 min	$\text{Et}_4\text{N}^+ \text{TpMoO}_3^-$	(59)	210
	$\text{Et}_4\text{N}^+ \text{Tp}^*\text{Mo}(\text{CO})_3^-$	DMD, acetone, Ar, rt, 15 min	$\text{Et}_4\text{N}^+ \text{Tp}^*\text{MoO}_3^-$	(—)	210
		1. DMD, acetone, N ₂ , -78° , 15 min 2. -78° to rt, 2 h		(44)	217

C ₁₈		DMD, acetone, 20°, 24 h		(63)	204
		DMD, acetone, -78°, 1 h		(79)	490
C ₁₈₋₂₇		1. DMD, THF, acetone, -78°, 1 min 2. NH ₄ F, H ₂ O, rt, 1-12 h		R L ₃ Me (i-PrO) ₃ (45) Me (Et ₃ N) ₃ (90) Me Cp ₂ Cl (77) Ph Cp ₂ Cl (70)	212
323		DMD (1.2 eq), acetone, -78°, 10 min		I (80) + II (20)	208
		DMD (2.2 eq), acetone, -78°, 20 min		II (93)	208
C ₁₉		DMD, acetone, CH ₂ Cl ₂ , 20°, 45 min		(100)	211

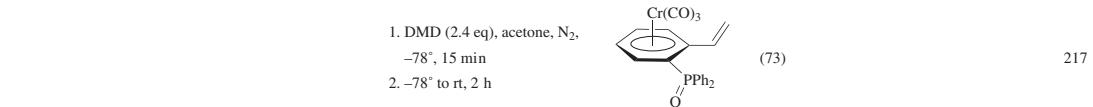
TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Ref.	
C ₁₉		DMD, acetone, CH ₂ Cl ₂ , 20°, 45 min		211	
C ₁₉₋₂₀		1. DMD, acetone, N ₂ , -78°, 15 min 2. -78° to rt, 2 h		R Ph (84-85) 4-MeOC ₆ H ₄ (81-95)	217
324	C ₂₀ 	DMD, acetone, 20°		(52)	206
		1. DMD, CH ₂ Cl ₂ , acetone, -30° 2. Et ₃ OB ₄ , CH ₂ Cl ₂ , acetone, -70°		(—)	206
C ₂₁		1. DMD, THF, acetone, -78°, 1 min 2. NH ₄ F, H ₂ O, rt, 1-12 h		(65)	212

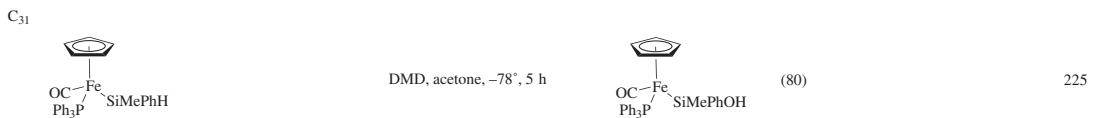
C ₂₁₋₂₄		DMD, acetone, CH ₂ Cl ₂ , 20°, 0.5 h		(100)	211
		TFD, TFP, CH ₂ Cl ₂ , 0°	I (83)		211
325		DMD, acetone, CH ₂ Cl ₂ , N ₂ , -20°, 20 h		R Ar ₁ Ar ²	215
		TFD, TFP, Et ₂ O, rt		H Ph Ph (30) Me Ph Ph (25) H 4-MeC ₆ H ₄ 4-MeC ₆ H ₄ (42) Me Ph 4-MeOC ₆ H ₄ (27) Me 4-MeOC ₆ H ₄ Ph (—) Me 4-MeC ₆ H ₄ 4-MeC ₆ H ₄ (41) Me 4-MeOC ₆ H ₄ 4-MeC ₆ H ₄ (—) Me 4-MeC ₆ H ₄ 4-MeOC ₆ H ₄ (29)	
C ₂₂₋₂₄		DMD, acetone, rt		(—)	209
				I (20) II (75) (47) (—)	491

TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₂₋₂₇		1. DMD, acetone, toluene, -78°, 30 min 2. rt, 1 h		224
C ₂₄		DMD, acetone, 0°, 45 min	 I (67) (—) 96 II (—) —	492
326		Time	I II % ee	
	BF ₄ ⁻	2.3 h	(67) (—) 96	
	BF ₄ ⁻	2.0 h	(49) (24) 100	
	BF ₄ ⁻	3.0 h	(84) (10) 91	
	BF ₄ ⁻	5.6 h	(100) (—) 85	
	TfO ⁻	2.6 h	(53) (21) 39	
	TfO ⁻	3.0 h	(84) (11) 38	
	TfO ⁻	2 d	(77) (—) 79	
C ₂₅	TfO ⁻	4 d	(58) (—) 100	
	TfO ⁻	—	(32) (—) —	
327		1. DMD (0.95 eq), acetone, N ₂ , -78°, 15 min 2. -78° to rt, 2 h		217



 <i>L</i> ¹ -Ru-S- <i>R</i> ¹					DMD, acetone, -40 to 0°	 <i>L</i> ² -Ru-O=S- <i>R</i> ¹		127
<i>L</i> ¹	<i>L</i> ²	<i>R</i> ¹	<i>R</i> ²	Time		dr	dr	
	Me ₂ P(CH ₂) ₂ PPh ₂	Me	<i>i</i> -Pr	45 min		(100)	80:20	
Ph ₃ P	CO	Me	<i>i</i> -Pr	2 h		(45)	64:36	
	Me ₂ P(CH ₂) ₂ PPh ₂	Me	Ph	45 min		(100)	80:20	
	Me ₂ P(CH ₂) ₂ PPh ₂	Me	Bz	45 min		(100)	75:25	
Ph ₃ P	CO	Me	Ph	2 h		(100)	54:46	
	Me ₂ P(CH ₂) ₂ PPh ₂	<i>i</i> -Pr	Bz	45 min		(10)	67:33	
Ph ₃ P	CO	Me	Bz	2 h		(30)	62:38	
(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	Me	<i>i</i> -Pr		45 min		(100)	93:7	
(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	Me	Ph		45 min		(100)	73:27	
(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	Me	<i>c</i> -C ₆ H ₁₁		45 min		(70)	92:8	
(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	Me	Bz		45 min		(100)	> 99:1	
(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	Et	Bz		45 min		(5)	95:5	



Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
		<i>L</i> ¹	<i>L</i> ²	R	
C ₃₁₋₄₈ <i>L</i> ¹ -Ru-SR	DMD, acetone, CH ₂ Cl ₂ , -40°, 10 min	 <i>L</i> ¹ -Ru-SO ₂ R	(ca. 90)	CO Ph ₂ P(CH ₂) ₂ PPh ₂ Ph ₂ P(CH ₂) ₂ PPh ₂ Ph ₂ P(CH ₂) ₂ PPh ₂ PPh ₃ PPh ₃ PPh ₃ PPh ₃	486
C ₃₂ 	DMD (4.4 eq), acetone, -30°, 1 h		(—)	Et ₄ N ⁺	493
C ₃₄₋₃₅ 	DMD, acetone, 20°, 2-20 d		n 1 (69) 2 (73)	Et ₄ N ⁺	219
C ₃₄₋₄₂ 	DMD, acetone, 20°, 2-20 d		n 1 (69) 2 (73)	Et ₄ N ⁺	219

n	R ¹	R ²	R ³	R ⁴	dr
1	Me	H	H	H	(35) 61:39
1	Et	H	H	H	(24) 55:45
2	Me	H	H	H	(33) 70:30
1	Me	H	Me	Me	(50) 72:28
2	Et	H	H	H	(27) 55:45
1	Me	—(CH ₂) ₃ —	H	H	(37) 48:38:9:5
1	Et	H	Me	Me	(51) 74:26
2	Me	H	Me	Me	(46) 79:21
1	Et	—(CH ₂) ₃ —	H	H	(36) 47:43:6:4
2	Me	—(CH ₂) ₃ —	H	H	(41) 30:30:23:17
2	Et	H	Me	Me	(48) 71:29
1	Ph	H	H	H	(29) 72:28
2	Et	—(CH ₂) ₃ —	H	H	(32) 84:6:6:4
2	Ph	H	H	H	(32) 78:22
1	Ph	H	Me	Me	(35) 71:29
1	Ph	—(CH ₂) ₃ —	H	H	(32) 58:25:17
2	Ph	H	Me	Me	(43) 59:41

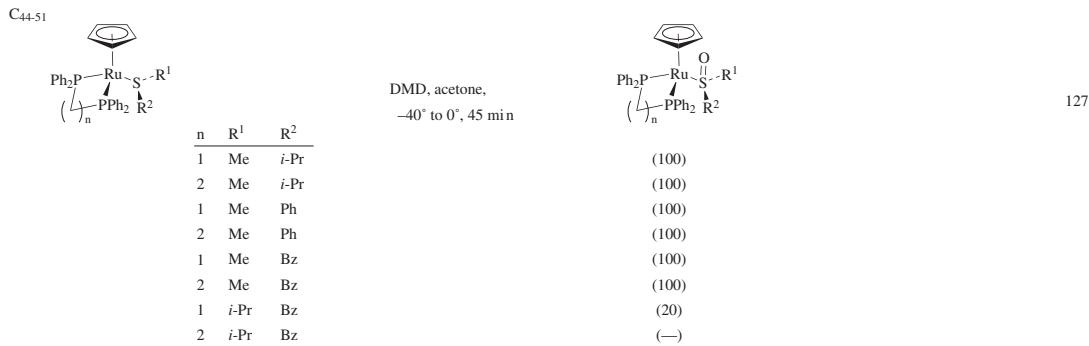


TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃₆		DMD, acetone, CH ₂ Cl ₂ , N ₂ , -78°		(74) 218
C ₃₇₋₃₈	Ar = 3,5-Me ₂ C ₆ H ₃		(> 90) 126	
C ₃₇₋₄₁		DMD, acetone, 0°, 45 min		R de i-Pr 86 Cy 84 Ph 46 Bz 98 492
		DMD, acetone, 0°, 45 min		I + II I:II (95) 7:93 (90) 73:27 (95) 99:1 126

C ₃₈₋₃₉		DMD, acetone, 0°, 45 min		(> 90)	126
C ₃₈₋₄₄		DMD, acetone, 20°, 2-4 d		R dr Me (39) 48:29:15:8 Bn (42) 58:17:14:11	219
C ₄₀		DMD, acetone, CH ₂ Cl ₂ , 0°, 40 min		(—)	494
331					
C ₄₄	Fe ^{II} (TPP) Mn ^{II} (TPP) ClMn ^{III} (TPP) HOMn ^{III} (TPP) Mn ^{III} (TPP)	DMD, acetone, -10° DMD, acetone, -50 to -20° DMD, acetone, -10° DMD, acetone, -10° DMD, acetone, -10°	[Fe ^{III} (TPP)] ₂ O (—) O=Mn ^{IV} (TPP) I (100) I (100) I (100) I (100)	198 198 198 198 198	

TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₄₄₋₄₆		DMD, acetone, 0°, 2 h		495	
	R ¹ Ph ₂ P---Ru---S---R ⁴				
	R ² PPh ₂				
	R ³				
	R ¹ R ² R ³ R ⁴				
	H H H H		(95)		
	H Me H Me		(90)		
	Me H Me H		(90)		
332	C ₅₆	Fe ^{II} (TMP)	DMD, acetone, -10°	O=Fe ^{IV} (TMP) (100)	198
	C ₈₈	[Fe ^{III} (TPP)] ₂ O	DMD, acetone, -10°	O=Fe ^{IV} (TPP) (—)	198
		[Mn ^{III} (TPP)] ₂ O	DMD, acetone, -10°	O=Mn ^{IV} (TPP) (100)	198

TABLE 7. MISCELLANEOUS OXIDATIONS BY ISOLATED DIOXIRANES

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																					
C ₄		1. DMD, MeI, acetone, -70° 2. -40° to rt	 (78)	170																					
C ₆		1. DMD, MeI, acetone, -70° 2. -40° to rt	 (85)	170																					
		1. DMD, MeI, acetone, -70° 2. -40° to rt	 (—)	170																					
C ₇		DMD, acetone, CH ₂ Cl ₂ , 0° or 15°	 (—)	496																					
		1. DMD, MeI, acetone, -70° 2. -40° to rt	 (72)	170																					
C _{8.9}		1. DMD, MeI, acetone, -70° 2. -40° to rt	 <table border="1"><tr><th>R¹</th><th>R²</th><th>Yield (%)</th></tr><tr><td>Cl</td><td>H</td><td>(82)</td></tr><tr><td>H</td><td>H</td><td>(85)</td></tr><tr><td>CF₃</td><td>H</td><td>(44)</td></tr><tr><td>H</td><td>Me</td><td>(72)</td></tr><tr><td>Me</td><td>H</td><td>(75)</td></tr><tr><td>MeO</td><td>H</td><td>(60)</td></tr></table>	R ¹	R ²	Yield (%)	Cl	H	(82)	H	H	(85)	CF ₃	H	(44)	H	Me	(72)	Me	H	(75)	MeO	H	(60)	170
R ¹	R ²	Yield (%)																							
Cl	H	(82)																							
H	H	(85)																							
CF ₃	H	(44)																							
H	Me	(72)																							
Me	H	(75)																							
MeO	H	(60)																							
C ₉		1. DMD, MeI, acetone, -70° 2. -40° to rt	 (82)	170																					

333

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉		1. DMD, MeI, acetone, -70° 2. -40° to rt	 (84) ^a	170
		1. DMD, MeI, acetone, -70° 2. -40° to rt	 (85) ^b	170
C ₁₃		DMD, acetone, THF, Ar, 20°, 5 min	 (43)	413
C ₁₄		1. DMD, MeI, acetone, -70° 2. -40° to rt	 (—)	170
C ₁₈		DMD, acetone, THF, Ar, 20°, 5 min	 (30)	413

334

^a These two products were obtained as a mixture in a ratio of 65:35.^b These two products were obtained as a mixture in a ratio of 50:50.

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