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Dioxiranes[1]

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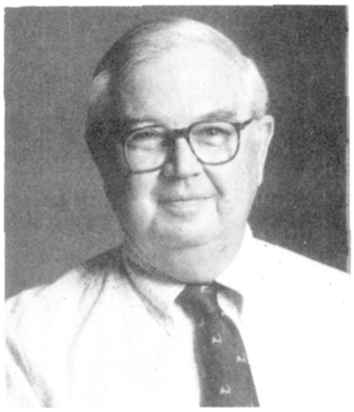
Contents

I. Introduction

The recent discovery[2] that solutions of dioxiranes can be prepared and used to carry out a variety of synthetically useful reactions has set the scene for a wide-ranging development of the chemistry of these interesting cyclic peroxides. This development will include synthetic, physical organic, and theoretical aspects. The purpose of this review is to recount the circumstances leading up to this discovery as well as to provide an account of literature reports in which evidence has been presented for the existence of dioxiranes. Such reports fall into the period from 1972 to the present. Thus the scope of this review does not include those many cases in which dioxiranes have been invoked as reaction intermediates, but without supporting evidence for their involvement. The author has written a book chapter[3] in which these latter cases have been surveyed. It may be that the chemistry described in this review will stimulate experiments that will permit the obtaining of supporting evidence for dioxirane involvement in some of these cases. The referenced earlier book chapter also contains some material on the solution method of dioxirane generation. However, that publication is much wider in scope and does not have the focus of this review. Finally, this review covers a number of recent publications that further illustrate the interesting chemistry of dioxiranes.

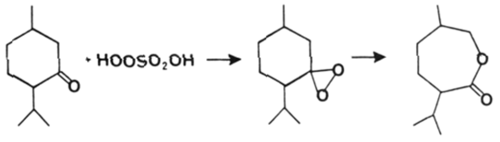
Kafaki, Martinez, and Herron have also written a review of dioxiranes[4a] and the related dioxymethylenes. Their review emphasizes gas-phase aspects as well as the thermochemistry and detailed computational studies of dioxiranes. In contrast, the current review emphasizes the organic chemistry of dioxiranes in solution.



Robert W. Murray was born in Brockton, MA, in 1928. He received an A.B. in chemistry from Brown University in 1951. After 3 years of active duty service with the U.S. Navy, he received an M.S. degree in chemistry from Wesleyan University and a Ph.D. degree from Yale University with Professor Martin Saunders. He was a member of the technical staff at Bell Telephone Laboratories from 1959 to 1968. In 1968 he became Professor of Chemistry at the University of Missouri—St. Louis. He served as department chairman from 1975 to 1980. In 1981 he was named Curators' Professor of Chemistry. He was a Visiting Professor of Chemistry at the Engler-Bunte Institute of the University of Karlsruhe in the Spring 1982 semester. In 1974 Murray was awarded the St. Louis Section ACS Award.

After this work was nearly complete, the author became aware of two additional reviews on dioxiranes recently submitted by Curci[4b] and Adam, Curci, and Edwards.[4c] While some of the material covered is the same, these reviews do differ in style and perspective from the present one. All of us involved in this exciting chemistry are convinced that we are only at the threshold of its development. In that sense these several reviews can perhaps be justified (and tolerated) as birth announcements from proud parents.

It is of historical interest that the first literature reference[5] to a dioxirane was made by Baeyer and Villiger in a publication describing a reaction that today bears their names. In 1899 these authors suggested that the intermediate in the conversion of the cyclic ketone menthone to its corresponding lactone by monoperoxysulfuric acid was a dioxirane (eq 1). The dioxirane



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mechanism for the Baeyer–Villiger reaction eventually lost out to a competing mechanism primarily as a result

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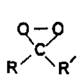
of an ^{18}O study by Doering and Dorfman.[6] Our success in isolating dioxiranes has prompted us to suggest[2,3] that the original formulation of the mechanism by Baeyer and Villiger could be viable for their ketone as well as other cases where cyclic ketones or dialkyl ketones are involved. This possibility would require reaction conditions supportive of dioxirane formation. The competing mechanism would still hold for those cases where the ketone contains a group of high migratory aptitude such as the Doering and Dorfman example. A second historical note comes from ozone chemistry. In 1905 Harries suggested[7a] that the 1,2,3-trioxolanes, formed when ozone adds to olefins, could decompose to a carbonyl compound and what he termed a "peroxide", to which he assigned the dioxirane structure.

As cyclic peroxides, dioxiranes (**1**) are related to the 1,2-dioxetanes (**2**)[7b] and the 1,2,3-trioxolanes[7c] (**3**). The



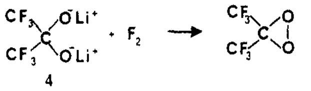
1a, R = R' = CF_3
1b, R = CF_3, R' = CF_2Cl
1c, R = R' = H
1d, R = R' = F
1e, R = R' = CH_3
1f, R = CH_3, R' = CH_3CH_2
1g, R = CH_3, R' = $CH_3CH_2CH_2$
1h, R = CH_3, R' = $CH_3CH_2CH_2CH_2$
1i, R = CH_3CH_2, R' = CH_3CH_2
1j, R = CH_3, R' = F
1k, R = F, R' = H
1l, R = CH_3, R' = H
1m, R = CH_3, R' = CF_3

chemistry of these close relatives is remarkably different, however. The major chemical path for the 1,2-dioxetanes is decomposition to give two carbonyl compounds. The 1,2,3-trioxolanes are the precursors to carbonyl compounds and carbonyl oxides in the Criegee mechanism[8a] of ozonolysis. To date the most common reaction of the dioxiranes is O-atom transfer, particularly to unsaturated materials. This latter reaction is observed only infrequently in the 1,2-dioxetanes[8b,c] or the 1,2,3-trioxolanes.[7c]

II. Preparation of Dioxiranes

A. Non-Peracid Methods

Apparently, the first report of the preparation of a dioxirane is that contained in a 1972 patent[9] issued to Talbott and Thompson. The authors describe the preparation of perfluorodimethyldioxirane (**1a**) and chloro(difluoromethyl)(trifluoromethyl)dioxirane (**1b**) by F_2 oxidation of the precursor dialkoxides, e.g., **4** (eq 2). The authors claim to have isolated the dioxiranes



(2)

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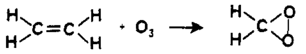
by low-temperature gas chromatography. The dioxiranes were pale yellow with λ_{max} of 306 nm for **1a**. The latter dioxirane was reported to be explosive and unstable. The authors also report infrared, ^{19}F NMR, and mass spectral data for **1a** and **1b**. The description of these dioxiranes as being yellow turned out to be an important clue for the developments in the present author's laboratory.

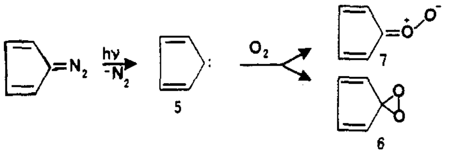
The field of ozone chemistry provided the next example of dioxirane formation. As mentioned above, beginning with the report of Harries in 1905,[7] dioxiranes have been considered as possible intermediates in the ozonolysis reaction. The success of the Criegee mechanism, based on the alternative proposal of a carbonyl oxide intermediate, led to reduced attention to the dioxirane possibility, at least in the case of solution ozonolysis. However, in 1977 Lovas and Suenram[10] presented critical evidence from microwave spectroscopy that parent dioxirane **1c** is produced in the reaction between ozone and ethylene (eq 3). The ozonolysis



(3)

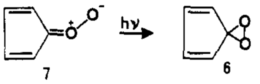
was carried out at low temperature (−130 to −75 °C). The microwave data were used to show that the dioxirane has C–O and O–O bond lengths of 1.3878 and 1.5155 Å, respectively. Kuczkowski had earlier shown[11] that ethylene ozonide has C–O and O–O bond lengths of 1.416 and 1.461 Å. Thus the dioxirane has a shorter C–O bond and a longer O–O bond than the ozonide. These differences were attributed to ring strain in the dioxirane by Suenram and Lovas. The microwave data also indicated that **1c** has a dipole moment of 2.479 D. This value is to be compared to that of 2.33 D for formaldehyde. Dioxirane **1c** was also detected among the products of ozonolysis of propene, vinyl fluoride, and 1-butene. Ozonolysis of propene and 1-butene could have given substituted dioxiranes, but they could not be detected. The low-temperature ozonolysis procedure also permitted[10] the detection of **1c** by photoionization mass spectrometry.

Matrix isolation spectroscopy has been used to obtain evidence that dioxiranes can be formed by the photooxidation of diazo compounds and diazirines. Chapman and Hess[12] photooxidized diazocyclopentadiene in an argon matrix at 10 K. The diazo compound loses nitrogen to give the carbene **5**, which reacts with oxygen to give a material that is either the dioxirane **6** or the carbonyl oxide **7** (eq 4). The authors[12] preferred the



(4)

carbonyl oxide structure based on the observed infrared spectrum. This material was itself photolyzed to give several products, including α-pyrone. Two reaction paths were considered to explain the products, including one involving dioxirane **6**. The authors favored the alternative pathway involving a dioxetane, however. Similar matrix isolation studies have been carried out by Dunkin and Bell[13,14] in which diazoindene and diazofluorene as well as diazocyclopentadiene were used. These workers also concluded that the intermediate carbenes are oxidized to oxygen-containing species, for which they considered both carbonyl oxide and dioxirane structures. They settled on the carbonyl oxide structure in the case of the diazocyclopentadiene oxidation. This conclusion was based on the observation of two nonequivalent oxygen atoms in the infrared spectrum of the oxygen-trapped species. In subsequent work Dunkin and Shields[15] showed that carbonyl oxide **7** can be photoisomerized to a new material (eq 5). The

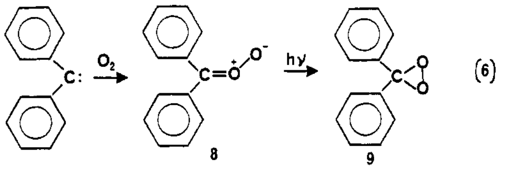


(5)

infrared spectrum of this material, prepared using

$^{16}O,^{18}O$, indicated that it contained two equivalent O atoms, and it was consequently assigned to the structure of dioxirane **6**.

Scaiano and co-workers observed[16] that the quenching of diphenylcarbene by oxygen produced a new species with an absorption spectrum different from that of the carbene. The authors favored a carbonyl oxide structure for this species but point out that they cannot rule out the dioxirane. Working with the same system, Sander showed[17] that the diphenylcarbene first reacts with oxygen to give benzophenone oxide (**8**), which is further photolyzed to diphenyldioxirane (**9**) (eq 6). The infrared spectrum of **9** had absorptions as follows: (Ar, 10 K) 760 (m), 698 (m), 629 (w), 590 (w) cm^{-1}. Irradiation at 515 nm brought about the conversion of **8** to **9**. When **9** is irradiated at 438 nm, it rearranges to phenyl benzoate (**10**) (eq 7). Sander has recently followed up[18] these studies by oxidizing 1-phenyl-2,2,2-trifluoroethylidene and bis(trifluoromethyl)methylene with molecular oxygen in an argon matrix. Here again the first-formed species were characterized as carbonyl oxides. One of them, trifluoroacetophenone oxide (**11**), could be further photolyzed to the dioxirane **12** (eq 8).



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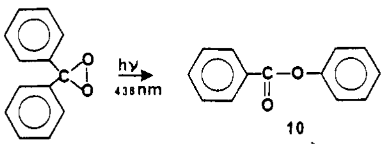

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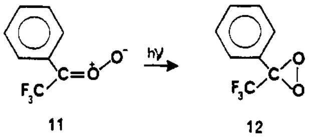
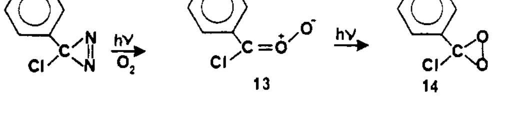


(8)

Dioxirane **12** had infrared absorptions at 1213 (s, C–F), 944 (s), 684 (m), and 643 (m) cm^{-1}. Irradiation of **12** caused isomerization to phenyl trifluoroacetate. In a related study Sheridan and co-workers[19] photolyzed phenylchlorodiazirine in an argon matrix in the presence of oxygen and obtained the carbonyl oxide **13** (eq 9). Photolysis of **13** with visible light gave the dioxirane **14**. Evidence for the structure of **14** comes from the infrared spectrum (1325 (m), 1318 (m), 1282 (s), 1162 (vs), 1075 (w), 982 (m), 900 (vs), 750 (m), 715 (m), 682 (s), 650 (m), 645 (w), 550 (w) cm^{-1}) and its photochemical isomerization to phenyl chloroformate.



(9)

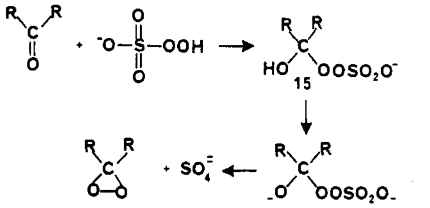
Finally, a recent report contains good evidence for the preparation of difluorodioxirane (**1d**). Shevlin, McKee, and co-workers[20] reacted arc-generated carbon atoms with tetrafluoromethane in the presence of oxygen. These conditions produce an oxidant that the authors believe arises from a reaction between difluoromethylene and oxygen. The oxidant epoxidizes olefins in a stereospecific manner. We have suggested[2] that this epoxidation behavior is one of several chemical criteria that can be used to distinguish dioxiranes from the isomeric carbonyl oxides. The authors conclude that their oxidant is difluorodioxirane on the basis of the epoxidation behavior as well as on the results of their ab initio calculations indicating that difluorodioxirane is more stable than the isomeric carbonyl oxide and that closure of the carbonyl oxide to the dioxirane should be rapid. The reviewer believes that this report contains sufficient evidence for the presence of the dioxirane to warrant its inclusion here.

B. Peracid Methods

1. *In Situ Generation of Dioxiranes*

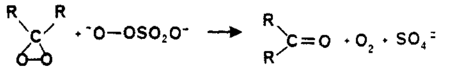
The most common current method of preparing dioxiranes involves the oxidation of ketones by peracids and, particularly, monoperoxysulfuric acid. As mentioned earlier, the connection between the peracid/ketone system and dioxiranes began with the suggestion of Baeyer and Villiger that a dioxirane was involved in the conversion of menthone to the corresponding lactone by monoperoxysulfuric acid.

The events leading up to the successful isolation of dioxiranes began with an observation by Montgomery[21] in 1974. Essentially, what Montgomery observed was that certain ketones enhance the rate of decomposition of monoperoxysulfuric acid (also referred to as caroate). Furthermore, he discovered that a number of oxidation reactions of caroate are catalyzed by the presence of ketones. These observations led Montgomery[21] to propose that the monoperoxysulfate anion was adding to the ketone to give an adduct, **15**. This adduct is in fact the "Criegee" intermediate proposed for the Baeyer–Villiger[5] reaction. Since a variety of ketones could enhance the caroate decomposition, Montgomery further proposed that intermediate **15** reacted further to give a dioxirane (eq 10). While convinced that dioxiranes were involved as intermediates in the catalyzed decompositions, Montgomery[21] was not prepared to say that these dioxiranes were acting as oxidants. Thus while he was working in slightly alkaline as opposed to the usual acidic conditions of the Baeyer–Villiger reaction, Montgomery had essentially revived the idea that dioxiranes could be involved in these reactions.



(10)

The next chapter in these developments was written by Edwards, Curci, and their co-workers.[22-26] Using a combination of kinetic and ^{18}O-labeling experiments, Edwards et al. presented a strong case for the presence of dioxiranes in the ketone/caroate system. Furthermore, they presented evidence that this intermediate was itself a very powerful oxidant. The reactions were run in an aqueous system containing the ketone, caroate (Oxone, Du Pont Co.),[27a] and the substrate. Efficient oxidation required strict pH control at 7.5. At higher pH values the yields of oxidation products dropped sharply. This latter observation was explained by postulating an increased concentration of caroate dianion which could attack the dioxirane to generate oxygen (eq 11). The critical ^{18}O-labeling experiment was carried out with doubly labeled caroate (OSO_2–^{18}O–^{18}OH). Attack of this caroate on the ketone should give dioxirane with 50% of the label in the caroate (eq 12). When a second labeled caroate attacks the dioxirane as shown in eq 11, the oxygen produced should contain 75% of the original labeling. In fact, the evolved oxygen was found to contain 73 ± 2% of the label, thus providing powerful evidence for the requirement of a dioxirane in these caroate/ketone decomposition reactions.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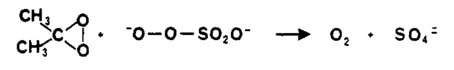
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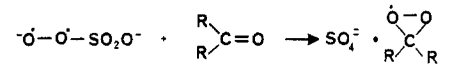
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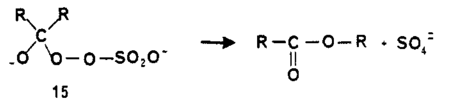
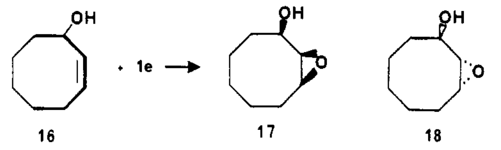
Subsequent events that led to the isolation of dioxiranes would not have occurred without this pioneering work of Edwards and Curci.[22-26] History will record that these careful experiments opened the door to an exciting new chapter in peroxide chemistry.

Another interesting observation made by Edwards and co-workers[22] was that with most of the ketones used, there was little competition from the Baeyer–Villiger reaction. With cyclobutanone, oxidation to the Baeyer–Villiger product, γ-butyrolactone, was the major reaction pathway, however. Significantly, cyclohexanone undergoes only a slight amount of Baeyer–Villiger oxidation at pH 7, while at pH 9 some 15–30% of the reaction occurs along this path. The authors chose to explain Baeyer–Villiger type products as arising from intermediate **15** rather than from the dioxirane (eq 13). This choice was based on the observation that when labeled caroate (HO^*O^*–SO_3^-) was used in the reaction with cyclohexanone, the ε-caprolactone obtained[23] contained label only in the ether oxygen. We subsequently showed[2] that dioxiranes also rearrange to Baeyer–Villiger type products when treated with Lewis acids (vide infra).



(13)

Edwards and co-workers also showed[22] that their in situ method of preparing dioxiranes could be used to carry out a number of O-atom-transfer reactions of the dioxiranes. For example, olefins were shown to be epoxidized in a syn stereospecific manner and in high yield. Use of their aqueous generation conditions was extended[23] to water-insoluble olefins by the use of phase-transfer catalysis. Curci and co-workers later examined[25] the stereoselectivity and regioselectivity of dioxirane epoxidations. The stereoselectivity observed was similar to that given by peracids. For example, (*Z*)-cyclooct-2-en-1-ol (**16**) was converted into the epoxy alcohols **17** and **18** in a ratio of 1:99 (eq 14). The regiospecificity of the epoxidation was shown by oxidizing geraniol (**19**) to the mixture of epoxides **20**, **21**, and **22** (eq 15). At high conversions the diepoxide **20** was the major product. However, at moderate conversions the 6,7-epoxide **21** becomes the major product.



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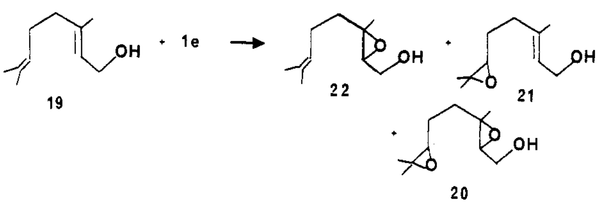


(15)

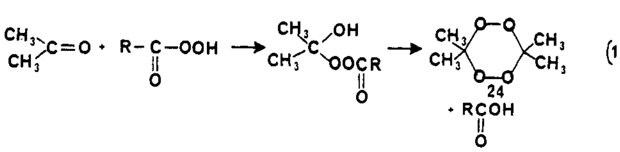
The synthetic utility of in situ generated dioxiranes was greatly expanded when Curci and co-workers reported[26a] that chiral ketones can be converted to dioxiranes by caroate and that these dioxiranes react with prochiral alkenes to give epoxides with enantiomeric excesses in the 9–12.5 range. The chiral ketones used were (+)-isopinocamphone (**23a**) and (*S*)-(+)-3-phenylbutan-2-one (**23b**). The prochiral alkenes epoxidized were 1-methylcyclohexene and (*E*)-β-methylstyrene. When 1-methylcyclohexene is epoxidized with **23a**, for example, the epoxides are obtained in 92% yield and with an enantiomeric excess of 12%. The predominant enantiomer had the (+)-(1*S*,2*R*) configuration. The authors point out that the chiral dioxirane method gives enantioselectivities that are superior to those given by such standard reagents as (+)-monoperoxycamphoric acid. Furthermore, unlike some more recently available methods, the dioxirane method is catalytic rather than stoichiometric. Indeed the optically active ketone catalyst can be recovered unchanged.

In addition to alkenes the in situ method has been used to carry out single oxygen atom oxidations of a variety of other substrates, including alkynes, pyridine, polycyclic aromatic hydrocarbons, sulfides, and sulfoxides. The reader is directed to ref 3 for a recent summary of individual reactions. In some instances the in situ method may be preferred over the method using the isolated dioxirane. Examples include cases where the substrate and/or product is not sensitive to alkaline aqueous conditions or where large-scale reactions are required.

2. *Isolation of Dioxiranes*

The work of Edwards and Curci[22-26] described above made a very strong case for the intermediacy of dioxiranes in the reaction between ketones and caroate. In the period in which they were gathering their important kinetic and ^{18}O data on these reactions, we were investigating the conditions of the Baeyer–Villiger reaction as a possible source of carbonyl oxides or dioxiranes. Our goal at the time was to find additional non-ozone sources of these species that would then be used in our longstanding work on the mechanism of ozonolysis. We were drawn to the Baeyer–Villiger reaction because of the, frequently overlooked, observation that many simple ketones, most notably acetone and methyl ethyl ketone, do not give the typical Baeyer–Villiger, that is, ester, product under the reaction conditions generally used.[27b] Instead these ketones give diperoxides; e.g., acetone gives acetone diperoxide

(**24**) (eq 16). In the field of ozone chemistry the formation of diperoxides has long been associated with the dimerization of carbonyl oxides, although this process has not been demonstrated in an unequivocal fashion. Thus the ketone/peracid reaction appeared to be a source of diperoxides whose chemistry could be compared to those obtained from ozonolyses. We had also recently shown[28] that carbonyl oxides could epoxidize olefins and were interested in pursuing this reaction further using an alternative source of carbonyl oxides.



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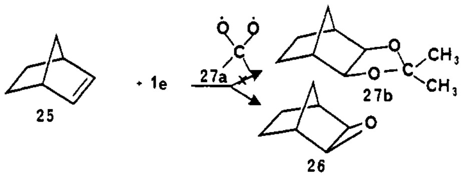
We first showed that no epoxidation occurred under a standard set of conditions, that is, using *cis*-3-hexene, peracetic acid, and diethyl ether solvent. We then showed that addition of a small amount of acetone led to epoxide formation and that increasing amounts of acetone led to higher yields of epoxide.[29a] It was clear then that the peracid and acetone interacted to give a new oxidant that epoxidizes olefins. At the time, we concluded that the oxidant was either the carbonyl oxide or the dioxirane. We[2] and others[22-26,33,40] have subsequently shown that dioxiranes epoxidize in a stereospecific manner. On the other hand, we had found that carbonyl oxides epoxidize in a stereoselective manner[28] and with much lower yields. We have suggested[2] that this epoxidation behavior is one of several chemical tests that can be used to distinguish between these two oxidants. Edwards, Curci, and co-workers had earlier[23] pointed out the differences between carbonyl oxides and dioxiranes in the epoxidation reaction. Since the *cis*-3-hexene in the peracetic acid/acetone experiment was converted exclusively to *cis*-3-hexene epoxide, it now seems very likely that the oxidant involved was the dioxirane.

Subsequent work (vide infra) using the ketone/caroate system indicates that this system generates the dioxirane and not the carbonyl oxide. Furthermore, while there are now several reports indicating that carbonyl oxides can be converted to dioxiranes (section II.A), there is no evidence to date that dioxiranes can be converted to carbonyl oxides. In the few cases studied to date[26b,29b] dioxiranes rearrange to the corresponding esters in the absence of reactive substrates. We had earlier reported[2] that **1e** gave some acetone diperoxide upon standing. While it is possible that the diperoxide was produced in the generation flask and then carried over to the receiver, the possibility that the diperoxide arises from **1e** has not been ruled out. In particular, if ester products are produced via the methylenebis(oxy), e.g., **27a**, then it is possible that **27a** could serve as the precursor to diperoxide under some reaction conditions. Experiments relative to this point are being pursued in our laboratory.

At about the same time that we were making our observations on the peracetic acid/acetone system, Edwards and co-workers[22-26] had made similar observations in the caroate/acetone system, as described above, namely, that the peracid and acetone interact to produce a new oxidant, now shown to be dimethyldioxirane (**1e**). The work that led to the isolation of the dioxirane began with the in situ generation method using the caroate/acetone system and, initially, following the Edwards procedure.[22] The use of the in situ method was extended to several other classes of substrates including showing[30] that the dioxirane converted some polycyclic aromatic compounds to arene oxides in a very convenient way. Of particular interest to the question of the nature of the reacting dioxirane was the observation[2] that norbornene (**25**) was converted to *exo*-norbornene oxide (**26**) in 95% yield when the in situ conditions and a phase-transfer catalyst were used (eq 17). This substrate was used in order to encourage reaction to give the 1,3-dioxolane (**27b**) presumably via the methylenebis(oxy) **27a**. To date no dioxirane has exhibited this reaction mode. In fact, none of the dioxirane chemistry observed to date would seem to require a prior homolysis of the O–O bond that is so characteristic of other peroxides. Nevertheless, the intervention of methylenebis(oxy)'s such as **27a** cannot be ruled out at present. Kafaki, Martinez, and Herron[4a] have suggested that the observed solution chemistry of dioxiranes is best attributed to the methylenebis(oxy) form. In the opinion of this reviewer a definitive answer to the question of the reactive form must await further experimentation. Some examples of such experimentation currently being pursued in the author's laboratory are the following:



(17)

(a) As described above, dioxiranes are able[26b,29b] to undergo unimolecular conversion to the corresponding esters. Is this a case where the methylenebis(oxy) form is involved? We have made[29b] one observation that bears on this possibility. When **1e** is stored in a solution of acetone/2-butanone and the solution is subsequently treated with BF_3,[2] neither of the esters that could arise from dioxirane **1f** are detected. This suggests that **1e** does not transfer an oxygen atom to 2-butanone to give **1f**. At present this should be regarded as a preliminary observation that requires verification and the use of other dioxiranes.

(b) We have described the reaction of **1e** with saturated hydrocarbons to give alcohols or ketones (section III.E). Both relative rate studies and kinetic isotope effect studies would seem to argue against a radical mechanism for these oxidations. Nevertheless, such studies need to be continued under conditions where oxygen and light are excluded as well as under conditions where radical chemistry might be enhanced, i.e., with deliberate photolysis and the passage of an O_2 stream.

(c) Amines are oxidized by **1e** to a variety of products depending upon the type of amine (primary, secondary, tertiary) and the type of substituent (section III.C). The mechanisms of these reactions have not been established. It is possible that the methylenebis(oxy) form is involved in one or more of these reactions. This possibility is perhaps most worth pursuing in those cases in which nitroxides are formed.

In the course of working with the in situ method, we experimented with a large number of reaction conditions. On several occasions, and particularly while working at larger scale, we observed the appearance of a yellow color as the solid Oxone and water/acetone came into contact. Recalling the earlier observation of Talbott and Thompson[9] that their perhalodimethyldioxiranes were yellow, we concluded that dimethyldioxirane had a sufficiently long lifetime under the reaction conditions to permit its visual observation. This conclusion stimulated efforts to remove the dioxirane from the generating medium. As pointed out earlier by Edwards[22] and confirmed by our own work, the generation medium is a very hostile one for the dioxirane. The basic conditions that are necessary for directing the caroate–acetone adduct along the pathway to the dioxirane are also those that cause destruction of the dioxirane once formed (eq 11). An apparatus was devised in which vigorous bubbling of an inert gas is used to remove the dioxirane from the generation medium. The dioxirane–acetone gas is then condensed into a receiver. This solution is then dried to the degree necessary for the intended oxidation. Such solutions may be kept in the freezer for future use with little decomposition. These solutions are assayed for dioxirane content by reacting them with excess phenyl methyl sulfide. The sulfide is rapidly and quantitatively oxidized to the corresponding sulfoxide. These solutions may be used to carry out a wide variety of oxygen-atom-transfer reactions (section III). Most reactions are performed at room temperature or below. Since most of these reactions are quantitative or nearly so and the dioxirane is converted to acetone upon reaction, the procedure also provides for easy workup.

The procedure for isolation of the dioxiranes contains a number of variables, rate of addition of reagents, inert-gas bubbling rate, etc., which have not been optimized. The concentrations of dioxirane obtained are in the range 0.04–0.12 M. We have made some attempts at determining the influence of reaction variables on dioxirane concentration. We have one dioxirane generator in which some variables, that is, rate of inert-gas introduction as well as rate of acetone–water and solid Oxone additions, are controlled. In this case dioxirane concentrations from one run to another are fairly constant at ca. 0.08 M, but no higher concentrations have been achieved. Attempts to concentrate the dioxirane solutions lead to only very slight increases in concentration. The distillation behavior suggests that the dioxirane may form an azeotrope with the acetone. We are also investigating a related possibility, namely, that dioxirane **1e** may be heavily solvated by acetone. As mentioned earlier, Lovas and Suenram[10] used their microwave data to show that dioxirane has a larger dipole moment than the corresponding carbonyl compound, i.e., formaldehyde. If a similar situation holds for dimethyldioxirane, then its dipole moment could be larger than that of acetone. This situation could lead to an aligning influence of dioxirane molecules on neighboring acetone molecules, that is, a solvation effect. Several experimental observations support the solvation possibility. We have found[31] that gas-phase reactions of **1e** with supported polycyclic aromatic hydrocarbons are influenced by the accompanying solvent. Yields of products from these reactions are increased when dioxirane is carried into the reaction zone in a mixture of acetone and methylene chloride rather than in acetone alone. Also the rate of epoxidation of ethyl cinnamate is increased[32] as the amount of methylene chloride in an acetone–methylene chloride solvent system is increased. These observations suggest that the dioxirane becomes more reactive, i.e., less stable, as acetone molecules are replaced with those of another solvent. While further work is required, the indications to date suggest that the successful isolation of dioxiranes was critically dependent on this solvation phenomenon.

The isolation procedure was used to prepare solutions of several other dioxiranes, **1f–i**.[2] The concentrations achieved in these latter cases were always below those of **1e**. If the solvation postulate is correct, then it may be that these lower concentrations reflect poorer solvation by the precursor ketones because of increased steric interference in the dioxirane and ketone substituent. The availability of solutions of dimethyldioxirane has also made it possible to obtain a variety of spectroscopic data by ourselves[2] and others.[3,9,10,26b,33,40a,57,62] The available spectroscopic data on dioxiranes are summarized in section IV.

Adam and co-workers have reported[33] that the Murray and Jeyaraman procedure for isolation of the dioxirane can be modified for larger scale work (300 mL of solution) by substituting a mechanical stirrer for the magnetic one described in the original work. Under these conditions only the cooled receiver and one trap were used instead of the series of traps described in the original[2] preparation. They have also used either argon or nitrogen as the carrier gas. For small-scale preparations these workers used no inert gas but relied on the oxygen produced in the reaction. Eaton and Wicks have used[34] the isolation procedure at a scale requiring a 5-L generation flask. They also used a "substantial" mechanical stirrer.

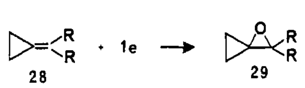
Curci and co-workers have recently described[26b] the isolation and characterization of methyl(trifluoromethyl)dioxirane (**1m**). This member of the series was found to be markedly more reactive than **1e** in its O-atom-transfer reactions.

The chemistry of dimethyldioxirane reported to date indicates that it is a very powerful oxidant. The dioxirane should be prepared in the hood and care taken not to inhale its vapor. This preparation has been carried out in the author's laboratory hundreds of times with no runaway decompositions or explosions occurring. As mentioned earlier, there is some reason to believe that the dioxirane may be stabilized in acetone solution. Neither the Adam[33] nor Eaton[34] groups have experienced any decomposition hazard while using the dioxirane solutions. The author is aware of a large amount of unpublished work involving several research groups in which the dioxirane solutions have been used without mishap.

III. Reactions of Dioxiranes

In this section the reactions of isolated dioxiranes are tabulated (Table I) and discussed. The reactions of dioxiranes using the in situ conditions are included in the discussion only if they were not cited in the earlier[3] review. The reader is reminded that two examples of photochemical reactions of dioxiranes were discussed in section II. In these cases the dioxiranes are photolyzed in matrices to give the ester rearrangement products, i.e., phenyl benzoate[17] in the case of diphenyldioxirane and phenyl trifluoroacetate[17] in the case of phenyl(trifluoromethyl)dioxirane. Of interest to the discussion of the Baeyer–Villiger reaction is the fact that phenyl migration was observed in the latter photolysis.

A very nice application of the in situ method was described[35] by Hofland, Steinberg, and de Boer, who showed that a series of cyclopropylidenes **28** could be converted to the oxaspiropentanes **29** in good yield (70–90%) using caroate–acetone in a buffered aqueous medium (eq 18). This achievement is particularly noteworthy since the standard acid epoxidation conditions lead to rearrangement of the oxaspiropentanes. Zebrowski and co-workers have used[36] the in situ method to oxidize a variety of aromatic amines to the corresponding nitro compounds. The authors had first attempted to employ the procedure for amine oxidation described by Murray and co-workers[37] using isolated dimethyldioxirane but found the in situ method better suited to their required large-scale reactions.



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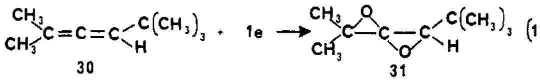
The reactions are discussed in the following paragraphs by class of reactant. When it is helpful in emphasizing special reaction characteristics, reference is made to a substrate or group of substrates by entry number(s).

A. Alkenes

Dimethyldioxirane converts alkenes to their corresponding epoxides in a rapid, high-yield process.[2,22-26,40] The reaction is stereospecific with retention with appropriate substrates. The isolated dioxirane method[2,26b,40] is particularly useful in cases where oxidation products are sensitive to the acidic conditions of the most commonly used epoxidation reagents or the basic conditions of the in situ method. A particularly pleasing example of such a case is contained in a recent report[38] by Crandall and Batal. These workers have used solutions of **1e** to convert a series of allenes to the corresponding spirodioxides in excellent yield (entry 5). Thus 2,5,5-trimethyl-2,3-hexadiene (**30**) was converted to the corresponding spirodioxide (**31**) in 84% yield in 10 min at room temperature (eq 19). The spirodioxide was obtained as a single diastereomer.



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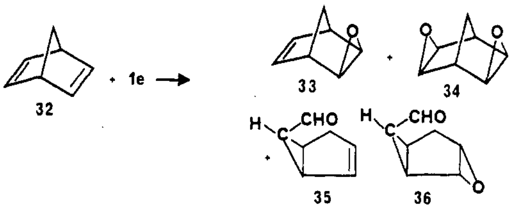
We have recently described[39] another example of the advantage of using dioxirane solutions where sensitive epoxides are involved. Treatment of norbornadiene (**32**) with **1e** leads to the formation of four products, namely, *exo*-norborna-2,5-diene monoepoxide (**33**), *exo,exo*-norborna-2,5-diene diepoxide (**34**), bicyclo[3.1.0]-hex-2-ene-6-*endo*-carboxaldehyde (**35**), and *exo*-2,3-epoxybicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde (**36**) (eq 20). The distribution of the products is dependent on the reaction conditions. When norbornadiene is added dropwise to a solution containing excess dioxirane, the sole product in 93% yield is the diepoxide **34**. On the other hand, use of less than the stoichiometric amount of **1e** led to a product mixture that was largely monoepoxide **33** (97%) contaminated with a small amount of aldehyde **35** (3%). The results obtained with the dioxirane method contrast sharply with those found when other epoxidation methods were used to synthesize monoepoxide. These methods give largely aldehyde product. Apparently the monoepoxide is sensitive to the acidic conditions of these reagents.



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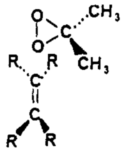
Second-order rate constants for the reaction of a series of alkenes have been reported[40a] by Baumstark and McCloskey (Table II). The relative reactivities of the alkenes studied are generally consistent with electrophilic O atom transfer by the dioxirane. Variations from the electrophilic trend suggest that dimethyldioxirane is more sensitive to steric factors than are peracids. Of particular interest is the observation that *cis*-alkenes were 7–9 times more reactive than their trans counterparts. The authors suggest that the peroxidation reaction has a transition state of the spiro variety, **37**, a possibility that accommodates the cis/trans rate difference particularly well.



37

A Hammett linear free energy study of the dimethyldioxirane-mediated epoxidation of a series of para-substituted ethyl cinnamates has been completed by Shiang.[41] The reagent was found to be electrophilic with a ρ value of −1.53. The second-order rate constants for the epoxidation of unsubstituted ethyl cinnamate were determined over the temperature range 10–30 °C and used to calculate E_a (=14.1 ± 0.4 kcal/mol) and log A (=7.41). It was felt that the large entropy requirement is consistent with the spiro type transition state and may also support the concept of a separate contribution to the entropy requirement from a heavily solvated dioxirane. Such solvation would lead to a large reordering of solvent molecules along the reaction coordinate to epoxide. Baumstark and Vasquez[40b] have completed a Hammett study of the epoxidation of a series of para-substituted styrenes and obtained a ρ^+ value = −0.90, again indicating the electrophilic nature of the O atom transfer. They also report second-order rate constants for the epoxidation of some additional alkenes.

B. Polycyclic Aromatic Hydrocarbons

As part of an ongoing research effort in the area of environmentally related mutagenesis and carcinogenesis, we have been interested in the oxidation of polycyclic aromatic hydrocarbons (PAH) by known or suspected atmospheric oxidants. We had earlier[30] used the in situ dioxirane method to show that some PAH are oxidized by dimethyldioxirane. With the availability of solutions of **1e**, we have gone on to study[42] the oxi-

TABLE I. Reactions of Isolated Dimethyldioxirane

entry	reactant	product(s)	yield, %	remarks	ref
		Alkenes			
1	ethyl *trans*-cinnnamate	*trans*-epoxide	85		2
2	4-X ethyl *trans*-cinnamates	*trans*-epoxides	*a*	kinetics measd	41
3	*cis*-stilbene	*cis*-epoxide	73		2
4	*trans*-stilbene	*trans*-epoxide	73		2
5	2,5,5-trimethyl-2,3-hexadiene	2,5,5-trimethyl-2,3-hexadiene spirodioxide	84	*b*	38
6	tetramethylallene	tetramethylallene spirodioxide	44		38
7	norbornadiene	monoepoxide, diepoxide, and others	*c*		39
8	1,2-dimethylcyclohexene	epoxide	*a*	rate const detd	40a
9	tetramethylethylene	epoxide	*a*	rate const detd	40a
10	2-methyl-2-butene	epoxide	*a*	rate const detd	40a
11	1-methylcyclohexene	epoxide	*a*	rate const detd	40a
12	(*Z*)-3-methyl-3-hexene	(*Z*)-epoxide	*a*	rate const detd	40a
13	(*E*)-3-methyl-3-hexene	(*E*)-epoxide	*a*	rate const detd	40a
14	cyclopentene	epoxide	*a*	rate const detd	40a
15	*cis*-3-hexene	*cis*-epoxide	*a*	rate const detd	40a
16	*cis*-3-hexene	*cis*-epoxide	>95	rate const detd	40b
17	*trans*-3-hexene	*trans*-epoxide	*a*	rate const detd	40a
18	*trans*-3-hexene	*trans*-epoxide	>95	rate const detd	40b
19	*cis*-2-hexene	*cis*-epoxide	*a*	rate const detd	40a
20	*trans*-2-hexene	*trans*-epoxide	*a*	rate const detd	40a
21	2-methyl-1-pentene	epoxide	*a*	rate const detd	40a
22	1-nonene	epoxide	*a*	rate const detd	40a
23	*cis*-4,4-dimethyl-2-pentene	*cis*-epoxide	>95	rate const detd	40b
24	*trans*-4,4-dimethyl-2-pentene	*trans*-epoxide	>95	rate const detd	40b
25	*cis*-2,5-dimethyl-3-hexene	*cis*-epoxide	>95	rate const detd	40b
26	*trans*-2,5-dimethyl-3-hexene	*trans*-epoxide	>95	rate const detd	40b
27	*trans*-2,2,5,5-tetramethyl-3-hexene	*trans*-epoxide	>95	rate const detd	40b
28	cyclohexene	epoxide	>95	rate const detd	40b
29	*cis*-1-phenylpropene	*cis*-epoxide	>95	rate const detd	40b
30	*trans*-1-phenylpropene	*trans*-epoxide	>95	rate const detd	40b
31	*cis*-stilbene	*cis*-epoxide	>95	rate const detd	40b
32	*trans*-stilbene	*trans*-epoxide	>95	rate const detd	40b
33	indene	epoxide	>95	rate const detd	40b
34	styrene	epoxide	>95	rate const detd	40b
35	4-X-styrenes	epoxides	>95	rate const detd	40b
36	3,3-dimethyl-1-butene	epoxide	>95	rate const detd	40b
37	3-methyl-1-buten-3-ol	epoxide	>95	rate const detd	40b
		Polycyclic Aromatic Hydrocarbons			
38	phenanthrene	9,10-oxide	83		2
39	phenanthrene	9,10-oxide	82	methylethyldioxirane used	2
40	phenanthrene	9,10-oxide and others	11.5 (oxide)	gas (**1e**)–solid reaction	31
41	pyrene	pyrene 4,5-oxide	35		42
42	pyrene	pyrene 4,5-oxide and others	11.5 (oxide)	gas (**1e**)–solid reaction	31
43	chrysene	chrysene 5,6-oxide	29		42
44	chrysene	chrysene 5,6-oxide and others	11.5 (oxide)	gas (**1e**)–solid reaction	31
45	benz[*a*]anthracene	5,6-oxide	65		42
		7,12-dione	25		
46	4*H*-cyclopenta[*def*]phenanthrene	8,9-dione	50		42
		others	*a*		
47	benzo[*a*]pyrene	unstable products	*a*		42
48	benzo[*e*]pyrene	4-hydroxybenzo[*e*]pyrene	20		42
49	benzo[*b*]chrysene	7,12-dione	70		42
50	dibenz[*a*,*h*]anthracene	5,6-oxide	51		42
		7,14-dione	trace		
51	dibenz[*a*,*h*]anthracene	5,6-oxide	trace	gas (**1e**)–solid reaction	31
		others	*a*		
		Nitrogen-Containing Compounds			
52	pyridine	amine oxide	75		2
53	aniline	nitrobenzene	97		37
54	*p*-anisidine	*p*-nitroanisole	94		37
55	*n*-butylamine	1-nitrobutane	84		37
56	*sec*-butylamine	2-nitrobutane	87		37
57	*tert*-butylamine	2-methyl-2-nitropropane	90		37
58	1-aminoadamantane	1-nitroadamantane	95		37
59	cyclohexylamine	nitrocyclohexane	95		37
60	1,4-diaminocubane	1,4-dinitrocubane	80		52
61	1,4-diisocyanatocubane	1,4-dinitrocubane	85	H_2O required	34
62	phenyl isocyanate	nitrobenzene	65	H_2O required	34
63	*n*-butyl isocyanate	nitrobutane	34	H_2O required	34

TABLE I (Continued)

entry	reactant	product(s)	yield, %	remarks	ref
64	cyclohexyl isocyanate	nitrocyclohexane	16	H_2O required	34
65	*tert*-butyl isocyanate	2-nitro-2-methylpropane	<5	H_2O required	34
66	1,3,5,7-tetraaminoadamantane tetrahydrochloride	1,3,5,7-tetranitroadamantane	91		52
67	*trans*-azobenzene	azoxybenzene	96		37
68	2,2,5,5-tetramethylpyrrolidine-3-carboxamide	3-carbamoyl-2,2,5,5-tetramethylpyrrolidin-1-yloxy	100		55
69	2,2,5,5-tetramethylpyrroline-3-carboxamide	3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy	98		55
70	2,2,5,5-tetramethyl-3-pyrroline-3-carboxylic acid	3-carboxy-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy	94		55
71	2,2,6,6-tetramethyl-4-piperidinol	4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy	100		55
72	2,2,6,6-tetramethyl-4-piperidone	4-oxo-2,2,6,6-tetramethylpiperidin-1-yloxy	98		55
73	2,2,6,6-tetramethyl-4-piperidone oxime	4-(hydroxyimino)-2,2,6,6-tetramethyl-piperidin-1-yloxy	99		55
74	3,3-dimethyl-1-oxa-4-azaspiro[4.5]-decane	3,3-dimethyl-1-oxa-4-azaspiro[4.5]dec-4-yloxy	100		55
		Sulfur Compounds			
75	phenyl methyl sulfide	phenyl methyl sulfoxide	98		2
76	*p*-tolyl methyl sulfide	sulfoxide	*a*	rate study	57
77	*p*-chlorophenyl methyl sulfide	sulfoxide	*a*	rate study	57
78	*p*-nitrophenyl methyl sulfide	sulfoxide	*a*	rate study	57
79	*p*-methoxyphenyl methyl sulfide	sulfoxide	*a*	rate study	57
80	*p*-tolyl methyl sulfoxide	sulfone	*a*	rate study	57
81	*p*-methoxyphenyl methyl sulfoxide	sulfone	*a*	rate study	57
82	*p*-chlorophenyl methyl sulfoxide	sulfone	*a*	rate study	57
83	*p*-nitrophenyl methyl sulfoxide	sulfone	*a*	rate study	57
84	thianthrene 5-oxide	sulfone	33[d]		
		disulfoxide	(84.9)[e]	rate study	33
			(15.1)[e]		
		Saturated Hydrocarbons			
85	adamantane	1-adamantanol	87		59
		2-adamantanol and 2-adamantanone	2.6		
86	*trans*-1,2-dimethylcyclohexane	*trans*-1,2-dimethylcyclohexan-1-ol	45		59
87	*cis*-1,2-dimethylcyclohexane	*cis*-1,2-dimethylcyclohexan-1-ol	100		59
88	*trans*-decalin	*trans*-9-decalol	20		59
89	*cis*-decalin	*cis*-9-decalol	84		59
90	toluene	benzaldehyde	3.3		59
		benzoic acid	1.8		
91	cyclohexane	cyclohexanol	23		59
		cyclohexanone	41		
92	cyclododecane	cyclododecanone	60		59
		cyclododecanol	3		
93	*n*-decane	2-decanone	20.3		59
		3-decanone and others	9.5		
		Miscellaneous			
94	triphenylphosphine	triphenylphosphine oxide	100		2
95	acetaldehyde	acetic acid	*a*		2
96	propionaldehyde	propionic acid	*a*		2
97	quadricyclane	norbornadiene	*a*	cat. isomerization	61

[a] Yield not determined. [b] The conversion of several other allenes to spirodioxides is reported. [c] Yield of each product depends upon reaction conditions. [d] Percent conversion. [e] Product distribution.

dation of eight PAH, all of which are known to be present in airborne particulate matter (entries 41, 43, and 45–50). In fact, five of these eight are known[43] to be at least weakly carcinogenic in small animals. The PAH are oxidized to a variety of products. Of particular note is the frequent occurrence of K-region oxides or products derived from these oxides in the product mixtures. PAH-related carcinogenesis is known[44-49] to require prior metabolic activation, that is, oxidation of the hydrocarbons. While the metabolites derived from the PAH contain a variety of functional groups, it appears that the arene oxide moiety is essential for binding the PAH to important biological substrates in the complex chain of events leading to cancer. In addition, in some cases use of the dioxirane method provides a useful synthesis of arene oxides for further study.

Airborne PAH undergo a variety of reactions in the atmosphere, but of interest here are oxidation reactions. It has been observed[50] that oxygenated fractions of atmospheric samples can be carcinogenic. It is of great interest then to determine what atmospheric oxidation reactions are contributing to the formation of carcinogens. As described in section II.A, the reaction of ozone with ethylene is known[10] to produce dioxirane. Since polluted atmospheres contain elevated amounts of ozone, alkenes, and PAH, we have suggested[31,42] that dioxirane–PAH reactions may be contributing to the production of carcinogens in these atmospheres.

In order to better simulate actual atmospheric conditions, we have also carried out PAH oxidation studies[31] in which the PAH is supported on a model particulate (silica gel, glass, etc.). A gas stream containing the oxidant being studied is then passed over the sup-

TABLE II. Second-Order Rate Constants for the Epoxidation of Alkenes by Dimethyldioxirane (1e) in Acetone at 25 °C[a]

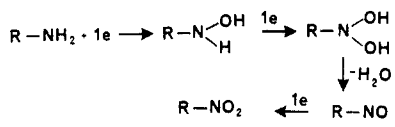
alkene	k_2, $M^{-1}\,s^{-1}$ [b]	rel react
$Me_2C{=}CMe_2$	7.1 ± 0.6	106
1,2-dimethylcyclohexene	2.0 ± 0.1	30
$Me_2C{=}CHMe$	2.4 ± 0.1	36
1-methylcyclohexene	1.59 ± 0.06	23.7
(*Z*)-3-methyl-3-hexene	1.61 ± 0.06	24.0
(*E*)-3-methyl-3-hexene	1.08 ± 0.04	16.1
cyclopentene	0.62 ± 0.01	9.3
cis-3-hexene	0.57 ± 0.02	8.5
trans-3-hexene	0.067 ± 0.001	1.0
cis-2-hexene	0.61 ± 0.01	9.1
trans-2-hexene	0.084 ± 0.002	1.3
2-methyl-1-pentene	0.31 ± 0.01	4.6
1-nonene	0.035 ± 0.005	0.5

[a] Data from: Baumstark, A. L.; McCloskey, C. J. "Epoxidation of Alkenes by Dimethyldioxirane: Evidence for a Spiro Transition State". *Tetrahedron Lett.* **1987**, *28*. [b] Determined under pseudo-first-order conditions with 1:10 and 10:1 alkene:1 ratios.

ported PAH. In the studies of interest here, the gas stream contains dioxirane **1e** in acetone or an acetone–methylene chloride mixture. Four PAH, phenanthrene, pyrene, chrysene, and dibenz[*a*,*h*]anthracene, were treated in this manner (entries 40, 42, 44, and 51). In all four cases the PAH were converted to reaction mixtures containing the K-region oxide and products derived from the oxide. These results add support to the suggestion that ozone-derived dioxiranes are excellent candidates for one type of atmospheric oxidant that can produce mutagens/carcinogens in polluted atmospheres.

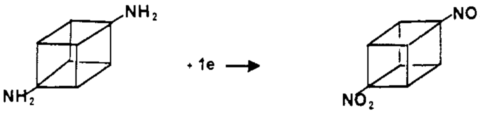
C. Nitrogen-Containing Compounds

Solutions of **1e** have been used to oxidize primary amines[36,37] to nitro compounds in a rapid and nearly quantitative fashion (entries 53–60). The process is believed to involve a succession of O atom transfers (eq 21). This view is supported by the observation that phenylhydroxylamine and nitrosobenzene can be separately oxidized to nitrobenzene. Since intermediate products can sometimes react with the starting primary amine, this procedure is most successful when a solution of the amine is added to excess dioxirane. This method has recently been extended to other aromatic amines by Zabrowski and co-workers.[36] Because they were interested in using mole quantities of the dioxirane, the Zabrowski group preferred the in situ method. They describe the conversion of a number of substituted aromatic amines to the corresponding nitro compounds in good to high yields. Yields were poorest when the amines were substituted with carboxylic acid or phenol groups. This group also studied the substrate selectivity of the dioxirane by carrying out amine oxidations in the presence of other substrates.



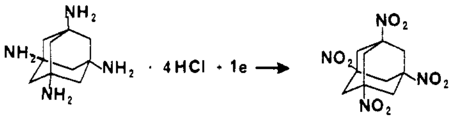
(21)

The primary amine oxidations have been extended to a large number of other cases in our laboratories.[51] Included are cases of aromatic amines containing two and three amino groups. In the case of aliphatic amines we have shown that dimethyldioxirane is particularly useful for converting 1,4-diaminocubane to 1,4-dinitrocubane in excellent yield (eq 22).[52] This procedure is thus much more attractive than the peracid method used earlier by Eaton and co-workers.[53] The Eaton group has gone on to use the dioxirane procedure very effectively in their work. They have described an important modification[34] in which the amine hydrochloride salt is oxidized directly by the dioxirane. This procedure eliminates the need to isolate sensitive amines such as 1,4-diaminocubane and also reduces the problem of starting amine reacting with intermediates along the path to nitro compound as described earlier. Eaton and co-workers have also reported[34] that 1,4-diisocyanatocubane is conveniently oxidized to 1,4-dinitrocubane by **1e**. The reaction also gives a high yield (85%). Interestingly, the isocyanate oxidation does not take place unless water is present. The authors have concluded that the cyanate is first hydrolyzed to the carbamic acid, which is then oxidized.



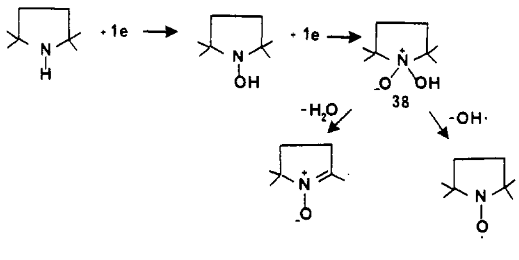
(22)

The device of oxidizing amine hydrochlorides by dimethyldioxirane has been used by Rajadhyaksha to efficiently synthesize a number of polynitro compounds.[52] A particularly striking example is the conversion of 1,3,5,7-tetraaminoadamantane tetrahydrochloride to 1,3,5,7-tetranitroadamantane in 91% yield (eq 23). The latter compound had been synthesized earlier by Sollott and Gilbert,[54] who used permanganate as oxidant and obtained a 45% yield.



(23)

In general, secondary amines are converted to the corresponding hydroxylamines by dimethyldioxirane.[51] The product obtained is very much a function of the reaction conditions and the structure of the secondary amine. When equimolar quantities of amine and dioxirane are reacted, the product is the hydroxylamine. When a second mole of dioxirane is available, further reaction occurs to give an intermediate **38**, which, if α hydrogens are present, loses water to give a nitrone (eq 24). If no α hydrogens are present, then the product is the nitroxide.[55] The latter procedure gives quantitative or near-quantitative yields of nitroxides in a fast and very convenient process that is apparently quite superior to existing methods.



(24)

Dimethyldioxirane oxidizes tertiary amines to the amine oxides (eq 25).[51] Here again the reaction con-

$$R_3N + 1e \longrightarrow R_3\overset{+}{N}\text{–}O^- + 1e \longrightarrow \underset{39}{R_3\overset{+}{N}\text{–}O\text{–}O^-} \xrightarrow{-O_2} R_3N \quad (25)$$

ditions are critical if the oxide is the desired product. We have discovered that excess dioxirane leads to an intermediate, presumably **39**, which loses oxygen (singlet?) to regenerate the amine. Thus dimethyldioxirane is one of only a few reagents that can be used to deoxygenate amine oxides.

A number of other nitrogen-containing functional groups have been oxidized by **1e**. Imines are oxidized[56] to the derived carbonyl and nitro compounds presumably through the intermediate oxaziridines. Azo compounds are converted to azoxy derivatives.[37]

D. Sulfur Compounds

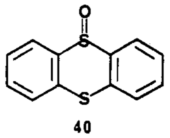
As indicated earlier in this review, solutions of alkyl dioxiranes are assayed for dioxirane content by reacting them with excess phenyl methyl sulfide. Under these conditions the sulfide is converted to the sulfoxide uncontaminated with sulfone. The sulfoxide content is then determined by gas chromatography and calibration using standard solutions of sulfoxide. The reaction with sulfides has been shown[57] to be electrophilic by reacting **1e** with a series of para-substituted phenyl methyl sulfides and treating the relative rate data with the Hammett linear free energy relationship. The linear correlation found gave a ρ value of -0.77. A similar study was carried out on the corresponding series of sulfoxides, which were oxidized to the sulfones. Dimethyldioxirane also acts as an electrophile in this case ($\rho = -0.76$). It may be that the sulfoxide to sulfone conversion is initiated by an attack of the dioxirane on the oxygen end of the sulfoxide dipole. Such an attack would parallel somewhat the attack of **1e** on the oxygen of an amine oxide in the reaction leading to deoxygenation described above.

Adam, Cremer, and co-workers[33] have also prepared solutions of **1e** in order to obtain spectroscopic data and compare them with calculated values. Adam and coworkers had earlier[58] developed a reaction designed to permit one to distinguish chemical differences between oxidants of interest but particularly carbonyl oxides and dioxiranes. The oxidants are allowed to react with thianthrene 5-oxide (**40**), where reaction can occur at either or both of the sulfide and sulfoxide functional groups. It was assumed that reaction at sulfide indicated electrophilic character, while reaction at sulfoxide would involve nucleophilic attack. Oxidants were then assigned numbers indicating their nucleophilic character. The numbers are calculated from product distributions in the various oxidations. Use of this reagent does distinguish between carbonyl oxides and dioxiranes. The authors had previously used this method to determine the nucleophilic character of **1e** formed in situ. When the method was used with the dioxirane solution, almost the same nucleophilicity ($X_{Nu} = 0.70$) was found. While pleased that both determinations indicated the same degree of nucleophilic character, the authors were puzzled by the apparently high degree of nucleophilicity exhibited by a reagent whose overall chemistry suggests that it is an electrophile. This apparent conflict may have its roots in the substrate chosen for determining the nucleophilicity scale. The substrate **40** has sulfide and sulfoxide groups whose character is modified by resonance interaction. Also, as indicated earlier, our results suggest that dioxirane may carry out an electrophilic attack on the sulfoxide via the negatively charged oxygen.

TABLE III. Relative Reactivity in C–H Reactions[a,d]

substrate[b]	rel rate of insertion by 1e	rel react toward H abstr[c]
toluene	(1)	(1)
ethylbenzene	24	3.2
cumene	91	6.8

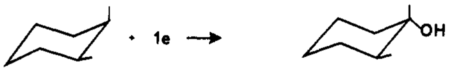
[a] Relative intensities are given per H. [b] In all cases only benzylic H is involved. [c] Taken from: Walling, C.; Thaler, W., *J. Am. Chem. Soc.* **1961**, *83*, 3877. H abstraction is by *tert*-butoxy radicals at 40 °C. [d] Data from: Murray, R. W.; Jeyaraman, R.; Mohan, L. *J. Am. Chem. Soc.* **1986**, *108*, 2470.



40

E. Saturated Hydrocarbons

Perhaps the most surprising chemistry of dimethyldioxirane to date is its ability to oxidize saturated hydrocarbons.[26b,59] The hydrocarbons are converted to alcohols or carbonyl compounds derived from the alcohols (entries 85–93). Unlike the reactions described in the immediately preceding sections, these oxidations require reaction times measured in hours rather than in minutes. The more reactive dioxirane **1m** is able to accomplish similar oxidations at a faster rate, however.[26b] With suitable substrates the reaction is found to be stereospecific with retention (entries 86–89). Thus, for example, *cis*-1,2-dimethylcyclohexane is converted to *cis*-1,2-dimethylcyclohexan-1-ol (eq 26).



(26)

A number of experimental observations suggest that these reactions of **1e** with hydrocarbons do not involve radical character. When the relative reactivity of **1e** with a series of alkylbenzenes (Table III) is compared[59] to that for hydrogen atom abstraction by *tert*-butoxy radical, it is found that the dioxirane is far more selective. Furthermore, when an equimolar mixture of cyclododecane and cyclododecane-d_{24} is oxidized by **1e**, the primary kinetic isotope effect measured, $k_H/k_D = 4.97$, suggests that the C–H bond is not completely cleaved in the transition state. The evidence to date is most consistent with a mechanism involving insertion of an O atom into a C–H bond by the dioxirane.

The hydrocarbon oxidation reaction may be particularly important in "activating" certain hydrocarbons that are otherwise difficult to derivatize. A prototype for this kind of reaction is the conversion[59] of adamantane to a reaction mixture containing an 87% yield of 1-adamantanol (entry 85). When n-decane is oxidized[59] by **1e**, a reaction mixture is obtained that contains 2-decanone and 3-decanone, with the former in greater amount. The reaction mixture also contains two other substances in smaller quantity which have not yet been identified. These materials could be 4- and 5-decanone. The early indication is that the dioxirane is sensitive to even the most subtle electronic effects in such hydrocarbons. This kind of sensitivity is similar to that exhibited by some microorganisms[60] and is not usually associated with simple organic oxidation reagents.

F. Miscellaneous Compounds

Dimethyldioxirane oxidizes triphenylphosphine to triphenylphosphine oxide[2] in a quantitative fashion. This reaction has been used as an alternate method to that using phenyl methyl sulfide for determining concentrations of dioxiranes. Acetaldehyde and propionaldehyde are converted[2] to acetic acid and propionic acid, respectively, by **1e**. This latter result has important consequences for ozonolysis mechanism studies. It is now well established that carbonyl oxides react with carbonyl compounds to give ozonides as originally proposed[8] by Criegee. From time to time there has been speculation that dioxiranes also might react with carbonyl compounds to give ozonides. While more aldehydes neet to be tested, it now seems likely that dioxiranes are not involved in ozonide formation.

It has recently been observed[61] that **1e** can catalyze the valence isomerization of quadricyclane to norbornadiene. The isomerization was studied by GPC and NMR techniques, and turnover numbers up to 60 have been measured. The mechanism by which the isomerization occurs is uncertain. It may be that the orbitals of **1e** interact with quadricyclane in a manner similar to that of metals, which also bring about the isomerization. Such interaction could lead to a symmetry-allowed process. Alternatively, the isomerization could involve electron transfer from the quadricyclane to the dioxirane, although no evidence for the involvement of radicals could be found.

IV. Spectroscopic Data and Theoretical and Computational Studies

A. Spectroscopic Data

Infrared spectra for several dioxiranes (four) have been measured in matrices at low temperature. These data are given in section II.A and will not be repeated here. Table IV contains a summary of reported spectroscopic data for those dioxiranes (five) for which data are available from solution or gas-phase studies.

Apparently, the first reported spectroscopic data on dioxiranes are those contained in a U.S. patent[9] issued to Talbott and Thompson. The patent describes the preparation of a large number of fluorinated cyclic peroxides, including the perhalogeno dioxiranes **1a** and **1b**. Infrared, ultraviolet, and ^{19}F NMR spectra were obtained on these compounds.

In 1977 and 1978 Suenram and Lovas[10] published microwave spectroscopic data on the parent dioxirane **1c**. These data permitted the calculation of bond lengths and bond angles as well as the dipole moment for the dioxirane. The dioxirane was produced by the low-temperature ozonolysis of ethylene. A comparison of the C–O bond length in **1c** with that of a variety of other compounds (ethylene ozonide, ethylene epoxide, tetrahydrofuran, etc.) indicates that the dioxirane has the shortest bond length of the compounds compared. On the other hand, the O–O bond length in **1c** is longer than that in ethylene ozonide or hydrogen peroxide. The authors concluded that the abnormal bond lengths in the dioxirane were due to ring strain.

TABLE IV. Spectroscopic Data on Dioxiranes

dioxirane	method	values	ref
1c	microwave	$r_{C-H} = 1.0903$ Å	10
		$r_{C-O} = 1.3878$ Å	
		$r_{O-O} = 1.5155$ Å	
		$\angle HCH = 117.32°$	
		$\angle OCO = 66.189°$	
		$\mu = 2.479$ D	
1a	^{19}F NMR	76.8 ϕ^a	9
	UV	$\lambda_{max} = 306$ nm	
	IR	7.39 (s), 7.84 (s), 8.10 (s), 8.25 (sh), 9.00 (w), 9.78 (w), 10.25 (s), 14.01 (m) μm	
1b	^{19}F NMR	65.0 ϕ (CF_2Cl)^a	9
		74.6 ϕ (CF_3)^a	
	IR	7.08 (w), 7.63 (m), 8.05 (s), 8.23 (s), 8.70 (m), 9.54 (m), 9.90 (w), 11.13 (m), 11.65 (m), 13.17 (w), 14.08 (w) μm	
1e[b]	^1H NMR	δ 1.65 (CH_3)	2
		δ 1.65 (CH_3)	33
	^{13}C NMR	δ 22.73 (CH_3)	2
		δ 22.68 (CH_3)^c	57
		δ 22.69 (CH_3)	33
	^{13}C NMR	δ 102.25 (ring C)^c	57
		δ 102.30 (ring C)	33
		δ 102 (ring C)	62
	^{17}O NMR	δ 302	62
	UV	$\lambda_{max} = 335$ nm (ϵ 260)	2
		$\lambda_{max} = 335$ nm (ϵ 10)	33
		$\lambda_{max} = 329$ nm (ϵ 10)	40a
	IR	3012 (s), 3005 (s), 2999 (s), 1209 (s), 1196 (w), 1094 (s), 1080 (w), 1059 (w), 1034 (w), 899 (s), 784 (s) cm^{-1}	2
1f[d]	^{13}C NMR	δ 103.9 (ring C)	3
	UV	$\lambda_{max} = 333$ nm (ϵ 126)	2
1m[e]	UV	$\lambda_{max} = 347$ nm (ϵ 9)	26b
	IR	1259, 1189, 971 (w), 839 (w), 731 (w), 669 (w) cm^{-1}	26b
	^1H NMR	δ 1.97	26b
	^{13}C NMR	δ 14.51 (CH_3)	26b
		δ 97.32 (ring C)	26b
		δ 122.2 (CF_3)	26b
	^{19}F NMR	δ −81.5	26b
	^{17}O NMR	δ 297	26b

[a] On ϕ scale $CCl_3F = 0$. [b] All measurements in acetone solution at ca. 0.1 M. [c] ^{13}C-enriched acetone used as precursor. [d] Measurements in methyl ethyl ketone. [e] Measurements in trifluoroacetone.

The availability of solutions of dimethyldioxirane permitted the obtaining of a variety of spectroscopic data on this compound. The report in 1985[2] describes infrared, ultraviolet, ^1H, and ^{13}C NMR data. All of the data were obtained in dilute solution in acetone. This far from ideal experimental condition caused some initial difficulty in obtaining the NMR data, particularly for the quaternary carbon in **1e**. This difficulty was ultimately resolved with the help of ^{13}C-enriched **1e**. The ultraviolet data have been verified by the later reports of Adam[33] and Baumstark,[40] although these latter groups have found a smaller extinction coefficient (Table IV).

In the original report the ring carbon was assigned to a resonance at δ 214. This assignment was not likely for the structure, yet this absorption was consistently present in the spectrum. The absorption at δ 214 was eventually concluded to be an artifact due to the low concentration and acetone solvent. When a sample of **1e** was prepared[57] using ^{13}C-enriched (C2) acetone, it clearly showed the ring carbon absorption at δ 102. With the correct assignment established, it became possible to determine appropriate NMR spectrometer settings to locate this absorption in unenriched dimethyldioxirane as well as in ethylmethyldioxirane. It is interesting that an absorption at δ 102 was described in the original report[2] as arising with time but was as-

TABLE V. Calculated Values of Dioxirane Structural and Spectroscopic Properties

dioxirane	property	values	method	ref
1c	^{13}C NMR	δ 82.6[a]	IGLO	33
		δ 89[a]	GIAO	*b*
	^{1}H NMR	δ 4.72	IGLO	33
	^{17}O NMR	δ 250	IGLO	33
	$r_{C\text{–}O}$	1.398 Å	RSMP/DZd	*c*
		1.428 Å	HF/3-21G	63
		1.366 Å	HF/6-31G	*d*
		1.411 Å	HF/6-31G	*e*
		1.428 Å	3-21G	66
		1.342 Å	MINDO/3	*f*
		1.390 Å	MP3/6-31G*//6-31G	4
	$r_{O\text{–}O}$	1.529 Å	RSMP/DZd	*c*
		1.448 Å	HF/6-31G	*d*
		1.522 Å	HF/3-21G	63
		1.533 Å	HF/6-31G	*e*
		1.522 Å	3-21G	66
		1.456 Å	MINDO/3	*f*
	IR absorptions	3061, 2978, 1378, 1319, 1226, 987, 947, 803, 765 cm^{-1}	3-21G* (scaled)	63
		3032, 2933, 1492, 1213, 1195, 1123, 961, 888 cm^{-1}	MP2/G-31G* (scaled)	*g*
1d	$r_{C\text{–}O}$	1.326 Å	HF/3-21G*	63
	$r_{O\text{–}O}$	1.483 Å	HF/3-21G*	63
	IR absorptions	1543, 1285, 1033, 964, 761, 637, 533, 508, 406 cm^{-1}	HF/3-21G* (scaled)	63
1e	^{13}C NMR	δ 99.2 (ring C)[a]	IGLO	33
		δ 105 (ring C)[a]	GIAO	*b*
		δ 17.0 (CH_3)[a]	IGLO	33
	^{17}O NMR	δ 330	IGLO	33
	$r_{C\text{–}O}$	1.417 Å	MP2/6-31G*	*h*
	$r_{O\text{–}O}$	1.521 Å	MP2/6-31G*	*h*

[a] Gas-phase calculations. [b] Allen, L. C.; Kitchen, D. B., to be published. [c] Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199. [d] Paz, J. L. G.; Yancz, M. *Theor. Chim. Acta* **1983**, *64*, 57. [e] Catalan, J.; Escudero, F.; Laso, J.; Mo, O.; Yancz, M. *J. Mol. Struct.* **1980**, *69*, 217. [f] Hull, L. A. *J. Org. Chem.* **1978**, *43*, 2780. [g] Gauss, J.; Cremer, D. *Chem. Phys. Lett.* **1987**, *133*, 420. [h] Cremer, D.; Schindler, M. *Chem. Phys. Lett.* **1987**, *133*, 293.

signed to acetone peroxide, now known to absorb elsewhere. At approximately the same time as our report,[57] the δ 102 assignment for the ring carbon was described by Adam, Cremer, and co-workers[33] and by Sciacovelli, Curci, et al.[62] The latter group also used ^{13}C-enriched **1e** to assist them in their determination. Perhaps the most significant spectroscopic observation relative to the structure of **1e** was the finding of a single ^{17}O resonance by the Sciacovelli–Curci[62] group. Furthermore, the ^{17}O resonance remained unchanged over the temperature range of 0 to 25 °C, thus eliminating the possibility that a dynamic process involving the isomeric carbonyl oxide was influencing the spectrum.

B. Theoretical and Computational Studies

A sampling of reported calculated values of structural and spectroscopic properties of some dioxiranes is given in Table V. Where more than one calculation method has been used by the same group of workers only one set of values is included in the table. The reader is referred to the original literature for further details. In most cases the calculated values are in good agreement with the available experimental values.

The values for infrared absorptions for dioxirane **1c** calculated by Francisco and Williams[63] have led them to suggest that some earlier unassigned experimental values may have been due to the dioxirane. Hull and co-workers[64] had measured infrared absorption spectra of the products of ozonolysis of ethylene at low temperature. They were able to assign some absorptions to 1,2,3-trioxolane, that is, the initial ozonide of ethylene. The unassigned absorptions (1355, 1340, 1214, 940, 803, 765 cm^{-1}) are in fair agreement with the calculated values for dioxirane. A somewhat similar situation exists for difluorodioxirane (**1d**). Christe and Pilipovich had suggested[65] that **1d** was a product of the low-pressure pyrolysis of bis(trifluoromethyl) peroxide on the basis of some measured infrared absorptions. Again the absorptions measured are in fair agreement with the values calculated for **1d** by Francisco and Williams.[63]

TABLE VI. Calculated Energy Differences between Dioxiranes and the Isomeric Carbonyl Oxides[a]

dioxirane	energy diff, kcal/mol	method	ref
1c	34.5	RSMP2	*b*
	29.7	GVG-CI	*c*
	36.7	HF	*d*
	34.5	MC-SCF	*e*
	33.2	MC-CI	*e*
	44.2	MP3/6-31G*//6-31G	4
	40.9	MP2/6-31G*(+ZPC)	20
	33.7	MINDO/3	*f*
1k	43.3	MP2/6-31G*	*g*
1d	67.0	MP2/6-31G*	20
1l	28.1	RSMP/basis B	*b*

[a] In all cases the dioxirane is the most stable species. [b] Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199. [c] Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 7180. [d] Ha, T. K.; Kuhne, H.; Vaccani, S.; Gunthard, Hs. H. *Chem. Phys. Lett.* **1974**, *24*, 172. [e] Karlstrom, G.; Engstrom, S.; Jonsson, B. *Chem. Phys. Lett.* **1979**, *67*, 343. [f] Hull, L. A. *J. Org. Chem.* **1978**, *43*, 2780. [g] Cremer, D.; Schmidt, T.; Gauss, J.; Radhakrishnan, T. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 427.

In addition to the values shown in Table V, Politzer et al.[66] have calculated some other parameters that are of significance with respect to the structure of dioxiranes. Calculation of a bond deviation index leads these workers to conclude that the O–O bond in dioxirane can be described as a bent bond similar to that in other strained compounds such as cyclopropane. The bond order of this bond is calculated to be less than that in hydrogen peroxide, indicating that it is a considerably weaker bond.

The differences in energy between some dioxiranes and their isomeric carbonyl oxides as determined by various calculation methods are given in Table VI. In all cases the dioxirane is the more stable of the two structure types. The presence of fluorine substituents as in **1d** and **1j** substantially increases the energy differences between carbonyl oxide and dioxirane isomers. On the other hand, the presence of fluorine substituents lowers the activation energy for the carbonyl oxide to dioxirane interconversion according to the calculations. Cremer and co-workers[67] calculate this barrier to be 17 kcal/mol for the monofluorodioxirane, while Shevlin[20] gives a value of 10.4 kcal/mol for the difluorodioxirane cyclization reaction. Values for the barrier to cyclization in the parent dioxirane are in the range 20–33.6 kcal/mol.[20,67–69] These barriers are such that they have led Herron, Martinez, and Huie to the conclusion[70] that closure of the carbonyl oxide to the dioxirane will not be competitive with the cycloaddition reaction of the carbonyl oxide with a carbonyl compound to give an ozonide.

V. Summary

The availability of solutions of dioxiranes has permitted the collection of spectroscopic data on some of these compounds as well as providing an opportunity for studying the chemistry of these smallest of the cyclic peroxides. To date this chemistry is rich and dramatically different from that of other cyclic peroxides. Some of the observed reactions show great potential in synthetic chemistry. The isolation of dimethyldioxirane and other dioxiranes has also revived interest in the in situ method of preparing dioxiranes, a method that may be more useful when larger quantities of dioxiranes are required and the desired reactions are not sensitive to base. There is some indication that the isolation of dimethyldioxirane may be assisted by stabilization from solvent acetone. This solvation may also account in part for the surprising stability of these solutions. Microwave data have been obtained on the parent dioxirane, thus providing valuable structural information. Infrared spectra have been obtained on several dioxiranes in matrices at low temperature.

VI. Acknowledgments

It is a pleasure to acknowledge the experimental talents and perseverance of my co-workers whose names are contained in the references to work from my laboratory. This work has been supported by grants from the National Institutes of Health, the Office of Naval Research, and Geocenters, Inc., for which I am very grateful. Thanks are also due to the University of Missouri—St. Louis for research support and to the National Science Foundation for partial support of the purchase of the 300-MHz NMR spectrometer used in some of the work. I also thank Professor R. Curci for providing prepublication copies of ref 4b and 4c.

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