and eventual formation of hydrocarbon products. Only the HFC mechanism is responsible for isotopic fractionation, since SOC does not depend on nuclear spin. Biradicals ^{37} that contain ^{13}C nuclei with large HFC undergo ISC faster and compete better with decarbonylation than biradicals that lack ^{13}C. The phenylacetyl radical has a ^{13}C HFC of 124 G at the carbonyl position,[22] much larger than the typical proton HFC of ≤30 G.

The mechanism above is consistent with experiment except for one flaw: it incorrectly predicts identical ^{13}C enrichments in all CO-containing products, including the starting material. To address this problem we consider the details of the SOC and HFC mechanisms. SOC in the biradical **7** is only effective in conformers with small R, while the HFC mechanism takes over at large R (Figure 2, bottom). Since only HFC is nucleus-selective, CO-containing products formed via ISC at large R are expected to have a higher β than products formed via ISC at small R. ^{37} is initially produced in conformations with relatively small R. SOC-dominated ISC at small R yields mainly recyclization to generate unenriched starting material. Formation of cyclophane **10**, however, requires the benzylic positions to be very far apart, and one expects and finds **10** to be highly enriched. Formation of the cis–trans isomer of **6** also requires a value of R large enough to accommodate internal rotation in the biradical.

This interpretation requires that whether one starts with *cis*-**6** or *trans*-**6**, the starting material must be *unenriched* while the cis–trans isomer and **10** must be *enriched*. This was confirmed for $\mathbf{6}_{12}$. Photolysis at 10 °C of *cis*-$\mathbf{6}_{12}$ gives β = 0, 90, 128% (±30%) for *cis*-$\mathbf{6}_{12}$, *trans*-$\mathbf{6}_{12}$, and $\mathbf{10}_{12}$, respectively, whereas photolysis of *trans*-$\mathbf{6}_{12}$ gives β = 68, 2, 131% for the same three compounds.[38] This confirmation strongly supports the above model.

In summary, the physical basis for the difference in ^{13}C enrichment among the products of biradical decay is the *inherent tendency of HFC and SOC to produce different products*, and this in turn comes from the R dependences of the different ISC mechanisms shown in Figure 2.

Conclusion. Through a combination of product studies, isotope effects, and transient absorption kinetics including the effect of biradical chain length and substituent, solvent, temperature, and magnetic field, we have made progress in elucidating the relation of the rates and product distributions to the spin interactions in the biradicals. Probably the most surprising result is the profound effect exerted by extremely small interactions such as the S–T gap, SOC, and HFC upon the dynamics and product distribution of triplet biradicals.

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Dioxiranes: A New Class of Powerful Oxidants

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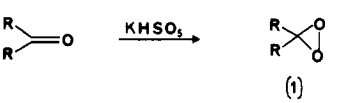
An oxidant that is efficient in transferring oxygen, selective in its reactivity, mild toward the oxidized product, and conveniently prepared from commercially available materials, possesses catalytic activity, and is recyclable and environmentally agreeable would unquestionably be the synthetic chemist's delight. Such an oxygen transfer reagent does not exist to this day, but an oxidant coming closest to these imposing characteristics is the dioxirane **1**.[1] The recent feat[2] of preparing dimethyldioxirane (**1a**) from the corresponding ketone and caroate ($KHSO_5$), as illustrated in eq 1, has provided convenient access to a powerful oxidant of unusual utility for synthetic purposes.[1-4]



(1)

(1)

Waldemar Adam received his B.Sc. in 1958 from the University of Illinois and his Ph.D. from MIT (F. D. Greene) in 1961. He was appointed Assistant Professor at the University of Puerto Rico in 1961, Associate Professor in 1965, and Professor in 1970. Since 1980 he has occupied the chair of Organic Chemistry at the University of Würzburg. Mechanistic organic chemistry, with emphasis on peroxides, photochemistry, and synthetic and biomedical applications, counts as his major research effort.

Ruggero Curci received a Doctorate Degree in Chemistry from the University of Bari in 1961. In 1964 he was appointed Assistant Professor, and in 1968 he moved to the University of Padova, where he earned the "Libera Docenza" (Associate Professorship, with tenure) in 1970. In 1975 he was appointed to the chair of Organic Chemistry at the University of Palermo, and three years later he returned to the University of Bari as Professor. His major research interests include synthesis and reaction mechanisms of organic and inorganic peroxides.

John O. Edwards conducted his studies (interrupted by a stint in the U.S. Marine Corps) at Colgate University (A.B. in 1947) and the University of Wisconsin. He held a postdoctoral position at Cornell University and was Research Chemist at the Du Pont Co., prior to coming to Brown University in 1952. As Professor Emeritus, he continues to carry out research on peroxide reactions and on the application of NMR to the study of transition-metal chemistry in solution.

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(1) For reviews, see: (a) Murray, R. W. In *Molecular Structure and Energetics: Unconventional Bonding*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York; Vol. 6, in press. (b) Curci, R. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI: Greenwich, CT; Vol. 2, Chapter 1, in press. (c) Murray, R. W. *Chem. Rev.*, in press.
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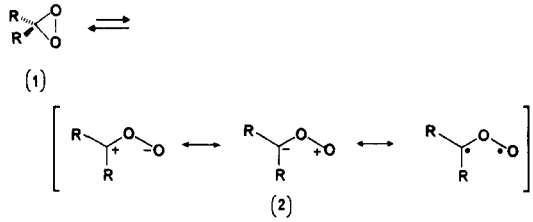
Pale yellow solutions of dioxirane **1a** (ca 0.1 M in acetone) are now routinely available in up to liter batches[4,5] storable at −20 °C for several days.[2,4] It is the purpose of this Account to convince the synthetic chemist of the scope and convenience of this new class of useful oxidants.

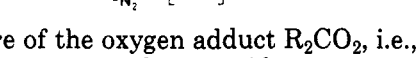
Historical Developments

Prior to the 1970s, only sporadic mention of the dioxiranes is to be found, and then only as elusive reaction intermediates in oxidation reactions.[1] As early as 1899, Baeyer and Villiger[6] postulated a dioxirane intermediate in the $KHSO_5$ oxidation of menthone into its lactone. Later ^{18}O labeling experiments clarified the mechanism of the Baeyer–Villiger oxidation of $Ph_2C{=}{}^{18}O$ as not to involve dioxiranes.[7] Independently, the "abnormal products" of ozonolysis, e.g., esters from ketones, were postulated to involve dioxiranes.[8] However, Criegee[9a] then convincingly established that ozonolysis of olefins proceeds via carbonyl oxides **2**, to be considered as valence isomers of dioxiranes **1** (eq 2). It is of historical significance that, much later, in the gas-phase ozonolysis of ethene, the parent dioxirane could be detected and its existence rigorously established.[10]



(1) (2) (2)

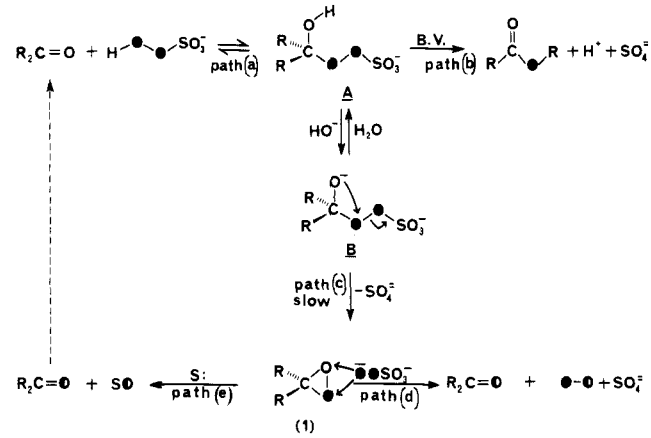
A third area of peroxide chemistry important for the development of dioxiranes as reaction intermediates concerns the photochemical oxygenation of diazoalkanes (eq 3).[11] Much controversy ensued[12] on the



(3)

structure of the oxygen adduct R_2CO_2, i.e., whether a dioxirane **1** or a carbonyl oxide **2** pertained. Careful matrix isolation work[13] has recently established that a complex reaction course obtains, the carbene first being trapped by dioxygen as a carbonyl oxide and subsequent photolysis resulting in its dioxirane.

Scheme I



The most significant historical fact in the development of dioxiranes as oxidants was the observation[14,15a] that acetone decomposes $KHSO_5$ with oxygen evolution. More important, this system exhibits remarkably efficient oxidizing action.[14,15] Once dioxiranes became accepted as relatively stable entities, numerous oxidations were performed in situ for synthetic purposes.[1]

A major breakthrough was the isolation of dimethyldioxirane (**1a**) in acetone solution, ca. 0.1 M.[2] A number of other low molecular weight dialkyldioxiranes could also be isolated.[2] Thus, a convenient, efficient, and useful oxidant was made available which holds great promise in synthesis.[1]

Generation and Isolation

Once it was recognized[14] that simple ketones accelerated the decomposition of caroate, it was essential to elucidate this catalysis as a function of pH, especially since $HOOSO_2OH$ has two widely different ionization constants, i.e., $pK_a(OH) < 0$ and $pK_a(OOH) \cong 9.4$. While the stoichiometry of the ketone-catalyzed decomposition was the same as that of the uncatalyzed process,[16] the pH dependence exhibited an S-shaped rate vs pH profile, instead of the typical bell-shaped one of the uncatalyzed reaction. Thus, the catalyzed rate of decomposition is first order in $[HSO_5^-]$ and in $[OH^-]$. Most important, the ketone is not consumed and thus catalytic in its action. Furthermore, experiments using doubly ^{18}O labeled caroate and unlabeled ketone, or ^{18}O labeled ketone and unlabeled caroate, confirmed the intervention of dioxiranes.[15a] The mechanism in Scheme I was postulated, accommodating all of the kinetic and labeling results.[15a]

As convincing as these experiments were for the intermediacy of dioxiranes in the ketone–caroate system, the infallible proof was its isolation and spectroscopic characterization. Since the labile, homologous 1,2-dioxetanes were isolated years ago,[17] it is surprising that

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Table I
NMR Chemical Shifts of Some Dioxiranes $R^1R^2CO_2$

dioxirane	R^1	R^2	temp, °C	chemical shifts,[a] δ ^1H	^{13}C	^{17}O	^{19}F	ref
1a	CH_3	CH_3	0	1.65 (s)	22.60 (CH_3)	302 (s)	–	2–4
1b	CH_3	CF_3	−20	1.97 (s)	14.51 (CH_3) 97.32 (C) 122.20 (CF_3)	297 (s)	−81.5 (s)	18
1d	CF_3	CF_3	–	–	–	–	−76.8 (s)	22

[a] Chemical shifts are relative to Me_4Si for ^1H and ^{13}C, to external $Me_2C{=}O$ and referred to H_2O for ^{17}O, and to $CFCl_3$ for ^{19}F.

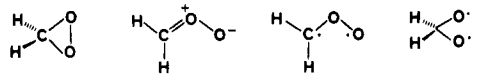
after their first postulation[14] and detection in the gas phase[10] 10 years[2] had to pass for sufficiently stable dioxiranes to become available.[1] This conquest was achieved by Murray and Jeyaraman, who were able to prepare a solution of ca. 0.1 M dimethyl dioxirane (**1a**) in acetone.[2] Most recently,[18] methyl(trifluoromethyl)-dioxirane (**1b**) was prepared in this way as a ca. 0.8 M solution in CF_3COCH_3.

Characterization, Structure, and Stability

Structural parameters (bond lengths and angles) are available on the parent dioxirane compound H_2CO_2 (**1c**) from microwave spectroscopy.[10] The peroxide bond is the longest (1.52 Å) so far known.[4,19] The bond length implies a rather unstable entity, easily undergoing homolysis of the O–O bond to afford bisoxymethylene diradical $^{\bullet}O{-}CR_2{-}O^{\bullet}$ (**3**).[19,20] Authentic members of the elusive dioxiranes have become available for spectroscopic characterization. The ^1H, ^{13}C, ^{17}O, and ^{19}F NMR data for the dioxiranes **1a**, **1b**, and **1d** are given in Table I. Characteristic is the dioxirane ring carbon atom ^{13}C resonance at ca. 100 ppm.[1,3,4,21] Most diagnostic of the dioxirane ring structure is the finding of a single ^{17}O resonance observed for both dioxiranes **1a** and **1b**.[18]

A weak ($\epsilon \cong 10$) n–π^* absorption is exhibited in the UV region 300–350 nm, with λ_{max} at 335, 347, and 306 nm for **1a**,[2,4] **1b**,[21] and **1d**,[18] respectively.[1] This absorption extends into the visible region out to ca. 440 nm, hence the pale yellow color.

In regard to the thermochemistry of dioxiranes, a number of theoretical analyses of the H_2CO_2 entity have been performed[20] These include carbonyl oxide (**2c**), peroxymethylene diradical (**2c′**), bisoxymethylene diradical (**3c**), and dioxirane (**1c**). The results are portrayed in the form of an energy diagram in Figure 1.



(1c) (2c) (2c′) (3c)

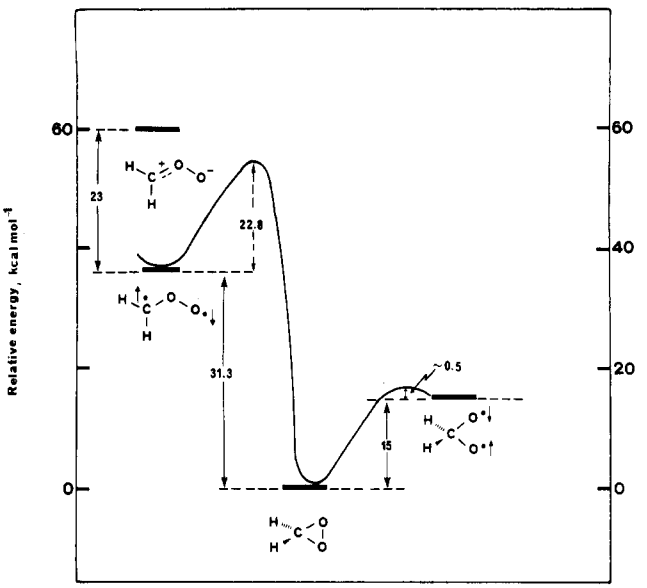


Figure 1.

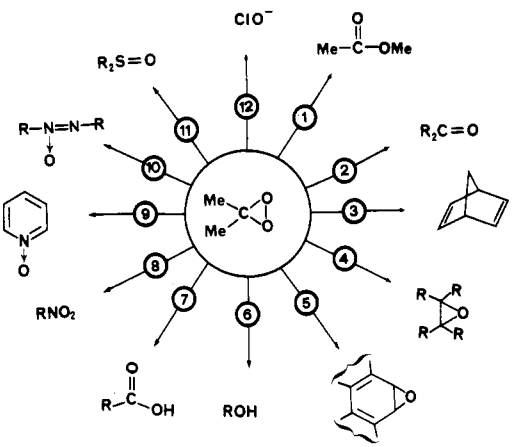


Figure 2.

Significant for the chemical reactivity of the H_2CO_2 species is that dioxirane (**1c**) is the lowest energy form; bisoxymethylene diradical (**3c**) is about 15 kcal/mol higher. In view of the low activation barrier (<1 kcal/mol) estimated for reclosure,[20,21] the highly strained dioxirane (**1c**) persists in the absence of oxidizable substrates.[1] Another significant feature of Figure 1 concerns the relative energy of carbonyl oxide (**2c**) and peroxymethylene diradical (**2c′**). In fact, both are significantly higher in energy than dioxirane (**1c**). Furthermore, an activation energy of ca. 22 kcal/mol is required for the **2c′** to **1c** cyclization. The chemical consequence is that a dioxirane should not readily open up to carbonyl oxides; neither do carbonyl oxides easily cyclize to the dioxiranes. Indeed, this cyclization could

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be achieved only on irradiation at 515 nm of matrix-isolated carbonyl oxides.[13] As it will be delineated in the next paragraph, another hint that dioxiranes and carbonyl oxides are to be considered as nonintercon-verting species comes from competitive oxygen transfer transfer to 9-thianthrene oxide (a useful mechanistic probe).[4,23]

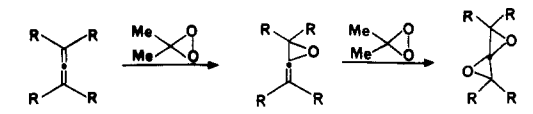
Chemical Reactivity

Much of the dioxirane chemistry so far established is summarized in Figure 2. Dimethyldioxirane (**1a**), whether in situ generated or in isolated form as acetone solution, displays impressive reactivity. For the sake of completeness, the transformations portrayed in the rosette begin with the rearrangement of dioxirane **1a** into methyl acetate (transformation 1).[1,2] Formally, oxidation of secondary alcohols into ketones (transformation 2)[24,25] does not involve oxygen atom transfer. Transformation 3 illustrates a most recent and interesting aspect of dioxirane chemistry, consisting in the ability of **1a** to act as a catalyst in the quadricyclane to norbornadiene valence isomerization.[26] The remaining transformations proceed under oxygen atom transfer. Effective epoxidations (transformations 4 and 5),[15,27-30] as well as insertions into C–H bonds of alkanes[24] and aldehydes[2] (transformations 6 and 7, respectively), have been recorded. Remarkable is the efficient conversion of primary amines into nitro compounds (transformation 8).[31] Nitro compounds are also formed in the reaction of **1a** with isocyanates.[5] Oxidation of tertiary amines, pyridine, and azo compounds gives the corresponding *N*-oxides (e.g., transformations 9 and 10);[1,2,5,15e] certain secondary amines yield nitroxides upon reaction with **1a**, a reaction that is likely to proceed via prior oxygen atom insertion into the N–H bond.[32] Organic sulfides[1,2,4,33] and chloride ion[14,15] are quantitatively oxidized to yield sulfoxides and hypochloride ion (transformations 11 and 12, respectively).

In this account, we shall focus on the oxygen transfer potential, classifying the processes into (i) epoxidations (transformations 4 and 5), (ii) carbon–hydrogen bond insertions (transformations 6 and 7), and (iii) lone-pair oxidations (transformations 8–12).

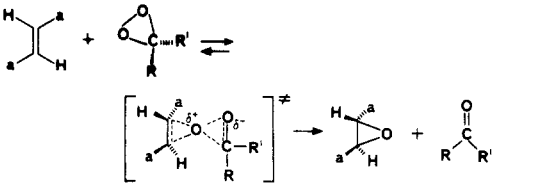
Epoxidations. This oxygen-transfer process is the most extensively used and unquestionably the most important for synthetic purposes. When in situ generated dioxirane is employed, it is critical to control the pH at 7.0–7.5 by means of phosphate or bicarbonate buffer. As it can be appreciated from Scheme I, oxygen transfer by the dioxirane to the substrate (path e) is competed for by peroxy anion $^{-}OOSO_3^{-}$ at high pH, leading to destruction of the dioxirane with formation of molecular oxygen (path d). At low pH, the crucial deprotonation A → B is suppressed and dioxirane formation path (c) improbable. Of course, such problems do not occur when isolated dioxirane is employed; however, isolated dioxirane is necessarily contained in the ketone as solvent from which the dioxirane was prepared. Efforts[4] to separate dioxirane **1a** from acetone have been so far unsuccessful.

With in situ dioxiranes, the epoxidations can be carried out in aqueous media for water-soluble substrates.[15] For water-insoluble alkenes, biphasic systems of water and organic solvents (CH_2Cl_2, $CHCl_3$, benzene, etc.) can be adopted; it is useful to employ phase-transfer catalysts such as $Bu_4N^+HSO_4^-$ or 18-crown-6.[15b] Subambient temperatures, typically 2–12 °C, are advantageous.[15] Numerous examples of alkene epoxidations with in situ or isolated dioxiranes have been reported,[1,15,27-30] in high yields and of broad scope. Most significant is that, in the essentially neutral media, even hydrolytically sensitive epoxides survive the mild reaction conditions, e.g., the epoxides of enol ethers.[34] Another impressive example is the epoxidation of allenes (eq 4).[35]



(4)

The chemoselectivity is illustrated by hex-1-en-5-one, which is cleanly epoxidized without Baeyer–Villiger rearrangement of the keto functionality.[15b] Actually, in this case the in situ epoxidation can be achieved without acetone as dioxirane precursor, because its own keto group can serve this function. High regioselectivity is manifested in the reaction of in situ **1a** with (*E*,-*E*)-1,3-pentadiene-1-carboxylic acid, which is exclusively epoxidized at the distal double bond.[15b] That dioxiranes transfer stereospecifically the oxygen atom via syn cycloaddition was convincingly demonstrated by the epoxidation of *cis*- and *trans*-cinnamic acids[15a,b] and of *cis*- and *trans*-stilbenes.[2] In both cases the cis olefins gave *Z* epoxides and trans olefins the *E* epoxides exclusively. This speaks for the "butterfly" transition state C in eq 5,[29] analogous to peracids.[36] Also, the anti stereoselectivity of the peracid epoxidation of medium-ring allylic alcohols applies for dioxiranes.[15c]



C

(5)

The "butterfly" transition state C (eq 5) implies that asymmetric induction should be achievable when op-

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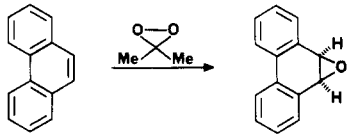
tically active dioxiranes are employed.[1b] Indeed, appreciable enantiomeric excesses (ee) of 9–20% were observed when optically active ketones were employed as precursors of dioxiranes in the epoxidation of simple alkenes such as 1-methylcyclohexene and β-methylstyrene,[15d] as well as of (*Z*)-octene-2.[37] For unfunctionalized prochiral alkenes, these enantioselectivities compare well[15d] with other epoxidizing agents and are more than twice those recorded for optically active peracids.[38] Of course, the advantage of enantioselective epoxidations by in situ dioxiranes is that such reactions require *catalytic* quantities of optically active ketones, instead of stoichiometric amounts of a chiral oxidant.[15d] Recently higher optical yields (up to 24% ee) have been recorded by employing 4,4,4-trifluoro-3-phenyl-3-methoxy-2-butanone.[37]

Analogous to peracids,[39] acetylenes give rather deep seated degradation products with dioxiranes.[15a,37] Thus, with the possible exception of dialkylacetylenes, which yield α,β-unsaturated ketones along with α-diketones,[37,39] this transformation is of little synthetic value. However, that substrates normally reluctant to be oxidized, such as the alkynes, readily react with dioxiranes speaks for the high oxidizing power of this new class of peroxides.

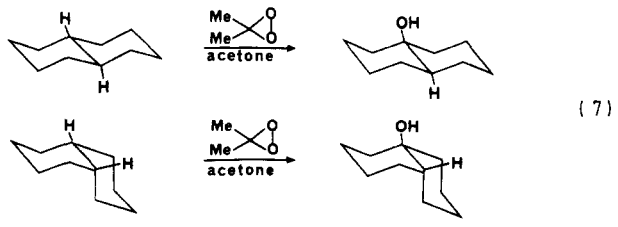
Therefore, it should not be surprising that oxygen atom transfer takes place with aromatic substrates, leading to arene oxides.[30] In situ dimethyldioxirane (**1a**) transforms phenanthrene, pyrene, and chrysene into the 9,10-oxide, the 4,5-oxide, and the 5,6-oxide, respectively.[30] Phenanthrene was also epoxidized by isolated **1a**, yielding phenanthrene 9,10-oxide in 83% yield,[2] during 45 min at 25 °C (eq 6).[18] Remarkably more



(6)

reactive is methyl(trifluoromethyl)dioxirane (**1b**), i.e., phenanthrene is consumed to the extent of ≥80% at −20 °C *within 5 min*, affording the 9,10-oxide in ≥93% yield![18] Clearly, for sluggish substrates dioxirane **1b** (Mello dioxirane)[18] is the oxidant of choice.

Insertion into Carbon–Hydrogen Bonds. The remarkable reactivity of dioxiranes is demonstrated by the fact that alkanes are directly oxidized into alcohols (transformation 6 in Figure 2).[24] As an example, *cis*- and *trans*-decalins afford the respective 9-decalols stereospecifically.[24] Such transformations are indeed rare for organic peroxides without the help of metal catalysts.[40]



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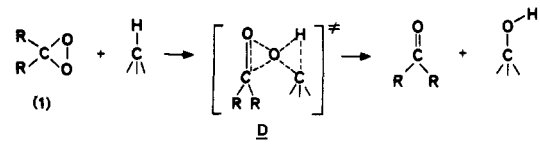
Scheme II



Even simple alkanes and cycloalkanes undergo such oxygen insertion by **1a**, although it was noted that this requires relatively long reaction times.[1c,24] However, methyl(trifluoromethyl)dioxirane (**1b**) transforms cyclohexane into cyclohexanone in less than 30 min in better than 95% yield![18] In these reactions the secondary alcohols are further oxidized to the corresponding ketones (transformation 2 in Figure 2), also an astounding oxidation.[18,24]

Murray and Jeyaraman[24] have also pointed to the high selectivity of dimethyldioxirane (**1a**) oxidations, as illustrated by the oxygen insertion with toluene, ethylbenzene, and isopropylbenzene. The reactivity at the benzylic position is in the order $PhCH(CH_3)_2 > PhCH_2CH_3 > PhCH_3$, but with much higher discrimination than observed for H abstraction by *tert*-butoxy radical in these substrates.[24] For mechanistic considerations, attention was called to the large kinetic isotope effect [$(k_H/k_D) = 4.97$, for cyclododecane-d_{24}], the high retention of configuration of the O atom insertion (e.g., eq 7), and the similarities with alkane ozonizations.[24] On the basis of these experimental findings, it is now tempting to propose the "butterfly" transition state D for the oxygen-insertion process (Scheme II).

It should be mentioned that more elaborate routes are also feasible, one envisaging H abstraction with formation of caged radical pairs [R•••O–CMe_2–OH]; however, these must couple prior to loss of stereochemistry, and the subsequent fast dissociation of the hemiacetal RO–CMe_2–OH would afford the products. Whatever the mechanistic uncertainties, the synthetic value of these powerful yet selective oxidants to perform direct oxyfunctionalization of hydrocarbons can hardly be overemphasized.[1]

As expected, aldehydes also undergo oxygen insertion with dioxiranes to yield the corresponding carboxylic acids (transformation 7 in Figure 2).[2] It is noteworthy that in these reactions no ozonides are formed, indicating that dioxiranes do not readily open up to the corresponding carbonyl oxides, followed by 1,3-dipolar cycloaddition with the aldehydes.[9]

Oxidation of Nucleophiles with Lone Pairs. Heteroatom substrates are good oxygen acceptors, the oxygen atom being attached at the side bearing the lone pair. In fact, one of the first such oxygen transfers was the oxidation of Cl^- to ClO^- (transformation 12 in Figure 2) by the $KHSO_5$/ketone system, which sparked the discovery of the dioxiranes.[14,15a] Oxidation of primary amines to nitro compounds (transformation 8 in Figure 2) is a stepwise process;[31,41] both hydroxylamines and nitroso compounds are oxidized by **1a** to their nitro derivatives and, therefore, are reasonable intermediates in the amine oxidation.[31] Eaton et al.[5] have described

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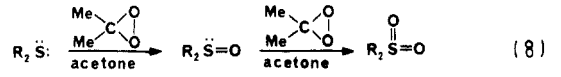
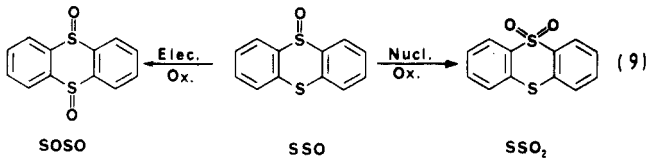
an important variation, in which primary amine hydrochlorides are converted directly into nitro compounds.[1c] In the conversion of pyridine into pyridine *N*-oxide (transformation 9 in Figure 2) by in situ dioxiranes, a careful kinetic analysis of the various mechanistic steps that obtain in this system was carried out.[15e] Examples of oxidations of other organic nitrogen substrates include the conversion of tertiary amines to their *N*-oxides and of azoalkanes to their azoxy compounds (transformation 10 in Figure 2).[31]

Among the sulfur nucleophiles, sulfides are oxidized by dioxiranes to sulfoxides (transformation 11 in Figure 2) and these, in turn, to sulfones (eq 8).[1-4,33] This oxidation can be controlled at the sulfoxide stage.



(8)

These results reveal the expected electrophilic character of dioxiranes. Indeed, when a series of para-substituted thioanisoles was used,[33] it was found that both the sulfide to sulfoxide and sulfoxide to sulfone oxidations by **1a** give negative ρ values of ca. −0.8. However, the question as to how electrophilic are dioxiranes relative to isomeric carbonyl oxides could be answered by means of the competition experiments shown in eq 9, using 5-thianthrene oxide (SSO).[4]



(9)

More electrophilic oxidants, e.g., ozone, oxidize the sulfide sulfur to give preferentially the 5,10-dioxide (SOSO), while more nucleophilic oxidants oxidize the sulfoxide sulfur to afford predominantly the 5,5-dioxide (SSO_2). A reactivity scale was defined for the nucleophilic character of the oxidant (X_{Nu}), ranging from 0.0 to 1.0. Values of X_{Nu} near 0 are associated with highly electrophilic oxidants [e.g., for *m*-chloroperoxybenzoic acid (MCPBA), X_{Nu} = 0.36], while X_{Nu} values near unity represent highly nucleophilic oxidants, e.g., carbonyl oxides (X_{Nu} > 0.80). On this scale, dimethyldioxirane (**1a**) has X_{Nu} = 0.68.[4] Qualitatively speaking, this is quite reasonable because dioxirane **1a** has been found to oxidize electron-poor olefins more efficiently than MCPBA; thus it is more nucleophilic than peracids.[4] On the other hand, while dioxiranes readily oxidize pyridine,[2,15e] carbonyl oxides do not,[42] and thus the former are more electrophilic.

Future Perspectives

The chemical transformations above bear witness to the great reactivity of dioxiranes as oxidants, especially their oxygen-transfer propensity.[1] The favorable combination of traits such as the convenient handling, potent and selective action under mild conditions, harmless byproducts, and catalytic activity make dimethyldioxirane (**1a**) and methyl(trifluoromethyl)dioxirane (**1b**) a synthetic chemist's delight. The current literature witnesses presently an intensive utilization of these unique oxidants in preparative applications.[1] Since significant progress is anticipated once the mechanistic details of dioxirane oxidations become elucidated, we sound out here with some pressing mechanistic incognita.

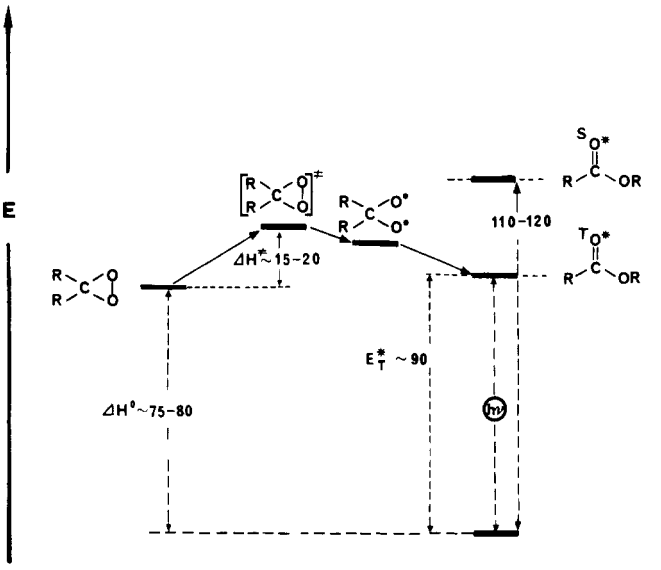


Figure 3.

Although in the company of suitable oxygen atom acceptors (π-systems, C–H bonds, lone pairs) dioxiranes transfer oxygen efficiently (Figure 2), their fate when left alone in solution is still open to debate. Clear is that at room temperature dioxirane **1a** solutions deteriorate within a few hours;[4] however, the claim[2] that significant amounts of tetramethyl-1,2,4,5-tetraoxane (its dimer) are produced could not be confirmed.[3,4] Also, in the decomposition of dioxirane **1b** no tetraoxane was observed,[18] but the main product was methyl trifluoroacetate; mass spectroscopy established that only traces of molecular oxygen are produced.[37] On the other hand, dioxygen production (presumably $^1O_2$*) is the major reaction course in the generation of dioxirane **1a** in situ, when the caroate/acetone system does not contain oxidizable substrates (Scheme I).[14,15] It should be instructive to elucidate the autodecomposition of dioxiranes into details.

Even the rearrangement of dioxiranes into carboxylic acids[10] or esters (e.g., transformation 1 in Figure 2) bears worthwile mechanistic facets to pursue.[1,9-12,43,44] Gas-phase ozonolysis[10] and matrix isolation work[13] established this rearrangement. What is especially intriguing about this isomerization is its high exothermicity (ca. 80 kcal/mol);[1b,10,20,44] consequently, it constitutes a potential chemiluminescent process.[1b,44] The qualitative energy diagram in Figure 3 conveys that at least triplet excited carbonyl products should be accessible, as it is well documented for 1,2-dioxetanes.[17]

However, in contrast to dioxetanes, the dioxiranes are much more powerful oxidants; then, for the detection of the triplet-state products by means of enhanced chemiluminescence,[17] suitable fluorophors will be necessary which resist destruction by oxygen transfer. In this context, the possibility of electron-transfer chemiluminescence must be mentioned (eq 10).

In this *c*hemically *i*nduced *e*lectron *e*xchange *l*uminescent process (CIEEL),[45] an electron is acquired by

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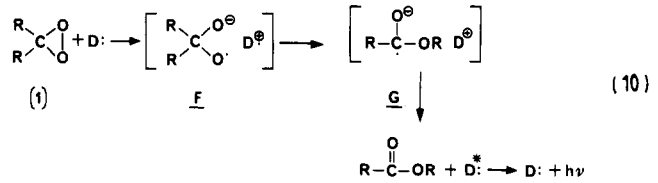

(10)

the dioxirane 1 from the fluorophor, resulting in the radical ion pair F. Conversion of the dioxirane radical anion to its ketyl radical and electron back transfer would generate electronically excited fluorophor. The latter would display its characteristic fluorescence. Such transformations have been postulated for putative dioxirane intermediates[46] and need to be rigorously established.

Quite generally speaking, it is possible that a number of the oxidations observed with dioxiranes that are outlined in the rosette in Figure 2 might proceed via electron transfer, but of course this does not necessarily entail production of excited states. A likely candidate appears to be the quadricyclane–norbornadiene isomerization,[47] which is efficiently catalyzed by dimethyldioxirane (**1a**).[26]

While dioxirane chemistry has been slowly maturing over the last 15 years into a prominent branch of oxidation processes, still numerous fascinating mechanistic and synthetic problems need to be attended.[1b] It is our contention that the fun has just begun!

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Base-Promoted, Imine-Forming 1,2-Elimination Reactions

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Base-promoted, bimolecular 1,2-eliminations are one of the fundamental reactions of organic chemistry. Synthetically, they are a common method for the introduction of π-bonds into saturated molecules. Mechanistically, they provide an important testing ground for methods and constructs with which bonding changes that take place during chemical reactions may be described in terms of detailed activated complexes.

The E2 transition state of a base-promoted 1,2-elimination is reached by the making/breaking of four bonds between five atomic centers in a concerted process. The activated complex is characterized structurally by the extents to which making/breaking of the four bonds have progressed. As shown in Figure 1, bond-making events include bond formation between the base and the β-proton and π-bond formation, while bond-breaking processes involve cleavage of the C_β–H bond and rupture of the C_α–leaving group bond. The variable E2 transition state theory[1,2] was developed to

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