# Rather Exotic Types of Cyclic Peroxides: Heteroatom Dioxiranes

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## 1. Introduction

This review discusses the heteroatom-containing dioxiranes in organic chemistry. Heteroatom-containing dioxiranes are three-membered ring peroxides with the form $XO_2$, where X is $R_3P$, RN, $R_2Si$, $R_2S$, $R_2Se$, $R_2Ge$, $R_2Sn$, $R_2Pb$, $R_2Te$, S, or Se. The R group represents hydrogen, halogen, alkyl, or aryl substituents. In light of the remarkable success that $R_2CO_2$ dioxiranes have had in oxygen-transfer reactions in organic chemistry, a review of $XO_2$ dioxiranes is expected to encourage and uncover new possible oxidation reactions. The synthetic utility for chemical oxidations with $XO_2$ dioxiranes is presently untapped.

## 2. Background

$XO_2$ dioxiranes are intermediates in photochemical and thermal reactions. In some cases, $XO_2$ dioxiranes have been detected with low-temperature techniques (e.g., matrix isolation, NMR, X-ray crystallography). In other cases, evidence for the existence of $XO_2$ dioxiranes comes from indirect studies, such as chemical trapping data or unimolecular rearrangements of the dioxirane congeners to more stable products.

An approach to the generation of $XO_2$ dioxiranes is often based on the reaction of an oxidant with mono-, di-, or trivalent (neutral) centers, such as nitrenes, silylenes, phosphines, phosphites, phosphoranide anions, phosphonium ion betaines, phosphine selenides, sulfides, selenides, and tellurides. Oxidants that have been used in the generation of these high-energy $XO_2$ dioxiranes include lowest excited singlet state oxygen ($^1O_2$), ground state triplet oxygen ($^3O_2$), ozone ($O_3$), superoxide ion ($O_2^{\bullet-}$), and hydrogen peroxide ($H_2O_2$).

Two general types of reactions give rise to $XO_2$ dioxiranes (Scheme 1). In the first case, $XO_2$ dioxiranes can arise from a "side-on" addition of the $O_2$ on the heteroatom center (e.g., reaction of $Ph_3P$ with $^1O_2$). In the second case, $XO_2$ dioxiranes originate from cyclization of the acyclic XOO form, which arose from an initial "end-on" addition of $O_2$ (e.g., reaction of $F_2Si$ with $^3O_2$). Methods that can generate $XO_2$ dioxiranes often do so in the presence of other reactive species, such as acyclic XOO or $^1O_2$.

The experimental requirements for producing $XO_2$ dioxiranes are not well defined, which leads to the question of how to develop this area. Our review of $XO_2$ dioxirane data in the solid-, solution-, and gas-phases will attempt to include substituent effects on the stability of $XO_2$ dioxiranes. The issues and challenges encountered in the synthesis of heteroatom-containing dioxiranes will be explored. Upon formation of $XO_2$ dioxiranes, subsequent intra- and intermolecular reactions take place. The analysis of structure and kinetics presented here can help guide thinking for the factors that underlie $XO_2$ dioxirane reactivity.

One aim of the review will be to consider the benefits of interplay between computational and experimental lines of evidence to help establish reactions that can generate $XO_2$ dioxiranes. Existing computational evidence will be summarized for $XO_2$ structures and their reactivities that are not yet characterized experimentally, such as in the cases where X equals $R_2Ge$, $R_2Sn$, $R_2Te$, S, and Se.

It should be noted that no comprehensive and critical coverage exists for cyclic $XO_2$ peroxide chemistry. Four previous reviews concerned with some aspects of $XO_2$ dioxiranes were published in 1995,[1] 1996,[2] 2000,[3] and 2005.[4] The metallodioxiranes, $MO_2$ (M = metal, e.g., Mo, etc.), will not be covered in this review. No comprehensive review exists for metallodioxiranes, $MO_2$.[5]

## 3. Scope

This review will treat sequentially heteroatom-substituted dioxiranes possessing a tetrahedral and trigonal bipyramidal geometry. In section 4.1, tetrahedral "pyramidal" dioxiranes are discussed based upon the order of heteroatoms in the

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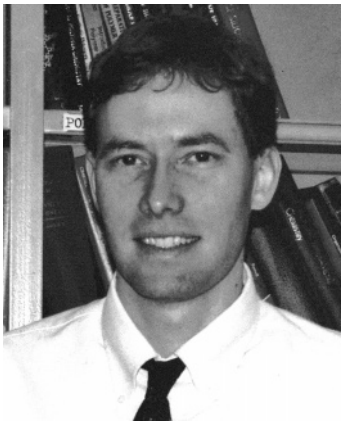
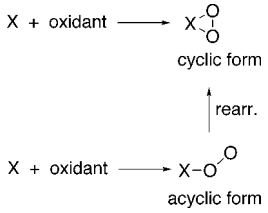
Nahed Sawwan was born in Gaza, Israel. After receiving her Pharmacy Assistant Diploma in 1991 and her B.S. degree in 1992 at the Islamic University in Gaza, she came to the United States. In 2000 she entered the Department of Chemistry at Long Island University—Brooklyn Campus, where she studied analogues of Kemp's triacid, leading to an M.S. degree in 2002. She is currently working toward her Ph.D. degree with A. Greer at Brooklyn College of the City University of New York, engaged in the synthesis and mechanistic studies of sulfur heterocyclic and dioxirane compounds. She enjoys activities with her children and family, such as hiking and climbing, and she is skilled in the sport of table tennis.



Alec Greer obtained his Ph.D. degree from the University of Wyoming under Edward L. Clennan. He was a postdoctoral fellow at University of California—Los Angeles with Christopher S. Foote, and then he moved to Brooklyn College of the City University of New York (CUNY) in 1999. His research interests are in physical organic chemistry, singlet oxygen and peroxide chemistry, as well as chemical evolution and natural products chemistry.

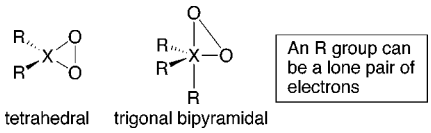
**Scheme 1. Formation of $XO_2$ Dioxiranes**



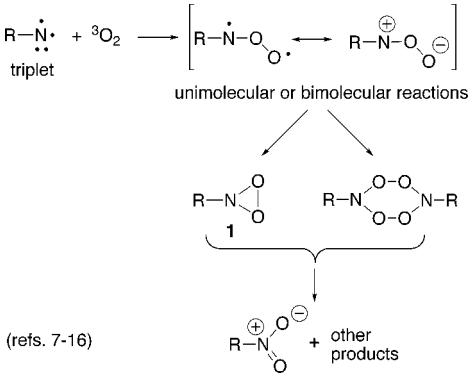

periodic table, with the exception of cyclic $SO_2$ and cyclic $SeO_2$. In section 4.2, a similar approach will be used for the trigonal bipyramidal (TBP) dioxiranes. Each subsection will describe the structure, generation, and reactions involving the $XO_2$ dioxiranes, where data is available. The description of a particular $XO_2$ dioxirane will vary in length based upon whether investigations involved direct spectroscopic, indirect trapping, and/or computational techniques.

In section 4.3, the energetics of the intercoversion between cyclic and ring-open $XO_2$ peroxides is discussed. A unimolecular reaction pathway is discussed in which $XO_2$ dioxiranes undergo an O−O bond homolysis to give the acyclic O−X−O isomer. In some cases $XO_2$ dioxiranes are thought to arise from the acyclic XOO form. Factors involved with intermolecular oxygen-transfer reactions of the $XO_2$ dioxiranes will be discussed in section 4.4. Lastly, the synthetic implications of $XO_2$ dioxiranes will be the topic of section 4.5.

**Scheme 2. Types of $XO_2$ Dioxiranes**




**Scheme 3. Reaction of Nitrene with $O_2$**




We intend to compare $R_2CO_2$ dioxiranes with $XO_2$ dioxiranes. Some examples of $R_2CO_2$ dioxiranes will be mentioned but not explicitly covered. There is substantial literature on $R_2CO_2$ dioxiranes. We emphasize that $R_2CO_2$ dioxiranes are a topic of their own, which has been previously reviewed[6] and is beyond the scope of this review. The restriction also applies to the carbonyl oxide/dioxirane pair. Carbon-based dioxiranes have proven to be highly useful in synthetic chemistry.

## 4. Heteroatom-Containing Dioxiranes

Heteroatom-containing dioxiranes, $XO_2$, possess either tetrahedral or trigonal bipyramidal geometry (Scheme 2). A trigonal bipyramidal structure where both oxygens are equatorial, as opposed to one apical and one equatorial, has only been suggested in one case. Evidence for the existence of these three-membered-ring $XO_2$ peroxides, their possible rearrangements, and their oxygen-transfer reactions are outlined. Different levels of confidence exist in the assignment of $XO_2$ structures.

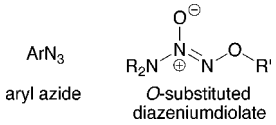
### 4.1. Tetrahedral Dioxiranes

Experimental evidence exists for tetrahedral $XO_2$ dioxiranes that take the form $RNO_2$ and $R_2SiO_2$, but it is not available for $R_2GeO_2$, $R_2SnO_2$, $R_2PbO_2$, $SO_2$, and $SeO_2$. The matrix isolation technique has played a key role in identifying $RNO_2$ and $R_2SiO_2$ dioxiranes. All of the tetrahedral $XO_2$ dioxiranes have been explored computationally except $SeO_2$.

#### 4.1.1. Dioxaziridine, $RNO_2$

**4.1.1.1. Background Information.** Dioxaziridine (azadioxirane, **1**, Scheme 3) has not been isolated as a pure compound but has been proposed as an unstable intermediate in glassy solutions (e.g., 2-methyltetrahydrofuran at 77 K)[7]

**Scheme 4. Dioxaziridine Precursors**

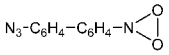
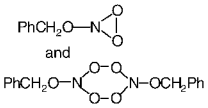
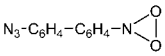
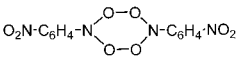
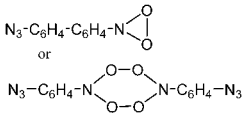



and in inert solvents (e.g., acetonitrile at 298 K).[8] Dioxaziridines are not stable at room temperature. To date, ten studies have proposed the formation of dioxaziridine via nitrene−$O_2$ chemistry from aryl azide and O-substituted diazeniumdiolate photooxidations (Scheme 4).[7−16] Tars also form in photooxidations of aryl azides.[17−22] A non-nitrene route to dioxaziridine has not been suggested. The idea of dioxaziridine as an intermediate in azide−ozone chemistry has not been put forward.[23]

Dioxaziridine may arise from the spin-allowed reaction of triplet nitrene with $^3O_2$, generated by cyclization of the initially formed nitroso oxide (Scheme 3). The reaction is analogous to the reaction of triplet carbenes with $^3O_2$. Owing to its ability to hydroxylate toluene,[8] nitroso oxide has been described as possessing diradical character ($RN^{\bullet}OO^{\bullet}$) rather than the zwitterionic character ($RN^+OO^-$); the latter is related to nucleophilic oxidants carbonyl oxides ($R_2C^+OO^-$) and persulfoxides ($R_2S^+OO^-$). However, there are differences of opinion as to the fate of the nitroso oxide. These differences may be reconciled based on nitroso oxide concentrations. High concentrations of nitroso oxide lead to dimerization to a six-membered-ring diperoxide, [1,2,4,5]-tetraoxa-3,6-diazinane, rather than intramolecular cyclization to the dioxaziridine. A compilation of the methods and reaction conditions proposed to generate dioxaziridine or tetraoxadiazinane is given in Table 1.

Matrix isolation has only been employed in one study to characterize structurally dioxaziridines.[7] Dioxaziridines have been directly detected by UV−visible spectroscopy.[7] Structural identification methods that use IR, EPR, luminescence, or NMR spectroscopy have not produced clear evidence for their detection. Dioxaziridines have so far not been trapped and are not capable of oxygen transfer to hydrocarbon molecules. This may be due to the powerful oxidation chemistry displayed by the precursor of the dioxaziridine, nitroso oxide.

**Table 1. Generation of Dioxaziridines ($RNO_2$ Dioxirane) or Tetraoxadiazinane (Diperoxide)**

| Year | Structure | Evidence of Formation | T(K) | Method of Preparation[a] | Ref. | Comments |
|---|---|---|---|---|---|---|
| 2004 |  | Luminescence data | 298 | A | 14, 15 | |
| 2002 |  | Luminescence data | 298 | C | 13 | Dioxaziridine contained within a rubber polymer was proposed |
| 2001 |  | Kinetic and product study | 298 | D | 10 | Light source power suggested to influence dioxaziridine-to-tetraoxadiazinane contribution |
| 2001 |  | Luminescence data | 293 | A | 16 | |
| 1999 | **1a - 1f** | UV-Visible detection | 77 | A | 7 | Presumably formed by nitroso oxide isomerization |
| 1996 |  Ar = *p*-$MeOC_6H_4$, Ph, *p*-$NO_2C_6H_4$ | $^{18}O_2$ labeling | 298 | B | 8 | Dioxiaziridine suggested to have a very short lifetime and convert rapidly to $ArNO_2$ nitrobenzene |
| 1991 |  | $^{18}O_2$ labeling | 298 | B | 11 | Suggestion of whether dioxaziridine was an intermediate or TS was not made |
| 1987 |  | $^{18}O_2$ labeling | 298 | B | 12 | Unimolecular isomerization of PhNOO to nitrobenzene suggested to go via phenyldioxaziridine |
| 1987 |  | Product study | 298 | B | 17 | Product distribution varies based upon high- vs low power light source. Intractable tarry polymer product also formed |
| 1971 |  | Product study | 77 | A | 9 | Suggested assignment of dioxaziridine or tetraoxadiazinane is only tentative |

[a] A, matrix isolation of $ArN_3$ photooxidation; B, room-temperature solution-phase $ArN_3$ photooxidation; C, substrates adsorbed to natural rubber; D, room-temperature solution-phase diazeniumdiolate photooxidation.

**Table 2. UV−visible Spectroscopic Data Obtained from Aryl Azide Photooxidations**[a]

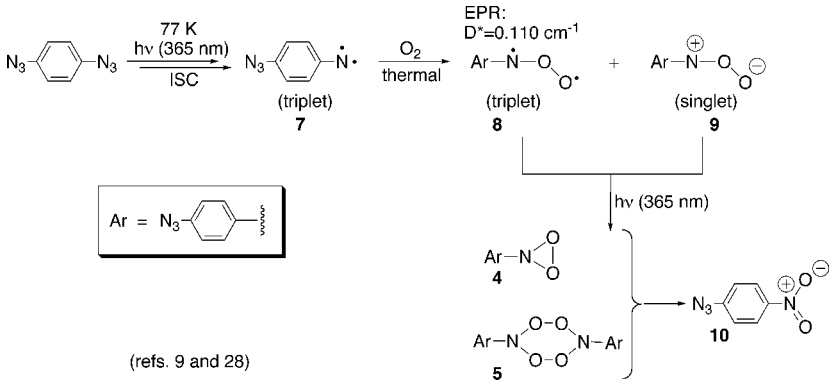
| R | 2 $\lambda_{max}$ (nm) | 1 $\lambda_{max}$ (nm) | 3 $\lambda_{max}$ (nm) |
|---|---|---|---|
| a | 514 | 333, 348 | 373 |
| b | 486 | 367 | 357, 374, 394 |
| c | 703 | 414 | 477 |
| d | 612 | 362 | 432 |
| e | 541 | - | 389 |
| f | 554 | 355, 371 | 379, 396, 425, 454 |

[a] Matrix detection of nitroso oxides, dioxaziridines, and nitro compounds at 77 K. Adapted with permission from ref 7. Copyright 1999 American Chemical Society.

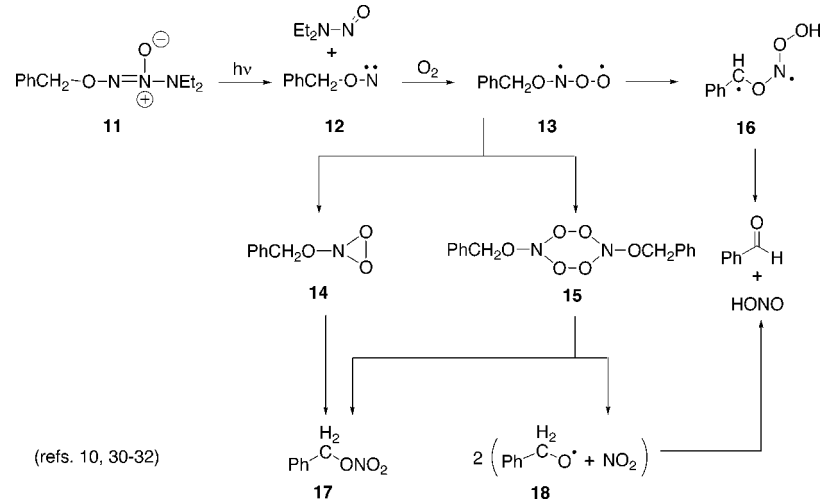
**4.1.1.2. Low Temperature.** *UV−Visible Spectroscopy.* We have only located one study that provided UV−visible spectroscopic evidence for the formation of dioxaziridines in the reaction of nitrenes with $O_2$ (Table 2). In 1999, the formation of 4-(dioxaziridinyl)stilbene (**1a**), 4-(dioxaziridinyl)-4′-nitrostilbene (**1b**), 4′-(dioxaziridinyl)-4-(dimethylamino)stilbene (**1c**), 4′-(dioxaziridinyl)-4-aminobiphenyl (**1d**), and 4-(dioxaziridinyl)-4′-(nitrene-substituted)stilbene (**1f**) was reported in rigid "glassy" 2-methyltetrahydrofuran (MTHF) at 77 K.[7,24] UV or visible irradiation of various aryl azides in air-saturated MTHF solution produced the corresponding triplet nitrene precursors,[25] which can be detected by EPR and UV−visible spectroscopy.[24,26,27] The reaction between the triplet nitrenes and $O_2$ is a thermal process and gives the corresponding nitroso oxides **2a**−**2e**, respectively, where **2f** arises from subsequent loss of $N_2$. Upon irradiation at 95 K, nitroso oxides **2a**−**2f** rearrange unimolecularly to dioxaziridines **1a**−**1f**. This process has a large barrier (computed value 45 kcal/mol).[7] MTHF is a rigid medium at 77 K and thus bimolecular reactions leading to [1,2,4,5]-tetraoxa-3,6-diazinanes appear to be unlikely. The dioxaziridines **1a**−**1e** subsequently isomerize to give the corresponding nitro compounds (**3a**−**3e**).

*EPR Spectroscopy.* In 1971, the intermediacy of dioxaziridine **4** or tetraoxadiazinane **5** was proposed in a photooxidation reaction with *p*-diazidobenzene (Scheme 5).[9,28] The UV photolysis ($\lambda$ = 365 nm) of *p*-diazidobenzene in $O_2$-saturated hydrocarbon solvents (3-methylpentane, methylcyclohexane, or ethanol) at 77 K produced the triplet mono-nitrene (**7**) in an early step.[9,29] EPR, luminescence, and visible spectroscopy followed the course of the reaction. Interestingly, the thermal reaction between triplet nitrene and $O_2$ gave higher nitroso oxide concentrations in 3-methylpentane compared to methylcyclohexane glasses, likely due to enhanced $O_2$ solubility or diffusion in the 3-methylpentane matrix at 77 K. Compound **8** was suggested to possess triplet

**Scheme 5. Photooxidation of *p*-Diazidobenzene**



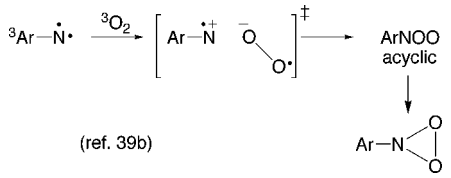

**Scheme 6. Photooxidation of O-Substituted Diazeniumdiolate**



character (based on an observed triplet species with $D^* = 0.110\ cm^{-1}$ in the EPR spectrum, a signal only present in $O_2$-containing samples), whereas **9** possessed singlet dipolar character (based on the observed diamagnetic yellow intermediate). On irradiation, the nitroso oxide(s) converted to the *p*-nitrophenyl azide product (**10**) via dioxaziridine or [1,2,4,5]-tetraoxa-3,6-diazinane intermediates. Only tentative evidence for dioxaziridine **4** was found, based on the possible interconversion of the nitroso oxide(s) to *p*-nitrophenyl azide **10**.

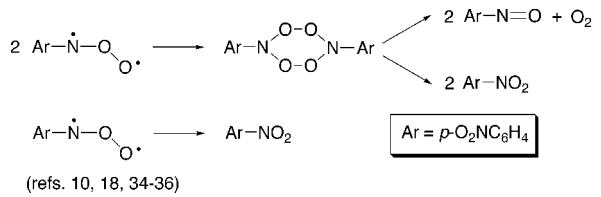
**4.1.1.3. Room Temperature.** *Time-Resolved Infrared Study: Oxynitrene−$O_2$ Reaction.* In 2001, a solution-phase O-substituted diazeniumdiolate (**11**) photooxidation reaction was conducted at room temperature.[10] Laser light ($\lambda = 266$ nm) was used to irradiate **11** in $O_2$-saturated acetonitrile-$d_3$, which led to an O-substituted nitrene (**12**) and $Et_2NN{=}O$ (Scheme 6).[10,30−32] Time-resolved infrared (TRIR) spectroscopy was used and provided kinetic insight that dioxaziridine (**14**) and tetraoxadiazinane (**15**) are both present as transient intermediates in the reaction. A first-order pathway for the nitroso oxide **13** leads to dioxaziridine **14**, whereas a second-order pathway for **13** afforded tetraoxadiazinane **15**. The relative contributions of the uni- and bimolecular pathways depended on the initial concentration of nitroso oxide **13**. A higher concentration of **13** was achieved from the use of high laser power, which then favored the bimolecular reaction to give **15**. Low laser power resulted in low steady-state concentrations of **13**. This consequently favored the unimolecular conversion of nitroso oxide to dioxaziridine **14** or diradical **16**. Formation of benzyl nitrate (**17**) is proposed to take place via dioxaziridine and tetraoxadiazinane. Benzaldehyde and nitrous acid (HONO) are additional products, thought to arise from **13** to **16** or produced by fragmentation of **15** into $^{\bullet}NO_2$ and benzyloxy radical **18** and subsequent coupling. Interestingly, oxynitrenes are known to react faster with $^3O_2$ compared to arylnitrenes due to a possible electron transfer to form an ion pair, coupling to generate the nitrene oxide, which cyclizes to the dioxaziridine (Scheme 7).[39b]

**Scheme 7. Formation of an Ion Pair Transition State**

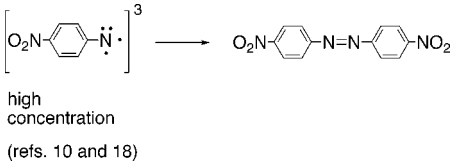



*Laser Flash Photolysis: Aryl Nitrene−$O_2$ Reaction.* In 1987, the photooxidation of *p*-nitrophenyl azide was reported in benzene and acetonitrile solution.[17] The reaction of *p*-nitrophenyl nitrene reacted with $O_2$ afforded the corresponding nitroso oxide. Dimerization of the nitroso oxide was suggested to give [1,2,4,5]-tetraoxa-3,6-diazinane (Scheme 8).[10,18,34−36] Cleavage of [1,2,4,5]-tetraoxa-3,6-diazinane yields ArN=O and $O_2$ (in a spin-forbidden process giving $^3O_2$ or in a spin-allowed process giving $^1O_2$), or it can fragment to give 2 equiv of $ArNO_2$. $ArNO_2$ may also come directly from nitroso oxide ArNOO. ArN=O reacts with triplet nitrene to give dinitroazobenzene [ArN(O)=NAr], or nitrene dimerizes when its concentration is raised, as in the case of the high-power irradiation (Scheme 9). The observation that variation

**Scheme 8. Reactions of Nitroso Oxides**



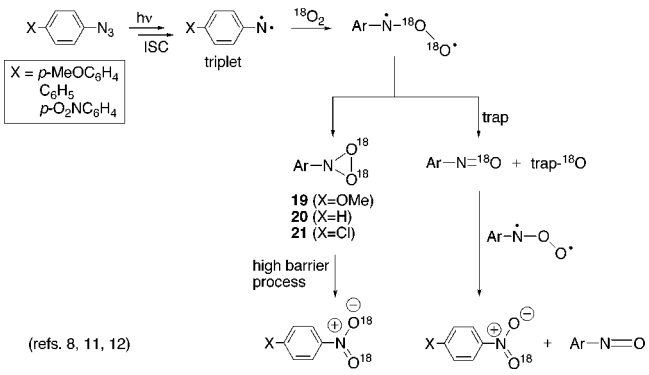

**Scheme 9. Nitrene Dimerization**




of the laser irradiation power leads to different product distributions constitutes an important discovery. One may anticipate that low-power irradiation conditions facilitate the unimolecular reaction of nitroso oxide **13** to dioxaziridine **14** (Scheme 6) by analogy with the *p*-nitrophenyl nitrene photooxidation reaction in dilute homogeneous solution (Scheme 8).[10]

*$^{18}O$ Isotope Labeling.* $^{18}O$ labeling experiments carried out from 1987 to 1996 suggested that *p*-methoxyphenyl dioxaziridine (**19**), phenyl dioxaziridine (**20**), and *p*-nitrophenyl dioxaziridine (**21**) arise in the photooxidation of *p*-methylphenyl azide, phenyl azide, and *p*-nitrophenyl azide, respectively (Scheme 10).[8,11,12] The $^{18}O$-tracer experiments

**Scheme 10. $^{18}O$-Labeling Study in Aryl Azide Photooxidations**




were conducted in acetonitrile solvent at 20 °C ($\lambda > 350$ nm) by using a mixture of $^{18}O_2$ and $^{16}O_2$ gas. GC/MS determined the content of $^{18}O$ and $^{16}O$ within the products. Indirect evidence pointed to a dioxaziridine intermediate, since retention of two $^{18}O$ atoms in the nitro product originated from one $^{18}O_2$ molecule. A unimolecular cyclization of nitroso oxide to dioxaziridine accounts for retention of the two oxygen atom labels in the nitro product (Table 3). Scrambling would have indicated that the oxygen atoms come from different $O_2$ molecules. Table 3 also shows that the unimolecular rearrangement of nitroso oxide to dioxaziridine is competitive with oxygen transfer (trapping) from the nitroso oxide to PhN=O, $Ph_2S$, $Ph_2SO$, and benzene. The work identified the electrophilic character in the phenyl nitroso oxide ($PhN^{\bullet}OO^{\bullet}$). $PhN^{\bullet}OO^{\bullet}$ is capable of hydroxylating toluene-4-*d* and anisole-4-*d* via an NIH shift to give the products 4-methylphenol-*d* (**23**; R = Me), 4-methoxyphenol-*d* (**23**; R = MMe), 4-methylphenyl-2-*d*-ol (**24**; R = Me), and 4-methoxyphen-2-*d*-ol (**24**; R = OMe) (Scheme 11).

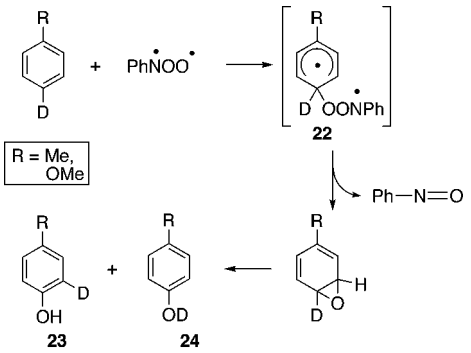
According to computations, a large energy barrier separates the nitroso oxide and dioxaziridine (∼45 kcal/mol) (section

**Table 3. $^{18}$O-Tracer Study in the Photooxidation of Aryl Azides[a]**

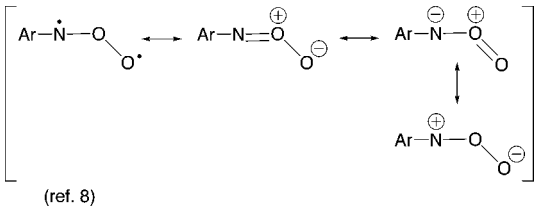
| $ArN_3$ | additive | conv (%) | yield (%) of $ArNO_2$ | mass data of $ArNO_2$: M/(M+2)/(M+4) | retention/ scrambling[b] |
|---|---|---|---|---|---|
| | | | | 100/0.6/8.4 | 100:0 (calculated) |
| | | | | 100/16.8/0.7 | 0:100 (calculated) |
| $p$-$MeOC_6H_4$ | $Ph_2S$ | 85 | 14 | 100/10.8/3.3 | 35:65 |
| $p$-$MeOC_6H_4$ | $Ph_2SO$ | 94 | 25 | >100/55.7/7.5 | 16:84 |
| $C_6H_5$ | | 41 | 28 | 100/10.7/4.0 | 41:59 |
| $p$-$O_2NC_6H_4$ | $Ph_2SO$ | 90 | 30 | 100/14.0/2.1 | 19:81 |

[a] Irradiation of $ArN_3$ ($\lambda$ = 350 nm) in acetonitrile under oxygen ($^{32}O_2/^{34}O_2/^{36}O_2$ = 100:0.6:8.4). Adapted with permission from ref 8. Copyright 1996 by the Royal Society of Chemistry. [b] Retention means the formation of $PhNO_2$ from one molecule of oxygen. Scrambling means that the two oxygen atoms in $ArNO_2$ are derived from two different oxygen molecules.

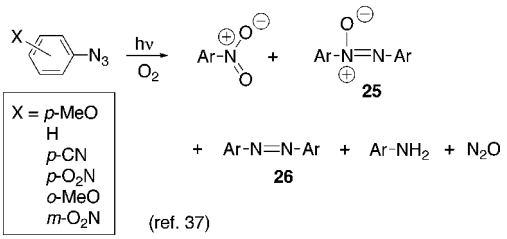
**Scheme 11. Oxygen Transfer from Phenyl Nitroso Oxide to Toluene-4-*d* and Methoxybenzene-4-*d***




**Scheme 12. Resonance Forms of Nitroso Oxide**




**Scheme 13. Photooxidations of Aryl Azides**




4.1.1.5). Thus, it is likely that a photochemical interconversion is necessary to overcome the high barrier,[7] although some authors argue that a greater diradical character (versus the zwitterion resonance form) will enable cyclization of the RNOO intermediate (Scheme 12).[8,11,12]

*Sensitized Reaction.* In 1983, a photooxidation reaction of aryl azides was conducted in acetonitrile, acetone, and benzene solvents at 30 °C (Scheme 13).[37] While dioxaziridine and tetraoxadiazinane were not suggested as intermediates in the reaction, this study is worth mentioning. This appears to be the only example of triplet sensitization in connection with the addition of oxygen during the photolysis of organic azides. A medium-pressure mercury lamp was used as the light source. When the triplet sensitizers acetone or acetophenone were added, an increased yield of nitrobenzene product resulted. Addition of a triplet quencher (piperylene) led to negligible yields of nitrobenzene product; however, addition of singlet oxygen sensitizers, Rose Bengal or methylene blue, had no effect on the product yields, which suggested that $^1O_2$ is not playing a role in the photooxidation. The presence of amine additives influenced the product distribution, in that primary or secondary amines increase production of tar while tertiary amines lower it.[38] Such effects with added amines have also been observed by others.[18,38−40]

**4.1.1.4. Miscellaneous.** In 2002, it was suggested that formation of dioxaziridine takes place in 4,4′-diazobiphenyl-containing rubber polymer samples which had been applied to a glass surface and dried before photolysis.[13] The photooxidation reaction has been proposed to proceed via a nitrene and then subsequently to dioxaziridine $N_3C_6H_4-C_6H_4NO_2$, where the dioxaziridine was suggested to luminesce at $\lambda_{max}$ = 456, 457, 461, 462, and 470 nm. Unfortunately, these rubber polymer experiments provide only tentative evidence for the presence of dioxaziridine, since the intermediate(s) responsible for the luminescence has(ve) not been detected. Other experiments have proposed the formation of dioxaziridines from photooxidations of phenylazide and 4,4′-diazodiphenyl in acetonitrile or ethanol solutions at room temperature.[14−16] It should be mentioned that reactions of molecular oxygen with imidogen (NH) have been studied in combustion processes. The addition of NH ($^3\Sigma^-$) and $O_2$ ($^3\Sigma_g^-$) is predicted to give imine peroxide, HNOO. Imidogen is generated in the laboratory, for example, by photolysis of hydrazoic acid, where NH ($^1\Delta$) is generated.[40,41] As yet, there are no experimental data that suggest the formation of unsubstituted dioxaziridine $HNO_2$ in the imidogen−$O_2$ reactions, although other $HNO_x$ species have been observed.

**4.1.1.5. Calculations.** *Structure.* Computational results for the dioxaziridine are addressed in this section. $HNO_2$ and $PhNO_2$ dioxiranes are minima at the G2(MP2), B3LYP/6-31G(d), MP2/6-31G(d), and multiconfigurational MC-SCF/6-31G(d) levels and have been used to explain the experimental data on the nitrene−$O_2$ reactions.[7,42−50]

Calculated bond distances and a bond angle are shown in Table 4. Dioxaziridine $HNO_2$ and $PhNO_2$ bond distances for O−O range from a high of 1.487 Å to a low of 1.404 Å. The sensitivity of the dioxaziridine geometry to the identity of the substituent R has not been examined in detail. Dioxaziridine $HNO_2$ and $PhNO_2$ bear a resemblance to each other independent of the computational method used. For example, at the B3LYP/6-31G* level, the O−O bond distance is 0.002 Å shorter and the N−O bond 0.002 Å shorter in the $HNO_2$ dioxirane than in the $PhNO_2$ dioxirane. However, the reported literature value for O−O is 1.404 Å at the MP2/6-31G(d) level and 1.487 Å at the MP2/6-31G(d,p) level. This represents a large difference in the predicted O−O bond distance, which has not been explained. The bond distances for the computed N−O range from a high of 1.451 Å to a low of 1.373 Å. The O−N−O bond angle ranges from a high of 61.8° to a low of 59.2°, with the exception of the MCSCF/6-31G(d) value of 68.3°. A sample computed structure for the unsubstituted dioxaziridine is given in Figure 1.

Dioxaziridines $HNO_2$ and $PhNO_2$ have $C_s$ symmetry and negatively charged oxygen atoms. The atomic charges, as predicted by Mulliken, indicate negative charge density at

**Table 4. Calculated Energies and Geometries of the Dioxaziridines**

| Year | Structure | State | Energy[a] | Method and Basis Set | O-O[b] | N-O[b] | O-N-O[c] | Ref. | Comments |
|---|---|---|---|---|---|---|---|---|---|
| 1999 |  | $S_o$ | -205.5670 | B3LYP/6-31G(d) | 1.461 | 1.431 | 61.4 | 7 | Both N-O bond distances are equal in length |
| 1999 |  | $S_o$ | -436.6261 | B3LYP/6-31G(d) | 1.463 | 1.443 | 60.9 | 7 | |
| 1998 |  | $S_o$ | -205.32839 | G2(MP2) | _ | 1.449 | 61.8 | 46 | |
| 1997 |  | $S_o$ | -205.07655 | MP2/6-31G(d,p) | 1.487 | 1.451 | 59.2 | 45 | |
| 1997 |  | $S_o$ | _ | MP2/6-311G (2df,2p) | 1.464 | 1.435 | 61.4 | 45 | |
| 1992 |  | $S_o$ | _ | MCSCF/6-31G(d,p) 6-electron-6-orbital | _ | 1.374 | 68.3 | 43 | Geometries also optimized for singlet and triplet acyclic HNOO |
| 1989 |  | $S_o$ | _ | MP2/6-31G(d) | 1.404 | 1.373 | 61.5 | 44 | Basis set dependence on HNOO dihedral angle also reported |
| 1987 |  | $S_o$ | _ | HF/4-31G(d) | 1.405 | 1.374 | 61.5 | 47 | Structure for dithiaziridine ($HNS_2$) also reported |

[a] Energies in atomic units. [b] Bond distances in angstroms. [c] Bond angles in degrees.

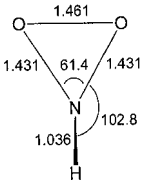



**Figure 1.** B3LYP/6-31G(d) computed structure of the unsubstituted dioxaziridine from ref 7. Bond lengths in angstroms; bond angles in degrees.

the oxygen atoms (−0.202) and positive ones on the hydrogen (+0.341) and nitrogen atoms (+0.063) (Table 5). Other properties that have been calculated for dioxaziridine $HNO_2$ include dipole moment (Table 6), energies of the HOMO and LUMO (Table 7), and vibrational frequencies (Table 8).

*Energetics.* Saddle points connecting the nitroso oxide and dioxaziridine have been located in four studies (Table 9). The cyclization barrier for MeO−NOO to $MeONO_2$ dioxirane is 21.6 kcal/mol at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level,[39b] that for PhNOO to $PhNO_2$ dioxirane is 40.9 kcal/mol at the B3LYP/6-31G(d) level, and that for HNOO to $HNO_2$ dioxirane is 43.8 kcal/mol at the MCSCF level.[43] The barrier is lower at the MP4/6-31G(d,p)//HF/6-31G(d) level, 12 kcal/mol.[49]

Dioxaziridine is apparently isoenergetic with the nitroso oxide in the gas phase. The interconversion of *trans* nitroso oxide HNOO to dioxaziridine $HNO_2$ has been calculated to be endothermic by 4.2 kcal/mol (MCSCF) and 4 kcal/mol [MP4/6-31G(d,p)//HF/6-31G(d)] and exothermic by −3.1 kcal/mol [MP2/6-31G(d,p)]. It should be worthwhile to compute the energetics and barrier for conversion of nitroso oxide to the six-membered diperoxide, [1,2,4,5]-tetraoxa-3,6-diazinane. Calculated structures on model systems provide evidence for the formation of dioxaziridine, but they have not been scrutinized against the dimerization pathway thus far.

The activation energies for the interconversion of dioxaziridine to the corresponding nitro compound are 33.2 kcal/mol [$MeONO_2$, B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)], 14.2 kcal/mol [$HNO_2$, B3LYP/6-31G(d)], and 18.8 kcal/mol [$PhNO_2$, B3LYP/6-31G(d)] (Table 9). However, a discrepancy exists since there is a reported value of 2 kcal/mol for $HNO_2$ [MP2/6-31G(d)]. The exothermicity of the reaction is −70.2 kcal/mol [$MeONO_2$, B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)], −74.0 kcal/mol [$HNO_2$, B3LYP/6-31G(d)], −80.7 kcal/mol [$PhNO_2$, B3LYP/6-31G(d)], −66 kcal/mol ($PhNO_2$), −64 kcal/mol ($PhNO_2$, MCSCF), −77.7 kcal/mol [$HNO_2$, MP2/6-31G(d,p)], −76 kcal/mol [$HNO_2$, MP4/6-31G(d,p)//HF/6-31G(d)]. For calculated energetics, isomerization and fragmentation are provided in Table 9. This includes conversion of dioxaziridine $HNO_2$ to acyclic HOON. The reaction of NH ($^3\Sigma^-$) and $O_2$ ($^3\Sigma_g^-$) to give acyclic HNOO has been investigated by SCF and MRD-CI calculations with the

**Table 5. Calculated Charge Densities of the Unsubstituted Dioxaziridine**

| Year | Structure | Mulliken Charge | | | | Method and Basis Set | Ref. | Comment |
|---|---|---|---|---|---|---|---|---|
| | | H | N | O | O | | | |
| 1997 |  | 0.341 | 0.063 | -0.202 | -0.202 | MP2/6-31G(d,p) | 45 | |
| 1987 |  | — | 0.094 | 0.090 | 0.090 | HF/6-31G(d,p) | 47 | A Mullliken gross population was calculated, where $q = d_{xx} + d_{yy} + d_{zz} + d_{xy} + d_{yz} + d_{xz}$ |

**Table 6. Calculated Dipole Moment of the Unsubstituted Dioxaziridine[a]**

| Year | Structure | μ (Debyes) | Method and Basis Set |
|---|---|---|---|
| 1989 |  | 2.22 | MP2/6-31G(d) |

[a] Adapted with permission from ref 44. Copyright Wiley.

6-31G(d,p) basis set.[43,49,50] The reaction between NH ($^1\Delta$) + $O_2$ ($^1\Delta_g$) has been suggested to give dioxaziridine $HNO_2$ in a concerted addition process, where acyclic HNOO does not intercede. The reaction of $HNO_2$ dioxirane to $^1$HNO + O($^3$P) is predicted to be endothermic by 7.0 kcal/mol from MCSCF calculations.[43] The activation energies for nitroso oxide or dioxaziridine to release an oxygen atom intramolecularly have not been computed to date. Formation of the dioxaziridine by the isomerization of peroxynitrite has not been proposed (Scheme 14), presumably due to the high instability expected; however, the isomerization of peroxynitrite to nitrate is known.[23e]

In conclusion, dioxaziridines do not arise as a primary species from a side-on attack of $^3O_2$ with electron-deficient triplet nitrene. Instead, these nitrene reactions with $O_2$ produce nitroso oxide, which subsequently may cyclize to dioxaziridine. Persistent isolable dioxaziridines have so far not been prepared. The generation of dioxaziridine as a transient intermediate has been achieved; however, other reactive species are also present, such as azide excited states, nitrenes, nitroso oxides, and tetraoxadiazinanes. To avoid the formation of such reactive intermediates in nitrene chemistry presents a challenge for the clean production of dioxaziridines.

### *4.1.2. Dioxasilirane, $R_2SiO_2$*

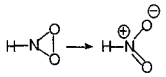
**4.1.2.1. Background Information.** Dioxasilirane (also known as siladioxirane or dioxasilacyclopropane, **27**) has not yet been isolated as a pure compound due to its instability. Dioxasilirane can be formed in a reaction of singlet or triplet silylene (silanediyl, $R_2Si$) with $^3O_2$. Silylenes generated from azo-, fluoro-, chloro-, methyl-, and methoxy-containing silanes in argon matrices have served as precursors to dioxasiliranes (Scheme 15).[51−58] Studies also suggest the intermediacy of dioxasilirane from solution-phase, $SiO_2$-surface, and combustion experiments.[59−74] A compilation of reaction conditions thought to give rise to dioxasiliranes is given in Table 10.

To date, three studies provide direct spectroscopic evidence for the formation of dioxasilirane intermediates. Surprisingly little indirect evidence has been collected to support the existence of dioxasiliranes. On reaction of silylene with $O_2$, silanone *O*-oxide (**28**) is thought to form initially and then rapidly interconvert to the dioxasilirane **27**, given the low barrier separating **27** and **28**. Silanone *O*-oxide is the congener of carbonyl oxide, but its oxygen transfer or other chemical reactivity is unknown, so that clarification about the importance of diradical character ($R_2Si^{\bullet}OO^{\bullet}$) and zwitterionic character ($R_2Si^{+}OO^{-}$) is not available. Bimolecular reactions of **27** or **28** are unknown in matrix and solution phases. 3,3,6,6-Tetrasubstituted-[1,2,4,5]-tetraoxa-3,6-disilinane and silanone [RSi(O)R] are not proposed as products formed in silyene−$O_2$ reactions; however, dioxasilirane can rearrange unimolecularly to a silaester [RSi(O)OR].

A large body of literature is available for silylenes, but only a fraction of it focuses on silylene−$O_2$ chemistry. The literature on silylenes under oxygen-free conditions will not be covered here.

**4.1.2.2. Low Temperature.** *Infrared Spectroscopy.* We have located three studies that provide IR spectroscopic evidence for dioxasilirane.[51−58] In 2000, the synthesis of methylphenyldioxasilirane ($MePhSiO_2$, **31**) in an oxygen-doped argon matrix at 10 K was reported (Scheme 16).[51] UV irradiation ($\lambda$ > 305 nm) of phenylsilyldiazomethane (**29**) in the argon matrix produces methylphenylsilylene via a 2-silapropene intermediate (**30**). Thermal annealing of the argon matrix to 30−45 K led to the reaction of silylene with

**Table 7. Calculated HOMO and LUMO Energies of the Unsubstituted Dioxaziridine[a]**

| Year | Structure | HOMO(au) | LUMO(au) | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|---|
| 1999 |  | -0.49245 | 0.20580 | HF/6-31G(d) | 7 | An orbital diagram for the conversion of the following is also given:  |
| 1989 |  | -0.49111 | 0.21799 | MP2/6-31G(d) | 44 | HOMO and LUMO values also reported for TS for NH inversion process |

[a] Both N−O bond distances are equal in length.

**Table 8. Calculated Vibrational Frequencies of the Unsubstituted Dioxaziridine**

| Year | Structure | Symmetry | a' | a" | a'[a] | a"[b] | a' | a'[b] | Method and Basis Set | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Scaled Harmonic Vibrational Frequencies (cm$^{-1}$) | | | | | | | | |
| 1997 |  | Scaled Freq. | 748 | 761 | 1035 | 1140 | 1344 | 3177 | MP2/6-31G(d,p) | 45 |
| | | Unscaled Freq. | 801 | 814 | 1107 | 1219 | 1437 | 3398 | | |
| | | IR intensity | 0.3 | 2.9 | 0.5 | 39.3 | 34.8 | 2.6 | | |

[a] Cyclic breathing vibration. [b] Exo N−H stretching vibration.

**Table 9. Calculated Relative Energies of Species on the Dioxaziridine Reaction Surface[a]**

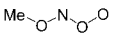
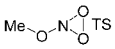
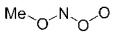
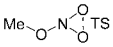
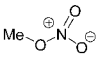
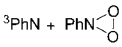
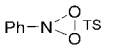
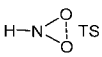
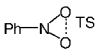
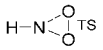
| Year | A | B | $\Delta E_{A \rightarrow B}$ | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|---|
| 2006 |  |  (Ring closing) | 21.6[b] | B3LYP/6-311+G(d,p)// B3LYP/6-31G(d) | 39b | Energies are given as ΔG(298K). Calculations were also performed at the CBS-QB3 level. |
| |  |  | 8.6 | | | |
| |  |  (Ring opening) | 33.2[b] | | | |
| |  |  | -70.2 | | | |
| | $^3$PhN + PhNOO | 2 PhN=O | -79.5 | | | |
| | $^3$PhN +  | 2 PhN=O | -93.5 | | | |
| 2002 |  |  (Ring closure) | 40.9[b] | B3LYP/6-31G(d) | 13 | Singlet-triplet gap for acyclic PhNOO is 19.0 kcal/mol with the CASSCF/6-31G(d) method |
| 1999 |  |  (Ring opening) | 14.2[b] | B3LYP/6-31G(d) | 7 | Zero-point energy (ZPE) correction included |
| |  |  (Ring opening) | 18.8[b] | | | |
| |  |  | -74.0 | | | |
| |  |  | -80.7 | | | |
| | $PhNO_2$ | $PhNO_2$ perpendicular Ph group | 3.5 | | | Energy represents the barrier to forcing the phenyl ring to be perpendicular to the dioxaziridine ring |
| 1998 |  + 2 $NH_2OH$ + HOOH | 2 $NH_2OOH$ + HON(H)OH | -28.0 | G2 (MP2) | 46 | Atomization energies were also reported |
| |  + 2$NH_3$ + 2$HO_2$ | 2 $NH_2OH$ + HOOH | 11.8 | | | |
| 1997 |  |  | -74.7 | MP4 SDTQ//MP2/ 6-31G(d,p) | 45 | ZPE corrected values also available |
| |  |  (trans) | -82.0 | | | |
| |  |  (cis) | -83.2 | | | |
| 1996 |  |  | -66 | | 8 | Computational method used was not mentioned |

**Table 9 (Continued)**

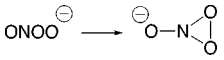
| Year | A | B | $\Delta E_{A \rightarrow B}$ | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|---|
| 1992 | H-NOO |  (Ring closure) | 43.8[b] | 6-electron/6-orbital MCSCF | 43 | A multiconfigurational SCF procedure was used and the transition state calculated with CI (full) |
| | H-NOO |  | 4.2 | | | |
| 1992 | H-NOO |  | 17.2[b] | 6-electron/6-orbital MCSCF | 43 | Favors route from HNOO to NOOH and then cleavage to NO+OH rather than less stable route of HNOO to cyclic $HNO_2$ |
| | H-NOO |  | -35.7 | | | |
| |  |  | -64.0 | | | |
| |  |  | -81.6 | | | |
| |  | HNO + O($^3$P) | 7.0 | | | |
| 1989 |  |  (Ring opening) | 60.7 | MP2/6-31G(d) | 44 | Values from the SCF method, the MP3 method and 6-31G, 6-31G+R. F., and 6-31G+(d) basis set were also reported. Inversion barrier of dioxaziridine is greater than 1H-azirine (46.3), oxaziridine(41.5), 1H-diazirine (34.7), and aziridene (19.9) at the MP2/6-31G(d) level. MP2/6-31G(d) inversion barrier reported on rotation about the HNOO dihedral angle. |
| |  |  (Ring opening) | 56.8 | MP2/6-31+G(d) | | |
| 1987 |  (cis) |  | -1.3 | MP2/6-31G(d,p) | 47 | Values also reported at the levels RHF/4-31G, RHF/4-31G(d), RHF/6-31G(d), and MP2/6-31G(d,p) |
| |  (trans) |  | -3.1 | | | |
| |  |  | -77.7 | | | |
| |  |  (cis) | -83.8 | | | |
| |  |  (trans) | -82.4 | | | |
| |  |  (cis) | -9.8 | | | |
| |  |  (trans) | -18.0 | | | |

**Table 9 (Continued)**

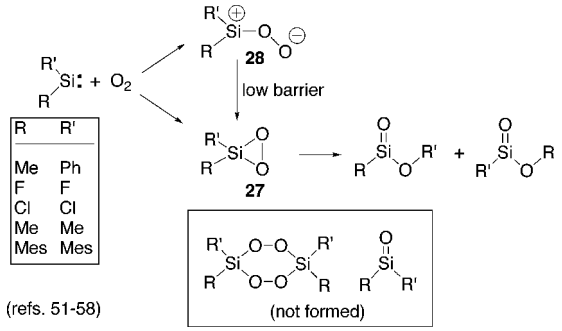
| Year | A | B | $\Delta E_{A \rightarrow B}$ | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|---|
| 1984 | HNOO |  (Ring closure) | 12[b] | MP4/6-31G(d,p)//HF/6-31G(d) | 49 | ZPE correction included. Bond additivity-type conections also included giving sufficient electron correlation contribution. Energy values are taken from a Figure in the original manuscript and are subject to errors of ± 3 kcal/mol. |
| | HNOO |  | 4 | | | |
| |  |  (Ring opening) | 2[b] | | | |
| |  |  | -76 | | | |
| | $^1$NH + $^1$O$_2$ |  | -20 | | | Path does not proceed through the HNOO species |
| |  | HONO | -81 | | | |

[a] Energies in kcal/mol. [b] Transition state energies in kcal/mol.

**Scheme 14. Cyclization of Peroxynitrite**

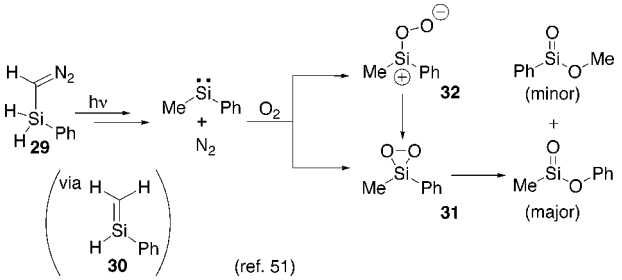


**Scheme 15. Reaction of Silylene with $O_2$**




$O_2$, giving dioxasilirane **31**. IR spectroscopy detected both silylene and dioxasilirane intermediates. Dioxasilirane **31**

**Scheme 16. Reaction of Silylene with $O_2$**




displays a strong Si−O stretching mode at 1002 cm$^{-1}$ (1005 cm$^{-1}$ predicted) and a weak O−O stretching mode at 577 cm$^{-1}$ (608 cm$^{-1}$ predicted) (Table 11). The predictions were made on the basis of B3LYP/6-311++G(2d,p) calculations. $^{18}O_2$ labeling confirms the assignment of methylphenyldioxasilirane, in which the Si−O stretching vibration is red-shifted by 25.3 cm$^{-1}$ (28 cm$^{-1}$ predicted) and the O−O stretching vibration by 23.5 cm$^{-1}$ (21 cm$^{-1}$ predicted). The DFT

**Table 10. Generation of Dioxasiliranes ($R^1R^2SiO_2$) or Silanone *O*-Oxides ($R^1R^2SiOO$)**

| year | $R^1$ | $R^2$ | evidence of formation | *T* (K) | method of generation[a] | ref | comments |
|---|---|---|---|---|---|---|---|
| 2000 | Me | Ph | IR spectroscopy | 30−40 | A | 51 | direct evidence for dioxasilirane obtained |
| 1996 | H | H | product analysis | | B | 74 | dioxasilirane proposed among other reactive intermediates |
| 1990 | F | F | IR spectroscopy | 10 | C | 52 | direct evidence for dioxasilirane obtained |
| 1990 | Cl | Cl | IR spectroscopy | 10 | C | 52 | direct evidence for dioxasilirane obtained |
| 1989 | Me | Me | IR spectroscopy | 35−42 | D | 53, 54 | direct evidence for dioxasilirane obtained |
| 1988 | Mes | Mes | IR spectroscopy | 16 | E | 82 | silanone *O*-oxide suggested as the intermediate rather than dioxasilirane |
| 1988−2004 | | | UV−vis and IR spectroscopy | 700 | F | 63−73 | conclusion for surface-bound silylene contradicts that of previous researchers |
| 1987 | Me | Ph | product analysis | 298 | G | 59 | tentative indirect evidence for the existence of dimesityldioxasilirane |

[a] A, matrix isolation from phenylsilyldiazomethane photooxidation; B, laser photolysis of a $SiH_4/O_2/CCl_4$ mixture; C, matrix isolation from $X_3SiSiX_3$ (X = F, Cl) pyrolysis and subsequent photooxidation; D, matrix isolation from diazidodimethylsilane photolysis and pyrolysis of 1,2-dimethoxytetramethyldisilane; E, matrix isolation from reaction of dimesitylsilylene with $O_2$; F, silica-gel reaction; G, solution-phase reaction of methylphenylsilylene with $O_2$.

**Table 11. IR Data for Matrix-Isolated Methylphenyldioxasilirane, $MePhSiO_2$**

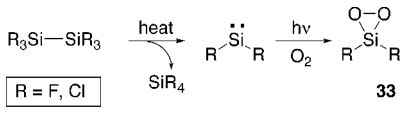
| argon, 10 K | | | B3LYP/6-311++G(d,p) | | | | |
|---|---|---|---|---|---|---|---|
| $\tilde{\nu}$, $cm^{-1}$ | $I^a$ | $\tilde{\nu}_i/\tilde{\nu}^b$ | $\tilde{\nu}$, $cm^{-1}$ | $I^a$ | $\tilde{\nu}_i/\tilde{\nu}^b$ | sym | assignment |
| 3086.3 | 2 | 1.000 | 3191 | 11 | 1.000 | A′ | C−H str |
| 3075.2 | 1 | | 3183 | 13 | 1.000 | A′ | C−H str |
| 3071.6 | 3 | 1.000 | 3175 | 5 | 1.000 | A′ | C−H str |
| 3058.7 | 2 | 1.000 | 3156 | 3 | 1.000 | A′ | C−H str |
| 3024.7 | 1 | | 3122 | 1 | 1.000 | A′ | $CH_3$ str |
| 3015.1 | 3 | 1.000 | 3099 | 2 | 1.000 | A″ | $CH_3$ str |
| 1596.8 | 17 | 1.000 | 1629 | 10 | 1.000 | A′ | ring str |
| 1435.0 | 30 | 1.000 | 1461 | 13 | 1.000 | A′ | skel ring, in pl C−H |
| 1432.5 | 2 | 1.000 | 1456 | 3 | 1.000 | A′ | HCH bend |
| 1429.5 | 7 | 1.000 | 1455 | 6 | 1.000 | A″ | HCH bend |
| 1336.9 | 3 | 1.000 | 1357 | 4 | 1.000 | A′ | skel ring, in pl C−H |
| 1307.5 | 5 | 1.000 | 1311 | 10 | 1.000 | A′ | HCH bend, ring str |
| 1260.3 | 10 | 0.998 | 1301 | 20 | 1.000 | A′ | HCH bend |
| 1218.0 | 4 | | 1211 | 2 | 1.000 | A′ | in pl C−H bend |
| 1135.6 | 92 | 0.999 | 1139 | 97 | 0.999 | A′ | skel ring, in pl C−H |
| 1033.7 | 4 | 0.999 | 1049 | 1 | 0.999 | A′ | skel ring, in pl C−H |
| 1013.1 | 1 | | 1013 | 3 | 1.000 | A′ | ring breathing |
| 1002.1 | 81 | 0.975 | 1005 | 100 | 0.972 | A′ | SiO str |
| 998.2 | 28 | | | | | | |
| 792.7 | 100 | 0.999 | 820 | 72 | 0.998 | A′ | $CH_3$ rock |
| 783.4 | 4 | 0.994 | 800 | 15 | 0.998 | A″ | $CH_3$ twist |
| 777.0 | 4 | | | | | | |
| 737.5 | 29 | 0.999 | 750 | 40 | 1.000 | A″ | C−H wag |
| 729.9 | 17 | 1.004 | 747 | 38 | 0.996 | A′ | SiC str, $CH_3$ def |
| 717.6 | 3 | 0.952 | 731 | 3 | 0.956 | A″ | SiC def, $CH_3$ def |
| 694.5 | 39 | 1.000 | 710 | 31 | 1.000 | A″ | C−H wag |
| 678.8 | 8 | 0.991 | 695 | 8 | 0.986 | A′ | |
| 576.7 | 28 | 0.959 | 608 | 25 | 0.965 | A′ | $O_2$ str, $CH_3$ def |
| 456.3 | 11 | 0.999 | 466 | 9 | 1.000 | A″ | C−H wag |

[a] Relative intensity based on the strongest peak. [b] Ratio of the frequencies of the $^{18}O$ versus $^{16}O$ isotopomers. [c] The assignment of experimental and calculated IR absorption is based on peak positions and peak intensities and is only tentative for the weak absorptions. Ref 51.

calculations reveal a barrier of about 1 kcal/mol for the cyclization of the silanone *O*-oxide **32** to dioxasilirane **31**. The silanone *O*-oxide **32** is not observed experimentally, probably because of a rapid interconversion to the dioxasilirane. Since silanone *O*-oxide **32** exists in a very shallow minimum and may not be chemically relevant, the generation of dioxasilirane **31** via MePhSi and $O_2$ is conceivable as a direct addition. Dioxasilirane **31** is photolabile and with 420-nm light interconverts to the silaester, MeSi(O)OPh via a [1,2]-phenyl migration or to PhSi(O)OMe via a [1,2]-methyl migration.

In 1990, the pyrolysis of hexafluorodisilane and hexachlorodisilane was reported (Scheme 17).[52,55,56] The loss of $SiF_4$

**Scheme 17. Pyrolysis of Hexahalodisilane**




(refs. 52, 55, 56)

and $SiCl_4$ takes place in an argon or argon−oxygen matrix, in which difluorosilylene and dichlorosilylene were subsequently trapped at 10 K. UV−visible photolysis of matrix-isolated difluorosilylene and dichlorosilylene in an $O_2$-containing matrix at 45 K yielded difluorodioxasilirane (**33**, R = F) and dichlorodioxasilirane (**33**, R = Cl). Isotopic labeling with $^{16}O_2/^{16}O^{18}O/^{18}O_2$ mixtures and HF/6-31G(d) calculations aided in the analysis of the IR spectra and in assigning the dioxasilirane structures (Table 12). $^{18}O$-isotopic

**Table 12. IR Spectroscopic Data of $F_2SiO_2$ and $Cl_2SiO_2$ Dioxiranes, Matrix-Isolated in $O_2$ at 10 K and ab initio Data of $F_2SiO_2$ Dioxirane Calculated at the HF/6-31G(d) Level[a]**

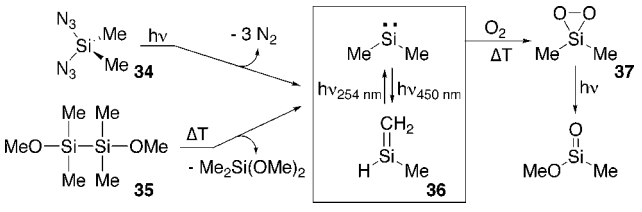
| matrix | | | | 6-31G(d) | | | | |
|---|---|---|---|---|---|---|---|---|
| $\tilde{\nu}^b$ | $I^c$ | $\Delta\tilde{\nu}_1{}^d$ | $\Delta\tilde{\nu}_2{}^e$ | $\tilde{\nu}^b$ | $I^c$ | $\Delta\tilde{\nu}_1{}^d$ | $\Delta\tilde{\nu}_2{}^e$ | assignment[f] |
| 1155.2 | | | | | | | | |
| 1153.5 | 1.00 | −9.6 | −19.3 | 1120.0 | 1.00 | −12.7 | −25.9 | δ(Si−F) |
| 1152.0 | | | | | | | | |
| 1150.8 | | | | | | | | |
| 1013.7 | 0.86 | −0.5 | −3.7 | 967.0 | 0.87 | −0.1 | −0.1 | δ(Si−F) |
| 862.7 | 0.02 | *g* | −32.4 | 800.0 | 0.12 | −9.0 | −26.2 | δ(Si−O) |
| | | | | 615.0 | 0.08 | −13.7 | −28.1 | δ(O−O) |
| 1054.4 | 1.00 | −14.5 | −30.9 | | | | | δ(Si−O) |
| 649.9 | 0.71 | 0.0 | 0.0 | | | | | δ(Si−O) |
| 647 | 0.63 | 0.0 | 0.0 | | | | | δ(Si−Cl) |
| 576.1 | 0.30 | −11.1 | 21.1 | | | | | δ(O−O) |

[a] References 52, 55, and 56. [b] Wavelength in $cm^{-1}$. [c] Relative intensity. [d] Isotopic shift if one $^{16}O$ atom is replaced by $^{18}O$. [e] Isotopic shift if two $^{16}O$ atoms are replaced by $^{18}O$. [f] Approximate description on the basis of observed isotopic shifts and the calculated mode vectors. [g] This weak peak of the O−O isotopomer could not be observed.

labeling reveals the equivalence of the oxygen atoms in $C_{2v}$-symmetric dioxasilirane **33**. When one $^{16}O$ atom in **33** (R = F) is replaced with $^{18}O$, the strong band at 1153 $cm^{-1}$ (four peaks) shifts to a lower frequency (by 9.6 $cm^{-1}$). Replacement of both oxygens by $^{18}O$ results in a shift to lower frequency by 19.3 $cm^{-1}$. A photolysis reaction was required to generate the dioxasiliranes **33** (R = F, Cl). Thermal reactions (up to 45 K) between $O_2$ and difluorosilylene and dichlorosilylene did not yield the corresponding dioxasiliranes. The dioxasilirane stability depends on substituent effects. Dioxasiliranes **33** (R = F, Cl) are stable to UV irradiation, unlike methylphenyldioxasilirane **31** and dimethyldioxasilirane **37**. The stronger Si−F and Si−Cl versus Si−C bonds play a role so that the [1,2]-fluoro or -chloro (rearranged) products, namely fluorine fluorosilanoate [FSi(O)OF] and chlorine chlorosilanoate [ClSi(O)OCl], are not easily formed.

In 1989, a matrix isolation study[53,54] demonstrated that dimethyldioxasilirane **37** forms in the 254-nm photolysis of diazidodimethylsilane [$Me_2Si(N_3)_2$, **34**] in $O_2$-doped argon at 10 K or by pyrolysis (700 °C) of 1,2-dimethoxytetramethyldisilane (**35**), followed by $O_2$ trapping in an argon matrix (Scheme 18).[55,56] A photochemical equilibrium exists

**Scheme 18. Generation of Silylene and a Subsequent Reaction with $O_2$**




(refs. 53, 54)

between 2-silapropene (**36**) and dimethylsilylene ($Me_2Si$),[75−80] in which dimethylsilylene is subsequently trapped by $O_2$.[81] IR spectroscopy revealed the splitting of an 1021 $cm^{-1}$ absorption with $^{18}O$ labeling, which when coupled with the propensity of the intermediate to rearrange to methoxymethylsilanone [MeSi(O)OMe] led to the assignment of the intermediate as dimethyldioxasilirane **37**. The strong Si−O stretching mode at 1013 $cm^{-1}$ and the weak O−O stretching mode at 554 $cm^{-1}$ for dimethyldioxasilirane **37** are consistent

with similar assignments made for methylphenyldioxasilirane **31** of 1002 and 577 $cm^{-1}$.[51] Dioxasilirane **37** is photochemically unstable and with 436 nm light rearranges to the corresponding silaester. MP2/6-31G(d) and HF/6-31G(d) calculations aided in the interpretation of the experimental IR data (Table 13). There is no evidence for the dimethylsilanone *O*-oxide intermediate.

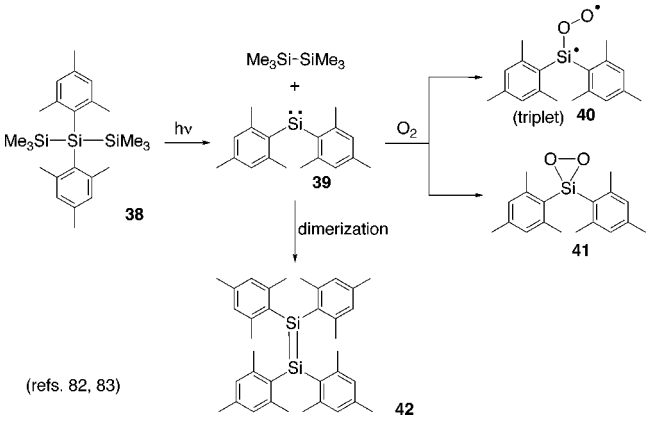
**Table 13. IR Spectroscopic Data of Dimethyldioxasilirane (37), Matrix-Isolated in Ar at 10 K ($\tilde{\nu}$ [$cm^{-1}$], $\Delta\tilde{\nu}$ Isotopic Shift)[a]**

| frequencies ($\tilde{\nu}$) | | | | | |
|---|---|---|---|---|---|
| [$^{16}O_2$]-**37** | [$^{16}O^{18}O$]-**37**[b] | $\Delta\tilde{\nu}$ | [$^{18}O_2$]-**37** | $\Delta\tilde{\nu}$ | assignment[c] |
| 1431.4 (w) | 1430.9 (w) | −0.5 | 1430.4 (w) | −1.0 | $\delta_{as}(CH_3)$ |
| 1260.3 (m) | 1260.0 (m) | 0.0 | 1258.8 (m) | −1.5 | $\delta_s(CH_3)$ |
| 1021.1 (s) | 1009.6 (s) | −11.5 | 997.0 (s) | −24.1 | $\tilde{\nu}_{as}$(Si−O) |
| 1012.9 (w) | 1005.2 (m) | −7.7 | 988.8 (w) | −24.1 | *d* |
| 1005.7 (w) | 993.2 (w) | −12.5 | 981.1 (w) | −24.6 | $\tilde{\nu}_{as}$(Si−O)[d] |
| 820.1 (m) | 814.8 (m) | −5.3 | 810.4 (m) | −9.7 | |
| 820.1 (m) | 814.8 (m) | −5.3 | 809.5 (m) | −10.6 | $\delta(CH_3)$[e] |
| 809.5 (m) | | | 800.8 (w) | −8.7 | $\delta(CH_3)$[e] |
| 554.4 (w) | | | 530.8 (w) | −23.6 | $\tilde{\nu}$(O−O) |

[a] References 53 and 54. [b] Due to the presence of three isotopomers in the spectra, not all bands could be assigned. [c] Approximate description on the basis of observed isotopic shifts and by comparison with ab initio calculations. [d] The assignment of the weak bands at 1012.9 and 1005.7 is not definite. [e] Rocking mode.

In one study, the formation of a silanone *O*-oxide was suggested instead of dioxasilirane. In 1988, the reaction of di-2,4,6-trimethylphenylsilylene (dimesitylsilylene, **39**) was conducted in a cryogenic solid-oxygen matrix at 16 K (Scheme 19).[82] An analysis of the products by IR spectros-

**Scheme 19. Irradiation of 2,2-Bis(2,4,6-trimethylphenyl)hexamethyltrisilane**

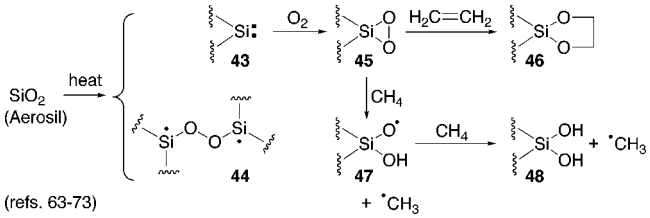



copy concluded that a triplet state silanone *O*-oxide **40** was present and not the dioxasilirane **41** based on data from isotopic mixtures of oxygen gas ($^{18}O_2$ and $^{16}O_2$) and HF/6-31G(d) computations. Dimerization of dimesitylsilylene **39** to form stable tetramesityldisilene **42** can take place in the absence of $O_2$.[83] This example for the intermediacy of silanone *O*-oxide stands in contrast to other reports of $O_2$ with silylenes (MePhSi, $F_2Si$, $Cl_2Si$, and $Me_2Si$), which point to a facile interconversion to the dioxasilirane.[51−54,61,62]

**4.1.2.3. Room Temperature.** *Silylene−$O_2$ Reaction.* While some work has been performed on the silylene−$O_2$ reaction in low-temperature argon matrices, little is known about the involvement of dioxasilirane in solution or at room temperature.[59−62] In 1987, laser photolysis ($\lambda$ = 266 nm) of $(Me_3Si)_2SiMePh$ was conducted in air-saturated cyclohexane solutions at 298 K. This reaction yielded methylphenylsilylene, which subsequently reacted with $O_2$.[59,61,62] Only a tentative suggestion was made for formation of the silanone *O*-oxide **32** or dioxasilirane **31** intermediates;[3,61,62,84] thus, there is some uncertainty as to whether the dioxasilirane had been generated in cyclohexane solution.

**4.1.2.4. Miscellaneous.** In work that has spanned the period from 1988 to 2004,[63−73] a surface-bound dioxasilirane [$(Si-O)_2SiO_2$, **45**] was suggested in the reaction of $O_2$ with silylene **43**, generated by vacuum pyrolysis of methoxylated silica (Scheme 20). Experiments were conducted on hetero-

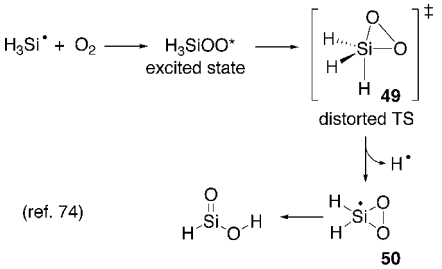
**Scheme 20. A Possible Surface-Bound Dioxasilirane**




geneous samples (aerosil $SiO_2$), in which defects in the aerosil were thought to give rise to silylene **43** in $SiO_2$. Previous EPR work came to a different conclusion about the identity of the silicon intermediate in $SiO_2$ pyrolysis reactions and suggested formation of diradical **44** rather than silylene **43**.[85−88] UV−visible and IR spectroscopy cannot easily identify reactive species (e.g., silylene **43**, $R_2Si^{\bullet}OOSi^{\bullet}R_2$ diradical **44**, and dioxasilirane **45**) on silicon surfaces, and there are difficulties in establishing the structure of intermediate(s) formed in the reaction. The surface-bound dioxasilirane **45** was suggested to react with ethylene to give **46** and not oxirane. A series of radical reactions were also proposed, such as the formation of **47** and **48**, in addition to reactions of dioxasilirane **45** with $H_2$, $D_2$, carbon monoxide, and ethane. In 2006, evidence suggested that dehydroxylation of either silica or hydroxylated silicon forms defects that lead to silylene and dioxasilirane at temperatures ranging from 100 to 400 °C.[58]

In 1996, a laser photolysis of silane ($SiH_4$)−oxygen ($O_2$) mixtures was reported.[74] The combustion reaction conditions generated silyl radical $H_3Si^{\bullet}$, which reacted with $O_2$ to give an excited acyclic $H_3SiOO$ species. It was proposed that acyclic $H_3SiOO$ cyclized to the unsubstituted dioxasilirane $H_2SiO_2$ radical (**50**), which then rearranged to silaformic acid [$H_2Si(=O)OH$] (Scheme 21). MP2(full)/6-31G(d)

**Scheme 21. Possible Reaction of the $SiH_3$ Radical with $O_2$**




and G2(MP2) calculations predicted dioxasilirane **50** to be a minimum on the potential energy surface, in which TS structure **49** involved the loss of a hydrogen atom. Silanoic acid is not the only product in the reaction, since silicon oxide (SiO) is also a final product that arises by high computed barriers (e.g., 67.6 kcal/mol), made possible by the combustion conditions.

**Table 14. Calculated Geometries of Dioxasiliranes**

| Year | Structure | State | Method and Basis Set | O-O[a] | Si-O[a] | Si-O-O[b] | O-Si-O[b] | Ref. | Comments |
|---|---|---|---|---|---|---|---|---|---|
| 2006 | $((HO)_3CO)_2Si$ | $S_o$ | B3LYP/6-31G(d) | 1.614 | 1.650, 1.666 | _ | _ | 58 | |
| 2005 | $H_2Si$ | $S_o$ | MP2(Full)/6-31G(d) | 1.628 | 1.672 | _ | 58.3 | 58 | Computed data also reported at the MCSCF (FORS) level with the 6-31G(d) basis set |
| 2000 | PhMeSi | $S_o$ | B3LYP/6-311++G(d,p) | 1.584 | 1.672 | 61.7 | 56.5 | 51 | Both Si-O bond distances are equal in length |
| 1999 | $H_2Si$ | $S_o$ | B3LYP/TZ2P | 1.571 | 1.678 | _ | _ | 90 | Computed data also reported at the B3LYP level with DZP and DZP-ECP basis sets |
| 1996 | $H_2Si$ | $S_o$ | SCF/6-31G(d,p) | _ | 1.632 | _ | 55.6 | 91 | |
| 1993 | $H_2Si$ | $S_o$ | MP2/6-31G(d) | 1.628 | 1.672 | _ | _ | 93 | |
| 1989 | $H_2Si$ | $S_o$ | MP2/6-31G(d) | 1.628 | 1.672 | 60.9 | _ | 92 | |
| 1989 | $H_2Si$ | $S_o$ | GVB/6-31G(d) | 1.81 | 1.66 | 57.0 | _ | 92 | CASSCF calculation also carried out with 6 electrons distributed in 6 active orbitals |

[a] Bond distances in angstroms. [b] Bond angles in degrees.

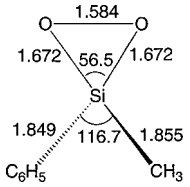



**Figure 2.** B3LYP/6-311++G(d,p) computed structure of the methylphenyldioxasilirane from ref 51. Bond lengths in angstroms; bond angles in degrees.

There is one recent report in the literature which suggests the formation of unsubstituted dioxasilirane $H_2SiO_2$ in a dihydrogensilylene−$O_2$ reaction. In 2006, the gas-phase reaction of silylene, $SiH_2$ (generated from the photolysis of phenylsilane), and $O_2$ was carried out at 297−600 K.[57] G3 calculations pointed to the formation of $H_2SiOO$ followed by cyclization to the dioxasilirane $H_2SiO_2$.

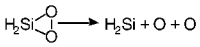
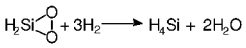
**4.1.2.5. Calculations.** *Structure.* Dioxasilirane structures optimize to minima at various levels of theory.[51,57,89−92] Calculated bond distances and bond angles are shown in Table 14. Dioxasilirane $((HO)_3CO)_2SiO_2$, $MePhSiO_2$, and $H_2SiO_2$ bear a resemblance to each other regardless of the computational method used. Dioxasilirane bond distances for O−O range from a high of 1.81 Å to a low of 1.571 Å. Bond distances for Si−O range from a high of 1.678 Å to a low of 1.632 Å. A sample computed structure for methylphenyldioxasilirane is given in Figure 2. Computed data for the Si−O−O and O−Si−O bond angles are also given in Table 14. The strain energy has been calculated for dioxasilirane $H_2SiO_2$ (Table 15). Bach estimated strain energies by using the CBS-Q method, along with cyclopropane and a six-membered ring Si-, O-, and C-containing heterocycle reference compound.[89] Calculated atomic charges are in Table 16, and the vibrational frequencies and infrared intensities are in Table 17. Dioxasilirane $H_2SiO_2$ possesses negative charge density on the oxygen atoms.

*Energetics.* Saddle points which connect silanone *O*-oxide and dioxasilirane have been located in four studies in the gas phase (Table 18).[51,57,90−92] The cyclization barrier for silanone *O*-oxide MePhSiOO to dioxasilirane $MePhSiO_2$ is 0.8 kcal/mol at the B3LYP/6-311++G(d,p) level.[51] The barrier for converting acyclic $Me_2SiOO$ to dioxasilirane $Me_2SiO_2$ is 6.5 kcal/mol at the HF/6-31G(d) level[53,54] and that for acyclic $H_2SiOO$ to dioxasilirane $H_2SiO_2$ is 6.5 and 2.2 kcal/mol at the HF/6-31G(d) and GVB/6-31G(d) levels.[92] Silanone *O*-oxide is predicted to be higher in energy than dioxasilirane. The conversion of singlet acyclic MePhSiOO to dioxasilirane $MePhSiO_2$ is calculated to be exothermic by −49.6 kcal/mol at the B3LYP/6-311++G(d,p) level.[51] Subsequent conversion of dioxasilirane $MePhSiO_2$ to silaester [PhSi(O)OMe] is calculated to be exothermic by −59.3 kcal/mol. The conversion of singlet acyclic $Me_2SiOO$ to dioxasilirane $Me_2SiO_2$ is calculated to be exothermic by −63.8 kcal/mol at the HF/6-31G(d) level, and the subsequent conversion from dioxasilirane $Me_2SiO_2$ to MeSi(O)OMe is exothermic by −63.8 kcal/mol.[53,54]

The computational work predicts a facile conversion of singlet silanone *O*-oxide to dioaxsilirane in an exothermic low-barrier process. In all cases, the dioxasilirane is calculated to be more stable than silanone *O*-oxide. A suggestion has also been made that this highly exothermic isomerization process could lead to vibrationally "hot" dioxasiliranes with excess energy.[92] The silanone *O*-oxide to dioxasilirane barrier height is much lower compared to that of the carbon analogue $H_2C^+OO^-$ to dioxirane $H_2CO_2$ (23 kcal/mol barrier at various levels of theory).[3,53−58] The relative energies for other bimolecular and isomerization reactions are listed in Table 18.[51,53,54,57,74,82,89,90,92−95]

In conclusion, section 4.1.2 provides evidence that is compelling for the direct detection of dioxasiliranes from matrix isolation experiments of the reaction of silylene with $O_2$. The generation of dioxasilirane has been achieved in the

**Table 15. Calculated Properties of the Dioxasilirane Ring[a]**

| Year | Structure | Estimated Strain Energy | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|
| 2006 |  | 36.0 | CBS-Q | 89 | Calculated from a 6-membered ring reference compound and a combination reaction of cyclopropane and dioxasilirane. In the same study, the strain energy for $H_2CO_2$ dioxarane was calculated to be 16-17 kcal/mol. |
| 1996 |  | 34.1 | MP2/6-31G(d,p) | 91 | Calculated from  |
| | | 44.9 | SCF/6-31G(d,p) | | |
| | | 27.7 | MP2/6-31G(d,p) | | Calculated from  |
| | | 26.6 | SCF/6-31G(d,p) | | |

[a] Energies in kilocalories per mole.

**Table 16. Calculated Properties of the Dioxasilirane Ring[a]**

| Year | Structure | Natural Atomic Charge | | | Natural Bond Order | | | Method | Comments |
|---|---|---|---|---|---|---|---|---|---|
| | | Si | O | H | Si-O | O-O | Si-H | | |
| 1999 |  | 1.82 | -0.56 | -0.34 | 0.42 | 1.00 | 0.66 | B3LYP/DZP | |
| | | 1.60 | -0.57 | -0.23 | 0.41 | 1.00 | 0.76 | B3LYP/DZP-ECP | ECP = effective core potential |

[a] Reference 90.

**Table 17. Harmonic Vibrational Frequencies ($\tilde{\nu}$) and Infrared Intensities of the Dioxasilirane $H_2SiO_2$[a]**

| MP2/6-31G(d) | | GVB/6-31G(d) | | | |
|---|---|---|---|---|---|
| $\tilde{\nu}$, cm$^{-1}$ | $I^b$ | $\tilde{\nu}$, cm$^{-1}$ | $I^b$ | | assignment |
| 490 | 0 | 526 | 0 | $a_2$ | $SiH_2$ twist |
| 613 | 21 | 284 | 10 | $a_1$ | OSiO bend |
| 734 | 97 | 755 | 126 | $b_1$ | $SiH_2$ rock |
| 792 | 11 | 822 | 1 | $b_2$ | OSiO a-str[c] |
| 871 | 141 | 923 | 192 | $b_2$ | $SiH_2$ bend |
| 976 | 2 | 956 | 40 | $a_1$ | OSiO a-str[c] |
| 1083 | 174 | 1123 | 206 | $a_1$ | $SiH_2$ bend |
| 2377 | 79 | 2464 | 106 | $a_1$ | $SiH_2$ a-str |
| 2393 | 168 | 2464 | 228 | $b_1$ | $SiH_2$ a-str |

[a] Reference 92. [b] Infrared intensities. [c] Strongly coupled with the bending of $SiH_2$.

absence of other reactive species such as silylenes and silanone *O*-oxides; however, formation of a stable isolable dioxasilirane has not yet been achieved.

### 4.1.3. Dioxagermirane, Dioxastannirane, and Dioxastilbirane

A photooxidation reaction of germanium has been conducted with deposited germanium chalcogenides with sulfur, selenium, and tellurium onto thin films, but peroxides were not suggested as intermediates.[96] Spectroscopic detection has been achieved for the heavy carbenes,[97−101] germylenes, and stannylenes (e.g., $H_2Ge$, $Me_2Ge$, and $Me_2Sn$), but there are no experimental reports of the corresponding dioxiranes. Dioxagermirane (**51**), dioxastannirane (**52**), and dioxastilbirane (**53**) have been examined with computational methods but have not been investigated experimentally (Scheme 22).[90,102]

**Structure.** In 1999, a computational study examined $H_2GeO_2$ (**51**), $H_2SnO_2$ (**52**), and $H_2SbO_2$ (**53**) at the B3LYP and CCSD(T) levels with various basis sets and an effective core potential (ECP) treatment.[90,102] These heteroatom-substituted dioxiranes optimize to minima on the potential energy surface (PES). Calculated bond distances are shown in Table 19. The B3LYP/TZ2P-ECP computed dioxirane structures show decreasing O−O bond distances in the order Ge > Sn > Pb with bond lengths of 1.566 Å ($H_2GeO_2$), 1.561 Å ($H_2SnO_2$), and 1.555 Å ($H_2PbO_2$). The O−O bond distances show a similar trend at the B3LYP/DZP-ECP level. The O−O bond distance decreases by increments of 0.005 and 0.006 Å in the series of $H_2GeO_2$, $H_2SnO_2$, and $H_2SbO_2$ dioxiranes. Other bond distances include Ge−O (1.778 Å), Sn−O (1.931 Å), and Pb−O (1.992 Å) at the B3LYP/TZ2P-ECP level. The natural atomic charges indicate a negative density at the oxygen and hydrogen atoms and a positive charge density on Ge, Sn, and Pb (Table 20). Natural bond order data are also presented in Table 20.

**Energetics.** Calculated energetics are provided in Table 21, in which data compare the higher homologue dioxiranes (cyclic $H_2YO_2$) with dihydroxycarbenes (HOYOH) and formic acid congeners [HY(=O)OH] (Y = Ge, Sn, and Pb). According to B3LYP/TZ2P-ECP calculations, the conversion of $H_2GeO_2$ dioxirane to HGe(=O)OH is exothermic by −76.9 kcal/mol. Similar exothermicities are calculated for

**Table 18. Calculated Relative Energies for Intramolecular and Intermolecular Reactions of Dioxasilirane[a]**

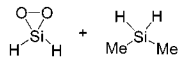
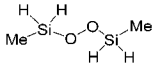
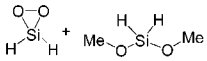
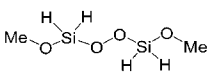
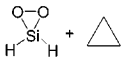
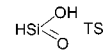
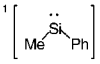
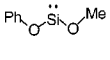
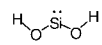
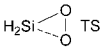
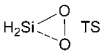
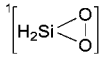
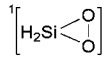
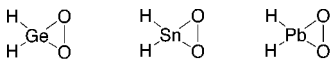
| Year | A | B | $\Delta E_{A \rightarrow B}$ | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|---|
| 2006 |  |  | -35.5 | CBS-Q | 89 | These represent homodesmotic reactions |
| |  |  | -36.0 | | | |
| |  |  | -31.2 | | | |
| 2005 | $H_2SiOO$ |  | -64.5 | G3 | 57 | |
| | $H_2SiOO$ |  | 4.5[b] | G3 | | |
| | | (ring closure) | | | | |
| |  |  | 14.4[b] | MRMP2/6-31G(d) | | Computed values vary widely depending on the theoretical method. Values also reported at the MCSCF level. Use of the Cc-pVTZ basis set also reported |
| | | (ring opening) | | | | |
| |  |  | 8.8 | MRMP2/6-31G(d) | | |
| |  |  | 1.4[b] | MRMP2/6-31G(d) | | |
| | | (H-rearrange) | | | | |
| |  |  | -85.9 | MRMP2/6-31G(d) | | |
| 2000 |  |  | 0.8[b] | B3LYP/6-311++G(d,p) | 51 | |
| | | (ring closure) | | | | |
| |  |  | -49.6 | B3LYP/6-311++G(d,p) | | |
| |  |  | -57.8 | B3LYP/6-311++G(d,p) | | |
| |  + $^3O_2$ |  | -77.4 | B3LYP/6-311++G(d,p) | | |
| |  |  | -61.7 | B3LYP/6-311++G(d,p) | | |
| |  |  | -59.3 | B3LYP/6-311++G(d,p) | | |
| |  |  | -49.1 | B3LYP/6-311++G(d,p) | | |
| 1999 |  |  | -81.1 | B3LYP/DZP | 90 | Calculations also performed at other levels of theory levels such as B3LYP/DZP-ECP, BLYP/ DZP, B3LYP/TZ2P, B3LYP/TZ2P-ECP, BLYP/DZ2P, BLYP/ TZ2P-ECP CCSD/TZ2P//BLYP/TZ2P, BLYP/DZ2P, BLYP/ TZ2P-ECP CCSD/TZ2P//BLYP/TZ2P, CCSD/TZ2P-ECP//BLYP/TZ2P-ECP, CCSD(T)/TZ2P-ECP//BLYP/TZ2P-ECP |

**Table 18 (Continued)**

| Year | A | B | $\Delta E_{A \rightarrow B}$ | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|---|
| |  |  | -80.1 | CCSD(T)/TZ2P-ECP//BLYP/TZ2P-ECP | | |
| |  |  | -88.6 | B3LYP/DZP | | |
| |  |  | -88.0 | CCSD(T)/TZ2P-ECP//BLYP/TZ2P-ECP | | |
| |  |  | 20.9 | B3LYP/DZP | | |
| |  |  | 24.6 | CCSD(T)/TZ2P-ECP//BLYP/TZ2P-ECP | | |
| 1996 |  |  TS (rearrangement) | 6.4[b] | CASSCF(6/6)/6-31G(d) | 74 | 6 electrons in 6 orbitals |
| |  |  | -8.3 | CASSCF(6/6)/6-31G(d) | | Predictions of the $SiH_3 + O_2$ reaction to give $SiH_3OO$ and then cyclization to $H_2SiO_2$ atom |
| | — |  | -28.1 | G2 | 93, 94 | Calculated heat of formation at 298 K |
| 1989 |  |  TS (ring closure) | 6.5[b] | HF/6-31G(d) | 53, 54 | |
| |  |  | -63.8 | HF/6-31G(d) | | |
| 1989 | $H_2SiOO$ |  TS (ring closure) | 6.5[b] | MP2/6-31G(d) | 92 | Single point values also calculated at various levels: MP3, MP4, CI with the 6-31G(2d,p) basis set |
| | $H_2SiOO$ |  TS (ring closure) | 2.2[b] | GVB/6-31G(d) | | Single point energies also calculated with GVB/6-31G(2d,p) and CASSCF/6-31G(d) |
| | $H_2SiOO$ |  | -63.8 | MP2/6-31G(d) | | |
| | $H_2SiOO$ |  | -62.1 | GVB/6-31G(d) | | |
| 1988 |  |  | -61.5 | MP4SDTQ/6-31G(d)//HF/6-31G(d) | 82 | |
| | $^1H_2Si + {}^3O_2$ |  | -84.2 | MP4SDTQ/6-31G(d)//HF/6-31G(d) | | |

[a] Energies in kilocalories per mole. [b] Transition state energies.

**Scheme 22. Dioxagermirane, Dioxastannirane, and Dioxastilbirane**



(ref. 90)

**51** **52** **53**

dioxastannirane (−70.6 kcal/mol) and dioxastilbirane (−71.8 kcal/mol) in their conversion to the corresponding formic acid congeners. $H_2YO_2$ dioxiranes vary in their Y−O bond strengths, namely 77.4 kcal/mol for Y = Ge, 63.6 kcal/mol for Y = Sn, and 34.0 kcal/mol for Y = Pb). The heteroatom-substituted dioxiranes are less stable for the heavier members of group 14. For example, the $H_2PbO_2$ dioxirane is 149.4 kcal/mol less stable than the corresponding dihydroxy species (plumbous hydroxide) according to B3LYP/TZ2P-ECP calculations. This instability correlates with a decrease in Y−O bond dissociation energies.

### 4.1.4. Cyclic Sulfur Dioxide, $SO_2$

The literature of the sulfur dioxide structure is enormous. Studies that have considered $SO_2$ structural isomers span a period of 50 years.[103−110] A variety of experimental methods have been used, but none have provided evidence for cyclic $SO_2$. Experimental methods have included, for example, flash photolysis of $SO_2$, gaseous $CS_2$−oxygen mixtures in explosions, and flash-initiated explosions of $H_2S$, $CS_2$, and COS. In 1996, an infrared absorption study of $SO_2$ in an argon

**Table 19. Calculated Geometries of Dioxagermirane, Dioxastannirane, and Dioxastilbirane[a]**

| Year | Structure | State | Method of Basis Set | O-O[b] | Y-O[b] |
|---|---|---|---|---|---|
| 1999 |  | $S_o$ | B3LYP/TZ2P-ECP | 1.566 | 1.778 (Y=Ge) |
| |  | $S_o$ | | 1.561 | 1.931 (Y=Sn) |
| |  | $S_o$ | | 1.555 | 1.992 (Y=Pb) |
| |  | $S_o$ | B3LYP/DZP-ECP | 1.555 | 1.785 (Y=Ge) |
| |  | $S_o$ | | 1.550 | 1.936 (Y=Sn) |
| |  | $S_o$ | | 1.544 | 2.001 (Y=Pb) |

[a] Reference 90. [b] Bond distances in angstroms.

**Table 20. Calculated Structural Properties of Dioxagermirane, Dioxastannirane, and Dioxastilbirane[a]**

| Year | Structure | Natural Atomic Charge | | | Natural Bond Order | | | Method and Basis Set |
|---|---|---|---|---|---|---|---|---|
| | | Y | O | H | Y-O | O-O | Y-H | |
| 1999 |  (Y=Ge) | 1.42 | -0.5 | -0.16 | 0.45 | 1.00 | 0.82 | B3LYP/DZP |
| | | 1.57 | -0.6 | -0.22 | 0.42 | 1.00 | 0.77 | B3LYP/DZP-ECP |
| |  (Y=Sn) | 1.88 | -0.6 | -0.32 | 0.37 | 1.00 | 0.67 | B3LYP/DZP-ECP |
| |  (Y=Sn) | 1.54 | -0.6 | -0.21 | 0.42 | 1.00 | 0.76 | B3LYP/DZP-ECP |

[a] Reference 90.

matrix was conducted using 193-nm light from an ArF eximer laser.[111] From $^{18}$O-labeling experiments, along with the analysis of IR intensities and B3LYP/cc-pVTZ calculations, it was concluded that the acyclic SOO was present, but not cyclic $SO_2$.[111] In 2006, cyclic $SO_2$ was suggested to form in a two-photon irradiation (248 nm) of acyclic $SO_2$ in a MTHF or ethanol matrix at 11 K, based on the temperature-dependent shift of the $SO_2$ $\lambda_{max}$.[112] There is uncertainty in the spectral assignment of the cyclic $SO_2$ structure due to the strong absorption of acyclic $SO_2$.

**Structure.** Given the absence of experimental data on cyclic $SO_2$, computational approaches have been used. Cyclic $SO_2$ optimizes to a minimum at many levels of theory, such as B3LYP/cc-pVTZ, BP86/cc-pVTZ, CCSD(T)/TZ2P(f), SCF/DZP, MRCI/cc-pVTZ, and GVB.[111,113−118] Calculated bond distances and a bond angle are shown in Table 22. The $O_1-O_2$ bond distances range from a high of 1.504 Å to a low of 1.479 Å,[111,113,114] the S−O bond distances range from 1.705 to 1.686 Å, and the O−S−O bond angle ranges from 52.7° to 51.9°. Calculated vibrational frequencies, IR intensities, and excitation energies for cyclic $SO_2$ are shown in Table 23.

**Energetics.** According to gas-phase CCSD(T)/TZ2P(f), B3LYP/cc-pVTZ, and BP86/cc-pVTZ calculations, cyclic $SO_2$ is 1−18 kcal/mol more stable than acyclic SOO. Cyclic $SO_2$ is highly unstable; the exothermicity on the ring opening to acyclic OSO is about 99−111 kcal/mol according to the above computed methods (Table 24).[111,114] The barrier to breaking the O−O bond of cyclic $SO_2$ is predicted to be 15.6 kcal/mol, based on MCSCF calculations.[117] The computed energetics and barrier for conversion of $SO_2$ to the six-membered ring diperoxide have not been determined, although DFT studies have focused on other combinations of dimers, trimers, and oligomers of sulfur oxides.[119−121] A series of calculations have been performed on the ground state PES of $SO_2$.[122−129] The activation energies for SOO or cyclic $SO_2$ to release an O-atom intermolecularly have not been computed to date. Additional work in this area is needed, such as the success found in the computed and still theoretical complexes $[S_3W(NO)_3]^{3+}$, $[O_3M(NO)_3]^{3+}$ (M = Cr, Mo, W, Fe, Ru, Os), and $[S_3W(NO)_2(CO)]^{2+}$ containing cyclic $O_3$ and $S_3$.[123,130]

**Table 21. Calculated Energies for Rearrangements of Dioxagerminane, Dioxastannirane, and Dioxastilbirane[a]**

| Year | A | B | $\Delta E_{A\rightarrow B}$ | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|---|
| 1999 |  |  | -72.3 | B3LYP/DZP-ECP | 90 | Calculations also performed at different levels of theory including single point calculations at the CCSD(T)/TZP-ECP level |
| | | | -76.9 | B3LYP/TZ2P-ECP | | |
| |  |  | -106.9 | B3LYP/DZP-ECP | | |
| | | | -109.7 | B3LYP/TZ2P-ECP | | |
| |  |  | -67.2 | B3LYP/DZP-ECP | | |
| | | | -70.6 | B3LYP/TZ2P-ECP | | |
| |  |  | -122.2 | B3LYP/DZP-ECP | | |
| | | | -125.9 | B3LYP/TZ2P-ECP | | |
| |  |  | -68.0 | B3LYP/DZP-ECP | | |
| | | | -71.8 | B3LYP/TZ2P-ECP | | |
| |  |  | -144.8 | B3LYP/DZP-ECP | | |
| | | | -149.4 | B3LYP/TZ2P-ECP | | |

[a] Energies in kilocalories per mole.

**Table 22. Calculated Geometries of Cyclic $SO_2$**

| Year | Structure | State | Method and Basis Set | O-O[a] | S-O[a] | O-S-O[b] | Ref. |
|---|---|---|---|---|---|---|---|
| 1997 |  | $S_0$ | CCSD(T)/TZ2P(*f*) | 1.500 | 1.690 | 52.7 | 113, 114 |
| 1996 |  | $S_0$ | B3LYP/cc-pVTZ | 1.479 | 1.686 | 51.9 | 111 |
| | | $S_0$ | BP86/cc-pVTZ | 1.504 | 1.705 | 51.9 | 111 |

[a] Bond distances in angstroms. [b] Bond angles in degrees.

**Table 23. Calculated Values of Cyclic $SO_2$**

(a) Vibrational Frequencies and IR Intensities

| year | $\tilde{\nu}_1$ ($A_1$)[a] | $\tilde{\nu}_2$ ($A_1$)[a] | $\tilde{\nu}_3$ ($B_2$)[a] | method and basis set | ref |
|---|---|---|---|---|---|
| 1996 | 1009 (13.3)[b] | 682 (3.9)[b] | 739 (9.8)[b] | B3LYP/cc-pVTZ | 111 |
| | 970 (11.0)[b] | 662 (4.0)[b] | 721 (8.8)[b] | BP86/cc-pVTZ | |

(b) Excitation Energies

| | state | energy (eV) MRCI | oscillator strength | energy (eV) MRCI + Q | ref |
|---|---|---|---|---|---|
| 2005[c] | $1^1A_1$ | 4.511 | | 4.465 | 118 |
| | $1^3A_2$ | 6.081 | 0 | 5.985 | |
| | $1^1A_2$ | 6.752 | 0 | 6.660 | |
| | $1^3B_1$ | 7.715 | 0 | 7.647 | |
| | $1^1B_1$ | 8.078 | 0.00124 | 8.033 | |
| | $2^3B_1$ | 8.887 | 0 | 8.738 | |
| | $2^3A_2$ | 9.170 | 0 | 8.85 | |
| | $1^3B_2$ | 9.930 | 0 | 9.824 | |

[a] Symmetries of vibrational modes are listed in parentheses. [b] IR intensities are listed in parentheses. [c] Cyclic $SO_2$ was computed for $C_{2v}$ symmetry.

**Table 24. Calculated Energies for the Rearrangements of Acyclic and Cyclic $SO_2$[a]**

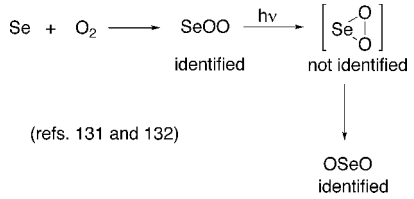
| Year | A | B | $\Delta E_{A \rightarrow B}$ | Method and Basis Set | Ref. |
|---|---|---|---|---|---|
| 1996 | OSO |  | 99.8 | B3LYP/ cc-pVTZ | 111 |
| | OSO |  | 98.2 | BP86/ cc-pVTZ | |
| | OSO | SOO | 107.3 | B3LYP/ cc-pVTZ | |
| | OSO | SOO | 99.7 | BP86/ cc-pVTZ | |
| 1995 | OSO |  | 104.3 | CCSD(T)/ TZ2P(*f*) | 114 |
| | OSO | SOO | 110.8 | CCSD(T)/ TZ2P(*f*) | |

[a] Energies in kilocalories per mole.

### 4.1.5. Cyclic Selenium Dioxide, $SeO_2$

A number of studies have been carried out on selenium oxide [$SeO_x$ ($x$ = 1, 2, 3)], but no experimental evidence exists for the cyclic $SeO_2$ intermediate. However, in 1996, a study of the reaction of selenium and $O_2$ provided evidence for various acyclic $Se_xO_y$ molecules, such as SeO, OSeO, SeOO, SeOOO, and OSeOO.[131,132] Complex infrared absorptions in solid argon identified the selenium oxide species. The observed frequencies were corroborated with B3LYP/LANL1DZ calculations, from which frequency, intensity, and isotopic-shift data for the absorptions of $Se_xO_2$ molecules were obtained. It was proposed that the formation of OSeO in the reactions of Se with $O_2$ and photolysis of SeOO may go through a cyclic intermediate (cyclic $SeO_2$) (Scheme 23). The open isomer OSeO product is considerably lower in energy than the acyclic SeOO or cyclic $SeO_2$ intermediates.

**Scheme 23. Reaction of Selenium with $O_2$**



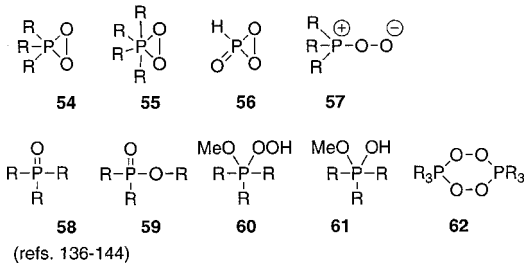

## 4.2. Trigonal Bipyramidal Dioxiranes

Trigonal bipyramidal (TBP) $XO_2$ dioxiranes are hypervalent peroxides of the form $R_3PO_2$, $R_2SO_2$, $R_2SeO_2$, and $R_2TeO_2$. Peroxide structures bearing two or more oxygen bonds to hypervalent phosphorus, sulfur, selenium, or tellurium centers are uncommon, although molecules such as phosphine and phosphite ozonides $R_3PO_3$ are known.[133−135] Spectroscopic evidence exists for the $R_3PO_2$ dioxirane, but not for $R_2SO_2$, $R_2SeO_2$, and $R_2TeO_2$. Computational studies have focused on the $R_3PO_2$ and $R_2SO_2$ dioxiranes, but not on $R_2SeO_2$ and $R_2TeO_2$.

### 4.2.1. Dioxaphosphirane, $R_3PO_2$

**4.2.1.1. Background Information.** A phosphoranide ion,[136] a sterically hindered aryl phosphine,[137] a 1,1′-binaphthyl phosphine,[138] and a $PH_3$−ozone complex[139] served as precursors to dioxaphosphiranes (**54**−**56**), for which direct spectroscopic evidence was obtained (Chart 1 and Table 25).

**Chart 1. Phosphorus- and Oxygen-Containing Compounds**

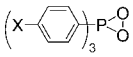
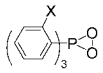
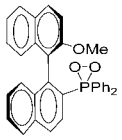
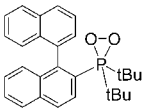
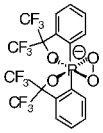



Dioxaphosphirane **55** is a hexacoordinated species. A number of other studies have provided indirect experimental evidence for the formation of dioxaphosphiranes. Various oxidants have been used in the generation of dioxaphosphiranes, such as, $^1O_2$, $^3O_2$, $O_3$, and hydrogen peroxide.[136−144] A previous review has summarized recent work on phosphine−$^1O_2$ reactions.[4] Early work on phosphine autoxidation reactions dates from 1962 to 1984,[145−147] although dioxaphosphiranes were not proposed as intermediates.

There is yet no evidence for the formation of peroxyphosphine oxide **57**, although it was proposed in a ring-closure phosphoranide−$O_2$ reaction.[136] Dioxaphosphirane **54** readily reacts with the substrate ($PR_3$) to form two equivalents of phosphine oxide **58**, but **54** also rearranges to the phosphonate **59** or is converted to hydroperoxyphosphine **60** and hydroxyphosphorane **61** in methanol. There is no experimental evidence that dioxaphosphirane dimerizes to a six-membered-ring diperoxide tetradiphosphinane (**62**).

**4.2.1.2. Low Temperature.** *NMR Spectroscopy.* In 2003, the synthesis of tris(*o*-methoxyphenyl)dioxaphosphirane was reported in $CH_2Cl_2$ and $CH_2Cl_2$/toluene solutions at 193 K and was followed by $^{31}P$ and $^{17}O$ NMR spectroscopy (Scheme 24 and Table 26).[137a] The reaction of singlet oxygen from irradiated air-saturated solutions containing tetraphenylporphyrin sensitizer in the presence of tris(*o*-methoxyphen-

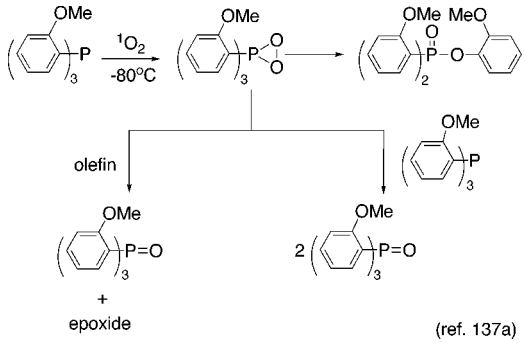
**Table 25. Generation of Dioxaphosphiranes ($R_3PO_2$ Dioxiranes)[a]**

| Year | Structure | Evidence of Formation | T (K) | Method of Preparation | Ref. | Comments |
|---|---|---|---|---|---|---|
| 2006 |  (X=MeO, H, F, Cl, $CF_3$) | Trapping and rate constant study | 298 | A | 137b | Phosphine oxide products formed |
| |  (X=MeO, Me, H) | Trapping and rate constant study | 298 | A | 137b | Phosphinate and phosphine oxide formed |
| |  | Intramolecular trapping | 298 | A | 138 | |
| |  | NMR spectroscopy and trapping | 218-258 | A | 138 | $^{31}P$ NMR spectroscopy was conducted in addition to trapping with cyclohexene |
| 2003 |  | NMR spectroscopy | 193 | A | 137a | $^{31}P$ and $^{17}O$ NMR spectroscopy was conducted along with olefin trapping studies |
| 2001 |  | Kinetic analysis | 298 | A | 140 | meta- and para-methoxyphenylphosphine reaction with singlet oxygen also conducted |
| 1999 |  | NMR and X-ray crystallography | 273 | B | 136 | Potassium 18-crown-6 was the counter ion |
| 1993 |  | Trapping and $^{18}O$ labelling | 298 | A | 143a | Peroxyphosphine oxide and [1,2,4,5,3,6]tetradiphosphinane are not formed |
| 1993 |  | Trapping and product study | 293 | A | 154 | Oxidation of olefins and thianthrene-5-oxide provide tentative evidence for the dioxaphosphirane |
| 1987 |  | IR spectroscopy | 12-18 | C | 139 | Other species formed such as HPO, HOOPO, and $HOPO_2$ |
| 1983 |  | Product study | 237 | D | 144 | |

[a] A, solution-phase phosphine or phosphite photooxidation; B, reaction between triplet oxygen and the phosphoramide ion; C, Ar-matrix irradiation of a $PH_3-O_3$ complex; D, reaction between $Ph_3P$, $H_2O_2$, and diethyl azocarboxylate.

yl)phosphine produced the dioxaphosphirane. Chemical quenching of $^1O_2$ by the phosphine was very efficient and led to phosphine oxide ($o$-$MeOC_6H_4)_3P{=}O$. The ability of phosphine to convert $^1O_2$ to $^3O_2$ (physical quenching) has not been observed in these reactions. The *ortho*, *meta*, and *para* isomers of $(MeOC_6H_4)_3P$ also show no physical quenching of $^1O_2$ regardless of the solvent.[137,143] With enriched $^{17}O_2$ gas used in the photooxidation, $^{17}O$ NMR data showed a broad peak at 740 ppm, which along with the $^{31}P$ NMR peak at −48.3 ppm was assigned to the three-membered ring system ($o$-$MeOC_6H_4)_3PO_2$. The $o$-methoxyphenyl groups exerted steric interactions that slowed the bimolecular reaction of the dioxaphosphirane with the substrate ($o$-$MeOC_6H_4)_3P$. For phosphines that possess small cone angles, as described for metal complexes,[148,149] the dioxaphosphirane has a longer lifetime by slowing bimolecular reactions. Alkene-trapping experiments showed that ($o$-$MeOC_6H_4)_3PO_2$ dioxaphosphirane transfers an oxygen atom to alkenes to yield epoxides, analogous to $R_2CO_2$ dioxiranes such as dimethyldioxirane (Table 27). As yet, no information is available whether the apical or the equatorial dioxaphosphirane oxygen is donated, although the equatorial oxygen should be the more electrophilic.[150−152] There is a reduced computed charge on $O_{eq}$ compared to the $O_{ax}$ atom. In the absence of an external trap, the intramolecular rearrangment of dioxaphosphirane afforded the phosphonate

**Scheme 24. Reaction of Tris(*o*-methoxyphenyl)phosphine with Singlet Oxygen**




**59**. In the presence of methanol as solvent, its addition leads to hydroperoxyphosphine and subsequently to hydroxyphosphorane and tris(*o*-methoxyphenyl)phosphine oxide, after reaction with the substrate.

In 2006, a dioxaphosphirane intermediate **63** was observed in the reaction of 1,1′-binaphthyl-di-*tert*-butyl-2-phosphine with $^1O_2$ in toluene at temperatures ranging from −40 to −80 °C (Scheme 25 and Table 26).[138] Evidence for the existence of the dioxaphosphirane came from an assignment of the $^{31}P$ NMR signal at −18.6 ppm and the subsequent decomposition of this intermediate upon warming to give the corresponding phosphine oxide. Warming of the mixture in the presence of cyclohexene afforded its epoxide. The intramolecular oxidation of dioxaphosphirane **63** gave naphthalene epoxide and subsequently a hydroxylated naphthalene product via an NIH-shift mechanism. A similar rearrangement was observed in the reaction of *R*-(+)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (**63′**) with $^1O_2$ according to $^{31}P$ NMR spectroscopy.[138]

*X-ray Crystallography.* In 1999, the synthesis of a hexacoordinate 12-P-6 dioxaphosphirane **68** was accomplished in a reaction of $^3O_2$ with 3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3H,2,1$\lambda^5$-benzoxaphosphoranide ion] (**65**), generated from a P−H phosphorane **64** at 273 K (Scheme 26).[136] Exposure of the 10-P-4 phosphoranide to $O_2$ in a thermal process involved electron transfer (phosphoranyl radical/superoxide radical pair, **66**) to give the corresponding dioxaphosphirane **68**. A cyclization of peroxyphosphine oxide **67** was proposed with pseudorotation to place the oxygen atom equatorial and the aryl carbons axial. On the basis of $^{31}P$ and $^{19}F$ NMR spectroscopy, the dioxaphosphirane structure was assigned (Table 26). The dioxaphosphirane crystallized with potassium 18-crown-6 as the salt and was found to be stable in the solid state at room temperature. With $Ph_3P$ it rapidly deoxygenated in solution to give oxidophosphorane **69** and $Ph_3P{=}O$. Except for $Ph_3P$, oxygen-transfer reactions to alkenes or other trapping agents were not explored. The synthesis of diasteromeric analogues was conducted, in which one of the $CF_3$ groups was replaced by $CH_3$. A slow interconversion of the *endo* and *exo* forms of the R side groups implies rigid three-membered peroxide rings in **68a′** and **68a″** and, thus, inefficient pseudorotation.

*IR Spectroscopy.* In 1987, the generation of a dioxaphosphirane [HP(=O)$O_2$] in the visible-light photolysis of a phosphine($PH_3$)−ozone complex in solid argon (12−18 K) was reported (Scheme 27 and Table 26).[139] The infrared study in an argon matrix of the reaction of $^{16,18}O_3$ with $PH_xD_{3-x}$ ($x$ = 0, 1, 2, 3) and subsequent decomposition of the phosphine−$O_3$ complex showed the presence of a number of compounds, which included phosphine oxide $H_3P{=}O$, phosphinic acid $H_2POH$, phosphonic acid $(HO)_2HP{=}O$, and metaphosphoric acid $HOPO_2$. The reaction is thought to produce the HP=O intermediate, which adds $O_2$ to give acyclic HOOP=O and the HP(=O)$O_2$ dioxaphosphirane upon further irradiation. The results do not support the interconversion between the acyclic HOOP=O and the dioxaphosphirane HP(=O)$O_2$. On the basis of the observed fundamental vibrational frequencies, HP(=O)$O_2$ and DP(=O)$O_2$ structures were assigned, which are given in Table 26. Rotationally, vibrationally, and electronically excited intermediates were suggested.

**4.2.1.3. Room Temperature.** Trapping, intramolecular rearrangement, and $^{18}O$-tracer experiments provided indirect evidence for the dioxaphosphirane intermediates in reactions of $^1O_2$ with phosphites and phosphines. Phosphites are less reactive and may be used as trapping agents in the $^1O_2$ reactions.[153] For example, trimethylphosphite traps the anethole−singlet oxygen intermediate(s) because it reacts slowly with $^1O_2$.[150]

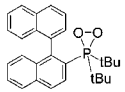
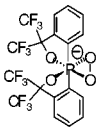
In 1993, the photooxidation of tributylphosphite and triphenylphosphine was conducted with sulfoxides [$(p\text{-}YC_6H_4)_2$-SO; Y = MeO, Me, H, and Cl] and sulfides [$(p\text{-}YC_6H_4)_2S$; Y = Me and H] as trapping agents (Scheme 28 and Table 28).[143]

Singlet oxygen was generated by irradiation ($\lambda$ > 400 nm) in air-saturated acetonitrile solutions with methylene blue as sensitizer. The reactivity of the intermediate in the reaction with these trapping agents correlated well with electrophilic dioxaphosphirane. A negative $\rho$ value of −0.63 for trapping by diaryl sulfide was obtained. Oxygen transfers to $Ph_2S$ and to $Ph_2SO$ were inefficient compared to the more oxophilic $(BuO)_3P$ molecule. The relative reactivity was 300:4:1 for $(BuO)_3P/Ph_2S/Ph_2SO$. An $^{18}O$-tracer experiment indicated retention of the two $^{18}O$ atoms, which suggests a unimolecular rearrangment of dioxaphosphirane ($Ph_3P^{18}O_2$) to phenyl diphenylphosphinate $Ph^{18}OP(^{18}O)Ph_2$. Retention indicates that the two oxygen atoms in the phosphinate product are derived from one $O_2$ molecule. Scrambling implies that the oxygen atoms come from different $O_2$ molecules. The labeling data do not rule out unimolecular rearrangment of an acyclic peroxyphosphine oxide (Scheme 29).

The reaction of $^1O_2$ with *para*-substituted arylphosphines was investigated in detail (Scheme 30).[137b] Formation of the corresponding phosphine oxides took place efficiently (no physical quenching of $^1O_2$), which showed a correlation with the Hammett $\sigma$ parameter ($\rho$ = −1.53 in $CDCl_3$) and with the Tolman electronic parameter.[148,149] The phosphine oxide products were proposed to arise from the reaction of phosphine with dioxaphosphirane intermediates.

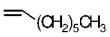
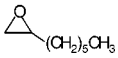
In 1993 and 1994, indirect evidence for the existence of a dioxaphosphirane came from the reaction of $^1O_2$ with a bicyclic phosphite (1-methyl-4-phospha-3,5,8-trioxabicyclo-[2.2.2]octane) in the presence of norbornene (Scheme 31).[154,155] The data point to a dioxaphosphirane intermediate in view of the epoxidation of norbornene. The bicyclic dioxaphosphirane would have no possibility for pseudorotation. The reaction was followed by GLC analysis, and the corresponding phosphate was formed as the product. Addition of the radical trap triphenylmethane did not influence the epoxidation reaction, which is similar to work on $(o\text{-}MeOC_6H_4)_3P$ in 2003.[137a] Less nucleophilic olefins such as stilbene and styrene are oxidized less efficiently. Analysis with the thianthrene 5-oxide probe also confirmed electrophilic oxidation behavior.[154,155,168−170]

**Table 26. Spectral Properties of Dioxaphosphiranes[a]**

| Year | Structure | $^{31}$P NMR (ppm) | $^{17}$O NMR (ppm) | Coupling Constants | X-ray structure | IR data (cm$^{-1}$) | | | Ref. | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | mode | observed | calculated | | |
| 2006 |  | -18.6 | | | | | | | 138 | |
| 2003 |  | -48.3 | 740 | | | | | | 137a | Also detected as the hydroperoxyphosphine and hydroxyphosphorane in MeOH |
| 1999 |  | -121.0 | | δ=-74.73 (q, $J_{PF}$=8.8Hz), -75.36 (q, $J_{PF}$=8.8 Hz) | a=10.446(5)Å<br>b=12.265(6)Å<br>c=15.206(6)Å<br>α=70.088(3)°<br>ß=80.669(4)°<br>γ=69.164(3)°<br>(R=0.047) | | | | 136 | $^{1}$H and $^{13}$C NMR data are also reported |
| 1987 |  | | | | | $\tilde{\nu}$ (P-H) | 2490.1 | 2489.8 | 139 | |
| | | | | | | | 2489.4 | 2489.7 | | |
| | | | | | | | 1370.3 | 1370.1 | | |
| | | | | | | | 1362.4, 1372.0 | 1366.8 | | |
| | | | | | | $\tilde{\nu}$ (P=O) | 1331.6 | 1330.4 | | |
| | | | | | | | 1368.1 | 1368.4 | | |
| | | | | | | | 1329.3 | 1328.1 | | |
| | | | | | | | 1326.9 | 1326.0 | | |
| | | | | | | $\tilde{\nu}_s$ (-PO$_2$) | 974.1 | 977.3 | | |
| | | | | | | | 939.4 | 943.5 | | |
| | | | | | | | 965.9 | 963.1 | | |
| | | | | | | | 959.0 | 961.5 | | |
| | | | | | | | 950.8 | 948.0 | | |
| | | | | | | | 931.8 | 932.4 | | |
| | | | | | | δ(HPO) | | 935.3 | | |
| | | | | | | | | 927.6 | | |
| | | | | | | $\tilde{\nu}_{as}$ (-PO$_2$) | | 853.6 | | |
| | | | | | | | 833.2 | 833.3 | | |
| | | | | | | | 833.2 | 833.1 | | |
| | | | | | | | | 813.8 | | |
| | | | | | | $\tilde{\nu}_s$ (-PO$_2$) | 587.3 | 586.8 | | |
| | | | | | | | 560.0 | 559.4 | | |
| | | | | | | ϖ(OPO$_2$) | 436.7 | 436.5 | | |
| | | | | | | | | 423.2 | | |

[a] Temperatures of the experiments range from 12 to 298 K.

**Table 27. Oxidation of Alkenes by in-Situ Generated Tris(*o*-methoxyphenyl)dioxaphosphirane[a]**

| Alkene | Epoxide | Yield (%) |
|---|---|---|
|  |  | 60 |
|  |  | 65 |
|  |  | 80 |
|  |  | 75 |

[a] Reference 137b.

In 1974, the formation of trialkyl phosphates was reported in the dye-sensitized photooxidation reactions of phosphites [$(MeO)_3P$, $(EtO)_3P$, $(i\text{-}PrO)_3P$, $(n\text{-}BuO)_3P$, (cyclic-$C_6H_{11}O)_3P$, and $(CH_2{=}CHCH_2O)_3P$].[156] Singlet oxygen was generated in benzene−methanol mixtures (4:1) with methylene blue or in acetone with Rose Bengal as sensitizer at 298 K. The transient formation of a phosphite−$O_2$ intermediate was implicated, but its structure was not suggested at that time.

**4.2.1.4. Miscellaneous.** *Diethyl Azodicarboxylate−$H_2O_2$ Reaction.* In one paper, the use of hydrogen peroxide was suggested to generate triphenyldioxphosphirane.[108] In 1983, a betaine(**70**)−$H_2O_2$ reaction was reported (Scheme 32).[144] Migration of the phenyl group to give **73** was taken as evidence for the presence of the dioxaphosphirane or tetradiphosphinane intermediate (Scheme 33). Further experiments to probe the nature of the intermediate(s) in the reaction have not been conducted.

*Arylphosphines Used as Jet-Fuel Stabilizers.* Over the past decade, arylphosphines have been examined as possible stabilizers of jet fuels.[158−163] The thermal oxidative and pyrolytic stability of the jet fuel was enhanced with additions of triphenylphosphine or dicyclohexylphenylphosphine over a temperature range of 190−250 °C. Oxophilic stabilizers such as phosphines are selectively oxidized rather than the jet fuel. Autoxidation of the phosphines has been suggested to take place by an electron-transfer and/or a charge-transfer process (Scheme 34). High temperatures were necessary to initiate a reaction between $Ar_3P$ and $^3O_2$ in view of the large activation energy ($E_a$ < 30 kcal/mol). Thus, decomposition of a possible dioxaphosphirane intermediate is expected to take place rapidly under the high-temperature conditions.

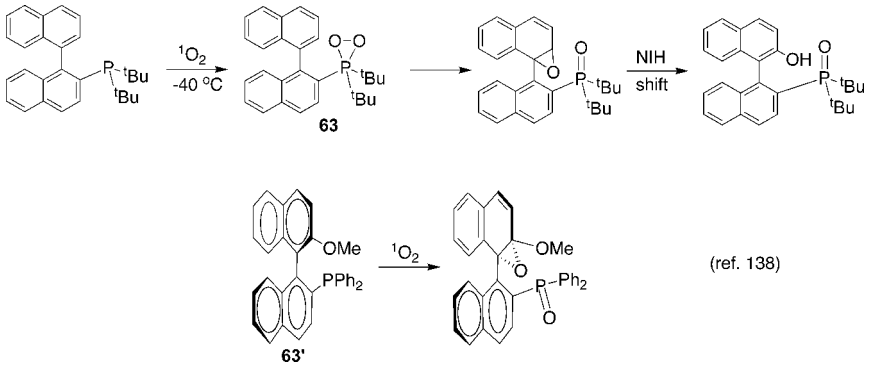
*Thermolysis of a Bisdiphenylphosphinic Peroxide.* In 1965, a reaction was reported which involved the thermal decomposition of a bisdiphenylphosphinic peroxide **74** (Scheme 35).[157] Decomposition of bisdiphenylphosphinic peroxide with phenyl migration occurred in chloroform, tetrachloroethane, DMF, and acetic acid, but not in alcohol solvents, in which an anhydride is formed. The result was interpreted tentatively in terms of a heterolytic cleavage reaction and production of transient peroxidic intermediates, such as the acyclic $Ph_2(RO)POO$ (**76**) and dioxaphosphirane $Ph_2(RO)$-$PO_2$ (**77**), prior to formation of the anhydride product. It is uncertain whether a dioxaphosphirane is formed in the reaction. Further experiments and computations are needed to validate the mechanistic suggestion.

**4.2.1.5. Calculations.** *Structure.* Dioxaphosphiranes $H_3PO_2$, $Me_3PO_2$, and $(HO)_3PO_2$ optimize to minima at various levels of theory and basis set extension, including HF/STO-3G(d), HF/3-21G(d), HF/6-31G(d), MP2/6-31G(d), and CASSCF/6-31G(d).[143,164] Calculated bond distances and bond angles are shown in Table 29. The parent dioxaphosphirane $HPO_2$ has also been studied and optimizes to a minimum at the SCF and SCF/CEPA-1 levels.[165] Calculations predict that peroxyphosphine oxide does not form in phosphine−$^1O_2$ reactions.[164] The acyclic peroxyphosphine oxides $(HO)_3POO$, $H_3POO$, and $Me_3POO$ are not found as minima at any level of theory.[143,164,165] Dioxaphosphirane $H_3PO_2$, $(HO)_3PO_2$, and $Me_3PO_2$ bond distances for the $O_1-O_2$ bond range from 1.599 to 1.560 Å. The dioxaphosphirane structure is calculated with one of the peroxide oxygens in an equatorial position and the other in an apical position. The apical $P-O_1$ bond is 0.059−0.202 Å longer than the equatorial $P-O_2$ bond, as would be expected for a TBP structure (Table 29). A sample computed structure for the unsubstituted dioxaphosphirane is given in Figure 3. The sensitivity of the dioxaphosphirane geometry to the R substituent has not been examined in detail.

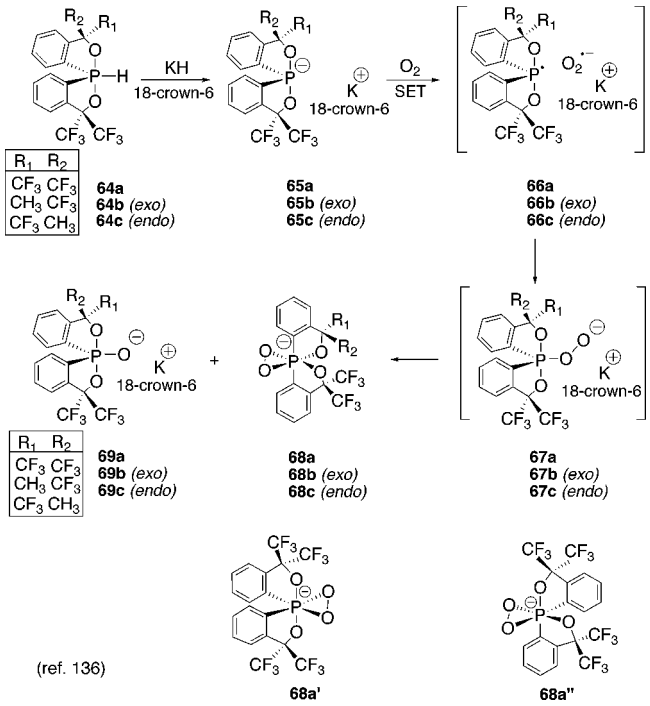
Wilke and Weinhold have recently calculated resonance bonding patterns in $H_3PO_3$ dioxaphosphirane (Scheme 36).[141] The use of Natural Resonance Theory (NRT) and Natural Bond Orbitals (NBOs)[166] predicted that the nonhypervalent ionic resonance forms II and III are more important than the valence-shell expanded[167] (octet-violating hypervalent structures) I, ionic IV, and $\pi$-complex V forms. The hypervalent form I, with participation of d orbitals in the hydridized structure, is a minor contributor in the structures I−V according to the NRT/NBO analysis.

**Energetics.** A computational investigation of the phosphine−singlet oxygen reaction appeared in 1993 (Table 30).[164] The barrier connecting $PH_3$ and $^1O_2$ with dioxaphosphirane $H_3PO_2$ is 24.8 kcal/mol at the MP2/6-31G(d) level. The conversion of $PH_3$ and $^1O_2$ to dioxaphosphirane $H_3PO_2$ is calculated to be −32.0 kcal/mol exothermic at the MP2/6-31G(d) level. The formation of dioxaphosphirane $Me_3PO_2$

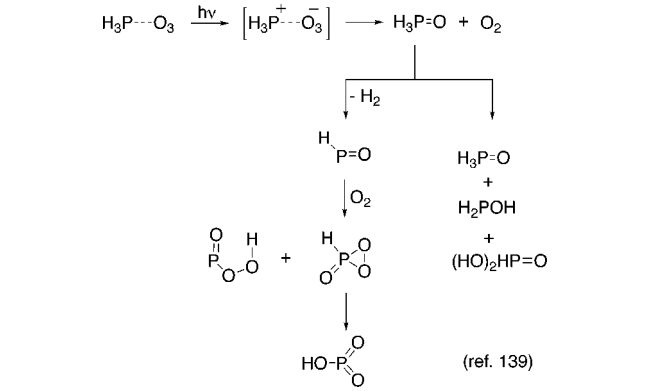
**Scheme 25. Reaction of Binaphthyl-Containing Phosphines with Singlet Oxygen**



**Scheme 26. Reaction of a Phosphoranide Ion with $O_2$**

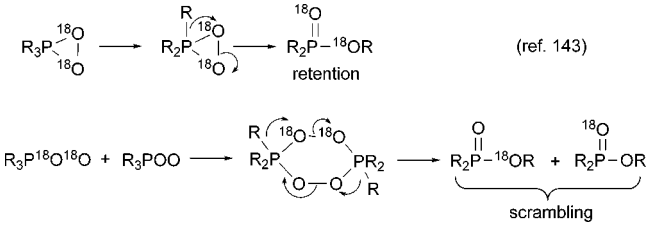



**Scheme 27. Photolysis of a Phosphine−Ozone Complex[a]**




[a] Paticipation of intermediates that are rotationally excited, vibrationally excited, or electronically excited is not noted here.

**Scheme 28. $^{18}O$-Labeling Study of a Dioxaphosphirane Rearrangement**




from $PMe_3$ and $^1O_2$ is calculated to be exothermic by −52.5 kcal/mol at the MP2/6-31G(d)//HF/6-31G(d) level, whereas the cyclization of the acyclic $HP(=O)_2$ to dioxaphosphirane $HPO_2$ is endothermic by 85.0 kcal/mol at the SCF level.

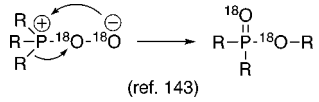
In conclusion, the spectroscopic evidence for dioxaphosphiranes **54**−**56** is now in hand. Dioxaphosphirane **54** arises from the reaction of phosphine or phosphite with $^1O_2$, but not from the primary formation of peroxyphosphine oxide. The singlet oxygen attaches in a side-on manner to the trivalent phosphorus center. Dioxaphosphiranes derived from sterically bulky phosphine ligands have synthetic versatility that should be further investigated.

**Table 28. $^{18}O$-Tracer Study of the Formation of Phenyl Diphenylphosphinate [$Ph_2P(=O)Ph$] from $Ph_3P$ and $^1O_2$[a]**

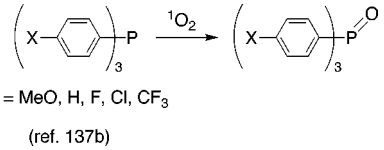
| entry | conditions[b] | product | masses[b] M | M + 2 | M + 4 | |
|---|---|---|---|---|---|---|
| | | | Observed | | | |
| 1 | 20 mM $Ph_3P/^{18}O_2$[c] | $Ph_2P(=O)Ph$ | 100 | 11.8 | 5.9 | |
| 2 | 20 mM $Ph_3P/^{18}O_2$[d] | $Ph_2P(=O)Ph$ | 100 | 10.5 | 0.3 | |
| | | | 100 | 1.3 | 5.6 | (difference between entries 1 and 2[e]) |
| | | | Calculated | | | |
| 3 | | | 100 | 0.5 | 6.2 | (retention) |
| 4 | | | 100 | 3.6 | 0.0 | (scramble) |

[a] Reference 143a. [b] Mass spectral data for $Ph_2P(=O)Ph$, $M = 294$. The observed values are the mean of two determinations. [c] Oxygen gas: $^{32}O_2/^{34}O_2/^{36}O_2 = 100:0.5:6.2$. [d] Control experiment with natural oxygen gas under the same conditions. [e] Net values for $^{18}O$ contents.

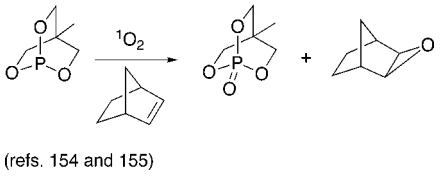
**Scheme 29. Peroxyphosphine Oxide Rearrangement**



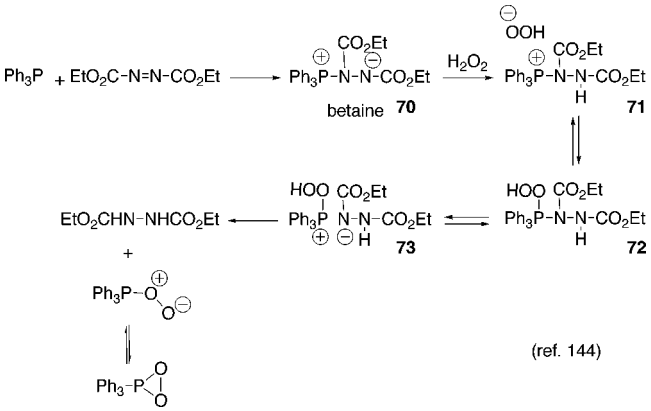

**Scheme 30. Reaction of Aryl Phosphines with Singlet Oxygen**




**Scheme 31. Reaction of a Bicyclic Phosphite with Singlet Oxygen**



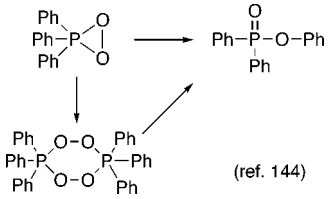

**Scheme 32. Reaction of a Betaine with Hydrogen Peroxide**



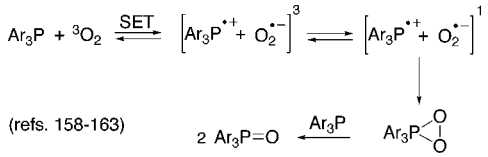

### 4.2.2. Dioxathiirane, $R_2SO_2$

**4.2.2.1. Background Information.** Dioxathiirane (thiadioxirane, **79**) has been suggested as an intermediate in sulfur oxidation reactions. Since seven previous reviews have focused on organic sulfide or metal thiolate−ligand photo-

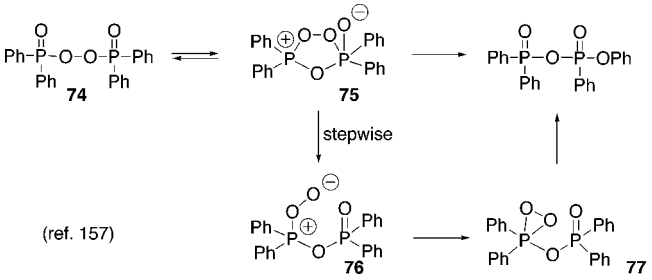
**Scheme 33. Phenyl Migration in Triphenyldioxaphosphirane**




**Scheme 34. Reaction of Triarylphosphine with $O_2$**




**Scheme 35. Thermal Reaction of Bisdiphenylphosphinic Peroxide**




oxidations and the possible formation of $R_2SO_2$ dioxathiiranes,[2,4,171−176] we shall focus our discussion on the new findings.

No direct spectroscopic data exist yet for the dioxathiirane $R_2SO_2$ intermediate. Routes that have been suggested to give

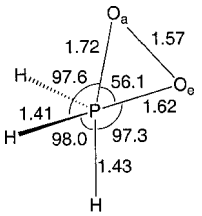
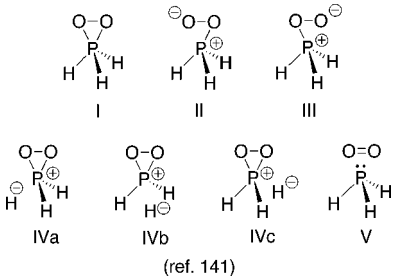



**Figure 3.** B3LYP/6-31+G(d) computed structure of the unsubstituted dioxaphosphirane from ref 141. Bond lengths in angstroms; bond angles in degrees.

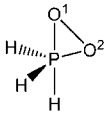
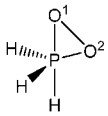
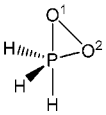
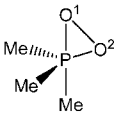
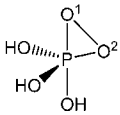
**Scheme 36. Resonance Forms of Dioxaphosphirane**




dioxathiirane include reagents such as $^1O_2$, $^3O_2$, and superoxide.[2,4,171−176] Dioxathiirane **79** may arise from the reaction of the sulfide radical cation with superoxide ion. There is no evidence that dioxathiirane is present in sulfide−$^1O_2$ reactions.

Experimental and computational data suggest that various species arise in sulfide oxidation chemistry, which include dioxathiirane **79**, persulfoxide **80**, sulfide radical ion superoxide pair **81**, *S*-hydroperoxysulfonium ylide **82**, sulfoxide **83**, and sulfone **84** (Chart 2). Sulfide photooxidations can lead to hydroperoxysulfurane **85** or a hydrogen-bonded

**Table 29. Calculated Energies and Geometries of Dioxaphosphiranes**

| Year | Structure | Energy[a] | Method of Basis Set | $O^1$-$O^2$ [b] | P-$O^1$ [b] | P-$O^2$ [b] | P-$O^1$-$O^2$ [c] | Ref. | Comments |
|---|---|---|---|---|---|---|---|---|---|
| 2006 |  | | B3LYP/6-31+G(d) | 1.570 | 1.720 | 1.620 | 58.6 | 141 | Calculations were also performed with other methods [HF, MP2, QC1SD(T)] and basis sets (3-21G, ang-cc-pVOZ, ang-cc-pVTZ) |
| 1993 |  | -492.53079 | MP2/6-31G(d) | 1.599 | 1.697 | 1.630 | 63.4 | 164 | |
| |  | -492.12798 | CASSCF/6-31G(d) | 1.630 | 1.681 | 1.622 | 62.3 | | Calculation on a 12-orbital system with 10 filled and 2 virtual orbitals |
| |  | -610.05313 | MP2(FC)/6-31G(d) | 1.560 | 1.782 | 1.580 | 69.2 | | |
| 1993 |  | -713.10466 | HF/3-21G(d) | 1.572 | 1.654 | 1.568 | -- | 143a | HF/STO-3G(d) calculations have also been reported |

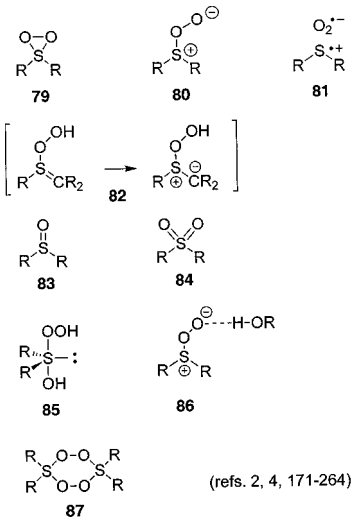
[a] Calculated for the $S_0$ state. [b] Bond distances in angstroms. [c] Bond angles in degrees.

**Table 30. Calculated Energies[a] for the Intramolecular and Intermolecular Reactions of Dioxaphosphiranes**

| Year | A | B | $\Delta E_{A \rightarrow B}$ | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|---|
| 1993 | $PH_3 + {}^1O_2$ | $H_3P$ | -32.0 | MP2/6-31G(d) | 164 | An energy minimum was not found for acyclic $H_3POO$ nor $Me_3POO$ at any theoretical level |
| | $PH_3 + {}^1O_2$ | $H_3P$ TS | 24.8 | | | |
| | $2\,PH_3 + {}^1O_2$ | $2\,H_3PO$ | -111.2 | | | |
| | $Me_3P + {}^1O_2$ | $Me_3P$ | -52.5 | MP2/6-31G(d)// HF/6-31G(d) | | |
| | $Me_3P + {}^1O_2$ | $H_3P$ TS | 20.7 | HF/3-21G(d) | | |
| | $2\,Me_3P + {}^1O_2$ | $2\,Me_3PO$ | -163.0 | MP2/6-31G(d)// HF/6-31G(d) | | |
| 1992 | H–P | H–P | 85.0 | SCF | 165 | |
| | | | 79.6 | SCF/CEPA-1 | 165 | Electron correlation was conducted with the CEPA-1 method by using SCF geometries |

[a] Energies in kilocalories per mole.

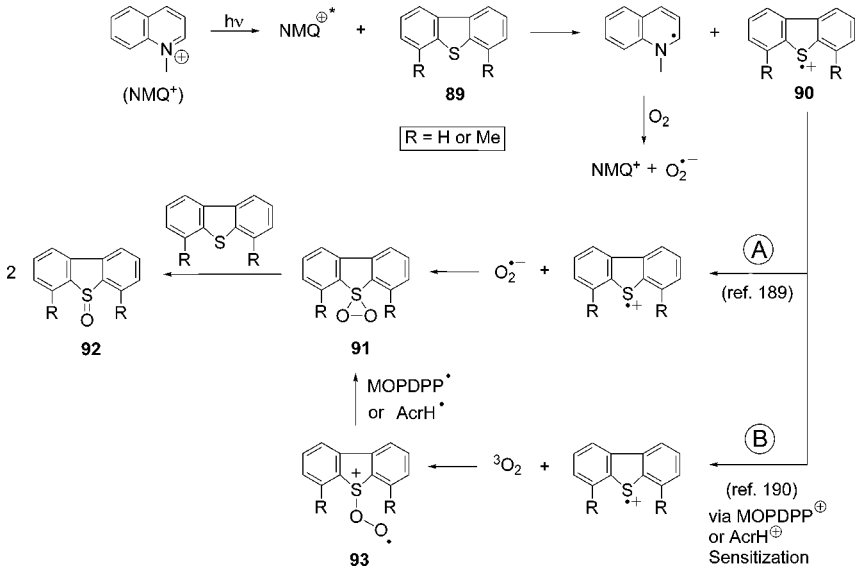
**Chart 2. Sulfur- and Oxygen-Containing Compounds**



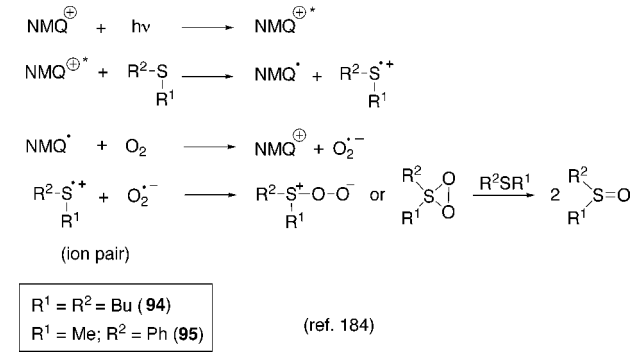

persulfoxide **86** in alcohol solvents.[4,171−187] The acidity of the medium and dependence on the trapping efficiency suggest the presence of **86**,[171] $^{17}$O-labeled substrates implied the participation of **85**. Alcohol adducts and nucleophilic oxygen-transfer chemistry suggest a dipolar form of the persulfoxide ($R_2S^+OO^-$) rather than a diradical form ($R_2S^{\bullet}$-$OO^{\bullet}$) in solution.[188] There is no evidence that $R_2S^+OO^-$ persulfoxide or $R_2SO_2$ dioxathiirane dimerize to a six-membered-ring diperoxide **87**. Quantum calculations have been used to predict the structures and energetics of intermediates generated in the oxidation of sulfur compounds.[164,176,184,188]

**4.2.2.2. Room Temperature.** *Electron-Transfer Photooxidation.* Dioxathiiranes may arise from electron-transfer photooxidations with the use of electron-deficient sensitizers.[184,185,189,190] In 2005 and 2006, experiments conducted in $O_2$-saturated acetonitrile implied that the sulfide radical ion **90** (R = H or Me), dioxathiirane **91** (R = H or Me), and sulfoxide **92** (R = H or Me) are generated in the photooxidation of dibenzothiophene **89** (R = H) and 4,6-dimeth-

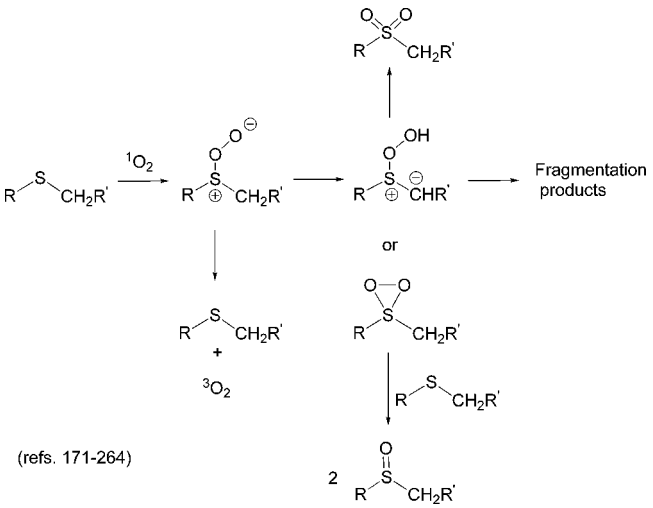
**Scheme 37. Electron-Transfer Photooxidation of Dibenzothiophenes**



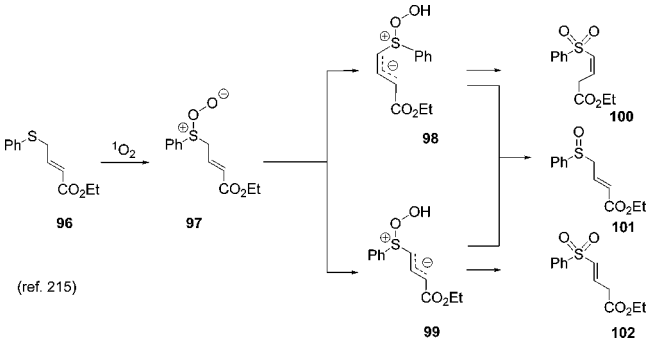
**Scheme 38. Electron-Transfer Photooxidation of Dibutylsulfide and Thioanisole**




**Scheme 39. Reaction of Sulfides with Singlet Oxygen**

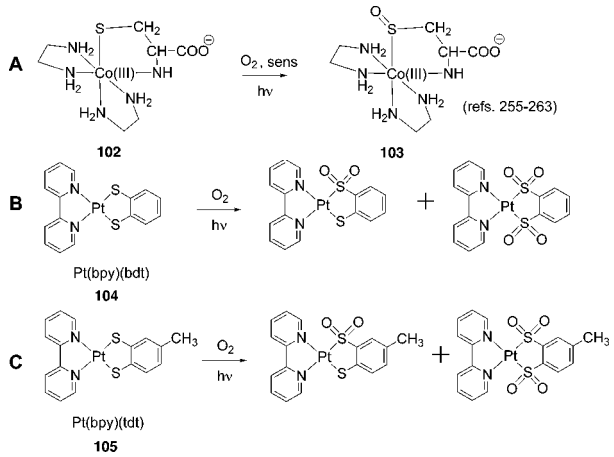



**Scheme 40. Reaction of γ-Phenylthiocrotonate with Singlet Oxygen**

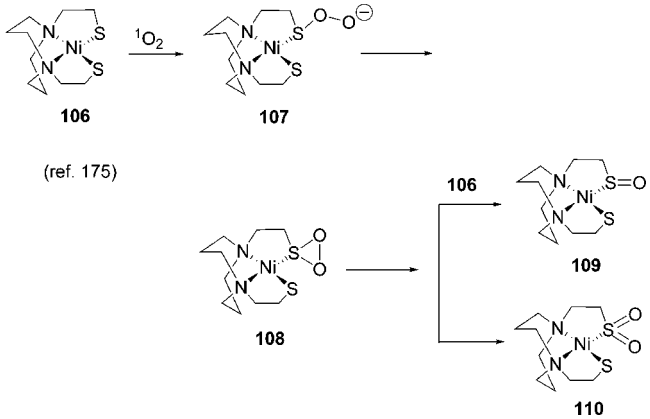



yldibenzothiophene **89** (R = Me), sensitized by *N*-methylquinolinium tetrafluoborate ($NMQ^+BF_4^-$), 10-methylacridine hexafluorophosphate ($AcrH^+PF_6^-$), or 2-(4-methoxyphenyl)-4,6-diphenylpyrylium ($MOPDPP^+BF_4^-$) in Scheme 37.[189,190] Laser photolysis, ESR, and fluorescence-quenching data were collected, and the formation of dioxathiirane **91** was proposed. It was speculated that the superoxide ion[189] added to the sulfide radical ion in one step (Scheme 37A). It was also suggested that ground state $^3O_2$[190] reacted with the sulfide radical ion in a stepwise manner (via **93** followed by back-electron transfer to $MOPDPP^\bullet$ or $AcrH^\bullet$, Scheme 37B). EPR data indicated that the superoxide ion is formed by electron transfer from the sensitizer radical (e.g., $NMQ^\bullet$). Sulfoxide production is reduced in the presence of the electron trap 1,4-benzoquinone, which reacts with $NMQ^\bullet$ and superoxide to give $NMQ^+$ and $O_2$. Compound **89** does not form the

**Scheme 41. Photooxidation of Cobalt- and Platinum-Thiolate Complexes**




**Scheme 42. Photooxidation of a Nickel-Thiolate Complex**




*S*-hydroperoxysulfonium ylide **82** due to the absence of α protons.

In 2003, the photooxidation of dibutylsulfide (**94**) and thioanisole (**95**) in $O_2$-saturated acetonitrile, sensitized by $NMQ^+$ and 9,10-dicyanoanthracene (DCA), was conducted at 298 K (Scheme 38).[184] Time-resolved laser flash photolysis of $NMQ^+$ revealed the formation of sulfide radical cations [dimeric $(Bu_2S)_2^{\bullet+}$, $PhSMe^{\bullet+}$, and dimeric $(PhSMe)_2^{\bullet+}$]. DCA photolysis also led to the production of radical ions for PhSMe, but not $Bu_2S$. The persulfoxide exists as a primary intermediate in sulfide$-^1O_2$ reactions,[188] but in the $NMQ^+$ and DCA systems, dioxathiirane was suggested to arise from a direct reaction between sulfide radical ion and the superoxide ion. The evidence for dioxathiirane derives from the electrophilic character of the intermediate in bimolecular trapping experiments, as confirmed by data from computations. The computations predict an energetically facile conversion of $R_2S^{\bullet+}$ (from **94** and **95**) with the superoxide ion to give the corresponding dioxathiiranes.[184]

Other work has also focused on generation of sulfide radical ions, some via electron-transfer photosensitizers [DCA (free or covalently bound to silica), triphenylpyrylium tetrafluoroborate, 2,3,5,6-tetrachloro-1,4-benzoquinone, $Ru(2,2'\text{-bipyrazine})_3^{2+}$, $TiO_2$, CdS, and acetone], although the intermediacy of dioxathiiranes is not suggested in these cases.[191−203]

*Singlet Oxygen Reactions.*[171−264] Early sulfide photooxidation work of Schenck (from 1962 to about 1970) suggested

**Table 31. Calculated Geometries of Dioxathiiranes**

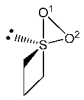
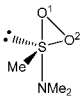
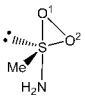
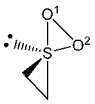
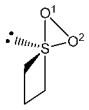
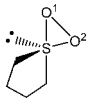
| Year | Structure | Method of Basis Set | $O^1$-$O^{2a}$ | S-$O^{1a}$ | S-$O^{2a}$ | S-$O^1$-$O^{2b}$ | Ref. |
|---|---|---|---|---|---|---|---|
| 1998 |  | B3LYP/6-31+G(d) | 1.535 | 2.077 | 1.597 | | 212 |
| 1998, 1996 |  | MP2/6-31G(d) | 1.556 | 1.811 | 1.651 | | 243, 244 |
| | | MP2/6-311+G(2df) | 1.531 | 1.817 | 1.609 | | |
| 1998 |  | MP2/6-311+G(3df,2p) | 1.542 | 1.755 | 1.607 | 67.7 | 176 |
| | | QCISD/6-31+G(d) | 1.562 | 1.982 | 1.597 | 77.7 | |
| |  | MP2/6-311+G(3df,2p) | 1.527 | 1.809 | 1.601 | 70.6 | |
| |  | MP2/6-311+G(3df,2p) | 1.53 | 1.798 | 1.603 | 70 | |
| 1997 |  | MP2/6-31G(d) | 1.556 | 1.811 | 1.652 | | 213 |
| |  | | 1.547 | 1.797 | 1.666 | | |
| |  | | 1.555 | 1.747 | 1.634 | | |
| |  | | 1.555 | 1.753 | 1.639 | | |
| |  | | 1.549 | 1.771 | 1.650 | | |
| |  | | 1.551 | 1.786 | 1.649 | | |
| |  | | 1.546 | 1.803 | 1.649 | | |
| |  | | 1.546 | 1.800 | 1.659 | | |
| |  | | 1.549 | 1.773 | 1.642 | | |
| |  | | 1.552 | 1.780 | 1.643 | | |
| 1996 |  | RHF-PM3 | 1.580 | 1.790 | 1.710 | | 242 |

**Table 31 (Continued)**

| Year | Structure | Method of Basis Set | $O^1$-$O^{2a}$ | S-$O^{1a}$ | S-$O^{2a}$ | S-$O^1$-$O^{2b}$ | Ref. |
|---|---|---|---|---|---|---|---|
| 1996 |  | | 1.564 | 1.793 | 1.648 | | 243 |
| |  | | 1.555 | 1.812 | 1.646 | | |
| |  | | 1.553 | 1.825 | 1.647 | | |
| 1992 |  | MP2/6-31G(d) | 1.555 | 1.809 | 1.648 | | 231 |

[a] Bond distances in angstroms. [b] Bond angles in degrees.

a sensitizer−oxygen complex (moloxide) rather than a diffusible $^1O_2$ species.[204,205] In the 1980s and 1990s, efforts were increased to understand the intermediates generated in the sulfide−$^1O_2$ chemistry. In these studies, the production of dioxathiiranes was searched for by using flash photolysis and competitive kinetic techniques. The reaction mechanism in Scheme 39 proposes the persulfoxide **80** as the first intermediate. The high-energy barrier computed for the formation of the dioxathiirane from the persulfoxide suggests that the *S*-hydroxysulfonium ylide is a key reaction intermediate. The *S*-hydroxysulfonium ylide is most likely an additional intermediate in the photosensitized oxidations of sulfides in aprotic solvents. The formation of a *S*-hydroperoxysulfonium ylide explains the experimental results in many cases.[207−216] For example, in 2002, the reaction of $^1O_2$ with ethyl $\gamma$-phenylthiocrotonate (**96**) was conducted in $C_6D_6$ at 298 K (Scheme 40).[215] From the observation of the sulfoxide **101** and sulfone **100** and **102** products by $^1$H NMR spectroscopy, the intermediacy of the *S*-hydroperoxysulfonium ylides **98** and **99** was implied. In this study, the source of $^1O_2$ was 1,4-dimethylnaphthalene endoperoxide.

Despite all the work conducted on the reactions of $^1O_2$ with nickel-, platinum-, and cobalt-thiolate complexes, little is known about the formation of the corresponding dioxathiiranes in these systems (Scheme 41 and 42).[255−263] The nickel- and platinum-thiolate ligand photooxidations were conducted in aprotic solvents (*N,N*-dimethylformamide, acetonitrile, and DMSO), which paralleled the organic sulfide−$^1O_2$ reactions observed in aprotic solvents.[175] Kinetic data and trapping experiments suggest a mechanism analogous to the photooxidation of organic sulfides. The singlet oxygen oxidizes the thiolato group of the complex [Co(III)-$(en)_2$(S-cys)]$^+$($BF_4$)$^-$ (**103**) in water to give the corresponding sulfenato complex (Scheme 41A). The Pt(bpy)(bdt) [bpy = 2,2′-bipyridine (**104**); bdt = 1,2-benzenedithiolate (**105**)] is oxidized by the $^1O_2$ to form the sulfinate [Pt(bpy)(bdt$O_2$)] and disulfinate [Pt(bpy)(bdt$O_4$)] products (Scheme 41B,C). Nickel dithiolate complexes react with $^3O_2$ or $^1O_2$ to generate the corresponding sulfenate and sulfonate products through the persulfoxide **107** and dioxathiirane **108** intermediates (Scheme 42).

**4.2.2.3. Calculations.** *Structure.* A number of computational papers have focused on the reaction of $^1O_2$ with sulfides. Theory suggests that the dioxathiirane is a minimum on the potential energy surface. The calculated O−O and S−O bond distances are shown in Table 31. The dioxathiirane structures resemble each other in many of the basic geometric trends. Dioxathiirane O−O bond distances range from 1.562 to 1.527 Å, which depends on the structure and the level of theory; the dioxathiirane ring is unsymmetric, with two nonequivalent S−O bonds. The oxygen atoms occupy apical and equatorial positions, with the apical bonds longer than the equatorial ones by ca. 0.08−0.48 Å. A sample computed structure for dimethyldioxathiirane is given in Figure 4.

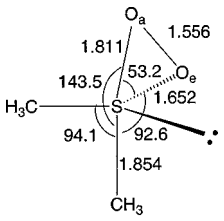
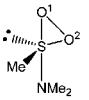
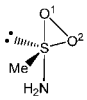



**Figure 4.** MP2/6-31G(d) computed structure of the dimethyldioxathiirane from ref 213. Bond lengths in angstroms; bond angles in degrees.

Dioxathiiranes have negative charges on the oxygen atoms. The atomic charges as predicted by the NBO method for a series of dioxathiiranes Me$S(O_2)$X (where X = Me, $NMe_2$, F, OMe, SMe, $NH_2$, NHMe, OH, and SH) indicate a greater negative charge at the apical oxygens ($O_1$) compared to the equatorial ones ($O_2$); see Table 32. MP2/6-31G(d) computed vibrational frequencies, IR intensities, and isotropic shifts of dioxathiirane $Me_2SO_2$ are shown in Tables 33 and 34.

*Energetics.* The transition state that connects the persulfoxide and the dioxathiirane is high in energy with a barrier of ∼20 kcal/mol; thus, the dioxathiirane is not expected to form as a reaction intermediate along this route. Once formed, the persulfoxide converts to the *S*-hydroperoxysulfonium ylide by a lower barrier process (∼10 kcal/mol). The strongest experimental evidence for the formation of dioxathiiranes comes from the use of electron-poor sensitizers in the photooxidation of sulfides. In contrast, the *S*-hydroperoxysulfonium ylide is in most cases the second intermediate formed in sulfide−$^1O_2$ reactions (Table 35).

**Table 32. Calculated Charges of the Sulfur and Oxygen Atoms in Dioxathiiranes[a]**

| Year | Structure | Natural Bond Order Charges | | | Method |
|---|---|---|---|---|---|
| | | S | $O^1$ | $O^2$ | |
| 1997 |  | 1.32 | -0.55 | -0.46 | MP2/6-31G(d) |
| |  | 1.45 | -0.55 | -0.46 | |
| |  | 1.59 | -0.51 | -0.41 | |
| |  | 1.34 | -0.47 | -0.39 | |
| |  | 1.52 | -0.52 | -0.44 | |
| |  | 1.20 | -0.52 | -0.42 | |
| |  | 1.45 | -0.55 | -0.46 | |
| |  | 1.45 | -0.55 | -0.46 | |
| |  | 1.52 | -0.52 | -0.43 | |
| |  | 1.22 | -0.51 | -0.41 | |

[a] Reference 213.

### 4.2.3. Dioxaselenirane and Dioxatellurirane

In 1994, the reaction of singlet oxygen with diaryl selenides and benzyl-substituted selenides was reported.[265] Surprisingly, the identities of the R groups of the starting selenides **111** were not explicitly stated in the publication.[265] The diaryl selenides yielded the corresponding selenoxides $Ar_2Se{=}O$, while the benzyl-substituted selenides afforded benzaldehyde and diselenide ArSeSeAr. Initial formation of a peroxyselenoxide **112** was proposed; however, the mechanism is not well understood. No mention was made of $R_2SeO_2$ dioxaselenirane **113** as a possible reaction intermediate (Scheme 43).

In 1976, a selenide photooxidation reaction was conducted in anhydrous methanol at room temperature.[266] Unfiltered light from an iodine lamp was employed, and Rose Bengal served as the sensitizer; the selenoxide yields are given in Table 36. No trapping reactions were conducted, although aryl selenides and selenoxides have been used as trapping agents[267] in other photooxidation processes.[268−270]

**Table 33. Calculated Vibrational Frequencies ($\tilde{\nu}$) and IR Intensities of Dimethyldioxathiirane[a,b]**

| $\tilde{\nu}$, $cm^{-1}$ | $I^c$ | $\tilde{\nu}$, $cm^{-1}$ | $I^c$ |
|---|---|---|---|
| 156 | 3.4 | 1083 | 39.0 |
| 235 | 0.1 | 1389 | 9.3 |
| 270 | 0.9 | 1422 | 8.1 |
| 326 | 5.5 | 1509 | 7.8 |
| 359 | 6.8 | 1517 | 2.0 |
| 366 | 6.5 | 1526 | 2.4 |
| 450 | 66.4 | 1536 | 19.5 |
| 649 | 54.8 | 3107 | 2.4 |
| 740 | 30.5 | 3123 | 3.7 |
| 807 | 56.9 | 3217 | 4.4 |
| 945 | 8.2 | 3226 | 3.0 |
| 963 | 9.2 | 3229 | 3.1 |
| 966 | 34.2 | 3258 | 0.8 |
| 1045 | 25.5 | | |

[a] Reference 231. [b] Calculated at the MP2/6-31G(d) level. [c] IR intensities.

**Table 34. Calculated Isotopic Shifts ($cm^{-1}$) of Selected Vibrations of Dimethyldioxathiirane[a,b]**

| $\tilde{\nu}$ | $\Delta\tilde{\nu}$ | $\Delta\tilde{\nu}$ | $\Delta\tilde{\nu}$ | $\Delta\tilde{\nu}$ |
|---|---|---|---|---|
|  |  |  |  |  |
| 156 | -4 | -2 | -6 | 0 |
| 326 | -3 | -2 | -5 | -1 |
| 359 | -3 | -3 | -6 | -3 |
| 366 | -1 | -3 | -4 | -1 |
| 450 | -7 | -15 | -21 | -1 |
| 649 | -2 | 0 | -2 | -5 |
| 740 | -6 | -2 | -8 | -7 |
| 807 | -15 | -4 | -18 | -8 |
| 945 | -4 | -8 | -28 | -1 |
| 963 | -14 | -17 | -18 | -4 |
| 966 | -3 | -4 | -4 | -1 |
| 1045 | -2 | -1 | -3 | -4 |

[a] Reference 231. [b] Calculated at the MP2/6-31G(d) level.

Little data exists on the dioxatellurirane, $R_2TeO_2$. Near-IR-absorbing tellurapyrylium dyes **114−118** have been suggested to form either $R_2Te^+OO^-$ pertelluroxide or $R_2TeO_2$ dioxatellurirane intermediates upon photooxidation with singlet oxygen,[271,272] but no distinction between the two intermediates was made (Scheme 44). The irradiation of the tellurapyrylium dyes was conducted in air-saturated aqueous solutions with unfiltered light from a tungsten bulb in the absence of trapping agents. A reaction between pertelluroxide or dioxatellurirane and substrate $R_2Te$ may take place, to account for the formation of the $R_2Te{=}O$ product, which is readily hydrated to the diol $R_2Te(OH)_2$. The tellurium-containing dyes **114−116** reacted with singlet oxygen 20−80 times faster than the corresponding selenium and oxygen derivatives **117** and **118**. The tellurium-containing dye **114** reacted two times faster with singlet oxygen than **116**. The impetus to study the photooxidation of the tellurapyrylium dyes was their potential use in photodynamic therapy (PDT). Theoretical studies on the photooxygenation of selenides and tellurides should be informative. The possible formation of $R_2SeO_2$ and $R_2TeO_2$ heterodioxiranes, their cleavage products, and Se-hydroperoxyselenium and Te-hydroperoxytellurium ylides should be of interest.

## 4.3. Cyclic and Ring-Opened Species

To assess the difference in stability between the various $XO_2$ heterodioxiranes, the computed energies between ring-

**Table 35. Calculated Energies for Intramolecular and Intermolecular Reactions of Dioxathiiranes[a]**

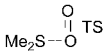
| Year | A | B | $\Delta E_{A \rightarrow B}$ | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|---|
| 2003 | $Me_2S^{\cdot+} + O_2^{\cdot-}$ |  | -158.6 | MP2/6-31+G(2d,p) | 184 | |
| | | | -151.2 | QCISD/6-31+G(2d,p) | | |
| |  |  | -1.7 | MP2/6-31+G(2d,p) | | |
| | | | 2.3 | QCISD/6-31+G(2d,p) | | |
| |  | $Me_2S + {}^1O_2$ | -11.1 | MP2/6-31+G(2d,p) | | |
| | | | -15.1 | QCISD/6-31+G(2d,p) | | |
| |  | $Me_2S + {}^3O_2$ TS | 9.9[b] | MP2/6-31+G(2d,p) | | |
| | | | 6.2 | QCISD/6-31+G(2d,p) | | |
| 1998 |  |  | -12.2 | B3LYP/6-31+G(d) | 212 | |
| | | | -7.4 | QCISD(T)/6-31+G(d) | | |
| | | | -5.9 | QCISD(T)/6-311+G(3df,2p) | | |
| |  | $Me_2S + {}^3O_2$ | -22.2 | B3LYP/6-31+G(d) | | 22 kcal/mol experimental value added to $^3O_2$ |
| | | | -13.9 | QCISD(T)/6-31+G(d) | | |
| | | | -3.5 | QCISD(T)/6-311+G(3df,2p) | | |
| |  |  | -87.6 | B3LYP/6-31+G(d) | | |
| | | | -85.9 | QCISD(T)/6-31+G(d) | | |
| | | | -101.8 | QCISD(T)/6-311+G(3df,2p) | | |
| |  |  | 3.0 | B3LYP/6-31+G(d) | | |
| | | | 0.9 | QCISD(T)/6-311+G(3df,2p) | | |
| |  |  | -6.7 | MP2/6-31G(d) | 176 | |
| | | | -7.2 | CCSD(T)/6-311+G(2df)[b] | | |
| |  | $Me_2S + {}^1O_2$ | -19.4 | MP2/6-31G(d) | | |
| | | | -3.2 | CCSD(T)/6-311+G(2df)[b] | | |
| |  |  | -94.5 | MP2/6-31G(d) | | |
| |  |  | -3.0 | MP2/6-31G(d) | | |
| | | | 1.4 | CCSD(T)/6-311+G(2df)[b] | | |
| | $Me_2S + {}^1O_2$ |  TS | 32.8[b] | MP2/6-31G(d) | | |
| | | | 11.2 | CCSD(T)/6-311+G(2df)[b] | | |
| |  |  TS | 19.0[b] | MP2/6-31G(d) | | |
| | | (Ring closure) | 20.6 | CCSD(T)/6-311+G(2df)[b] | | |
| |  |  TS' | 13.2[b] | MP2/6-31G(d) | | TS' represents a second pathway found to the dioxathiirane |
| | | (Ring closure) | 11.1 | CCSD(T)/6-311+G(2df)[b] | | |
| 1998 |  |  | -6.3 | MP2/6-31+G(d) | 176 | |
| | | | -0.1 | CCSD(T)/6-31+G(d)//MP2/6-31+G(d) | | |
| | | | 1.5 | QCISD/6-31+G(d) | | |
| | | | -7.9 | MP2/6-31++G(2d,p) | | |

**Table 35 (Continued)**

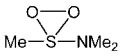
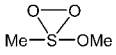
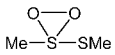
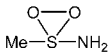
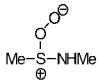
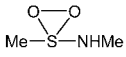
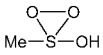
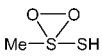
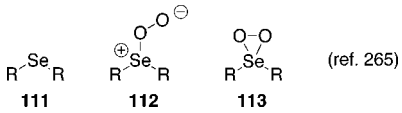
| Year | A | B | ΔE A→B | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|---|
| | | | -10.7 | MP2/6-31+G(2df,p) | | |
| | | | -10.6 | MP2/6-31+G(2df,p) | | |
| 1997, 1998 |  |  | -9.3 | MP2/6-31G(d) | 213, 214 | |
| |  |  | -31.1 | MP2/6-31G(d) | | |
| | | | -24.3 | CCSD(T)/6-31G(d) | | |
| | | | -30.1 | MP2/6-311G(2d) | | |
| |  |  | -13.6 | MP2/6-31G(d) | | |
| | | | -15.9 | CCSD(T)/6-31G(d) | | |
| | | | -14.4 | MP2/6-311G(2d) | | |
| |  |  | -19.7 | MP2/6-31G(d) | | |
| |  |  | -25.6 | MP2/6-31G(d) | | |
| |  |  | -12.2 | MP2/6-31G(d) | | |
| | | | -7.2 | CCSD(T)/6-31G(d) | | |
| | | | -10.8 | MP2/6-311G(2d) | | |
| |  |  | -11.8 | MP2/6-31G(d) | | |
| |  |  | -22.9 | MP2/6-31G(d) | | |
| | | | -16.7 | CCSD(T)/6-31G(d) | | |
| | | | -21.6 | MP2/6-311G(2d) | | |
| |  |  | -18.0 | MP2/6-31G(d) | | |
| | | | -10.9 | CCSD(T)/6-31G(d) | | |
| | | | -16.5 | MP2/6-311G(2d) | | |
| 1996 |  |  | 11.5 | MP2/6-31G(d) | 243 | |
| |  |  | 1.7 | | | |
| |  |  | -7.8 | | | |
| |  |  | -24.1 | | | |
| |  |  | -11.9 | | | |
| |  |  | -19.0 | | | |
| |  |  | -4.4 | | | |

**Table 35 (Continued)**

| Year | A | B | ΔE A→B | Method and Basis Set | Ref. | Comments |
|---|---|---|---|---|---|---|
| |  |  | -8.0 | | | |
| |  |  | -2.3 | | | |
| |  |  | TS 16.4[b] | | | |
| |  |  | TS 21.6[b] | | | |
| |  |  | TS' 13.2[b] | | 176 | TS' represents a second pathway found to the dioxathiirane |
| 1996 |  |  | -2.6 | PM3 | 242 | |
| |  |  | 17.6 | | | |

[a] Energies in kilocalories per mole. [b] Transition state energies.

**Scheme 43. Selenide, Peroxyselenoxide, and Dioxaselenirane**



(ref. 265)

**111** **112** **113**

**Table 36. Selenoxide Yields in the Reaction of Singlet Oxygen with Selenides ($R^1SeR^2$)[a]**

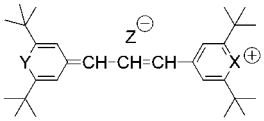
| $R^1$ | $R^2$ | Yield (%) |
|---|---|---|
| Ph | Me | 95 |
| Ph | $C_5H_7CH(OH)-CH(C_5H_7)$ | 70 |
| Me | $C_5H_{10}-CHMe$ | 85 |
| Me | $C_5H_7CH(OH)-CH(C_5H_7)$ | 70 |

[a] Reference 266.

closed and ring-opened structures shall be compared. With the exception of Sawaki's review,[3] no comparison of this sort exists for the $XO_2$ dioxiranes. The relative energetics of the $XO_2$ dioxiranes compared to O−X−O acyclic compounds are summarized in Table 37. Breaking of the O−O bond in $XO_2$ dioxiranes may lead, for example, to a nitro compound in the case of dioxaziridine (cf. entries 1−5, Table 37). In contrast, a Baeyer−Villiger reaction for some of the $XO_2$ dioxiranes may afford heteroatom-substituted esters or acids (cf. entries 6−11, Table 37). The above reactions are highly exothermic, favoring the acyclic structures rather than the corresponding $XO_2$ dioxiranes. We see that the energy difference is the greatest in the $SO_2$ system. Schaefer et al. have noted a decrease in this energy change for the heavier $XO_2$ dioxiranes ($H_2C$ > $H_2Si$ > $H_2Ge$ > $H_2Sn$ ∼ $H_2Pb$).[90] More systematic computational data is needed to recognize the factors that determine dioxirane stability. The data on the transition states for unimolecular O−O bond breaking processes in $XO_2$ dioxiranes are scarce.

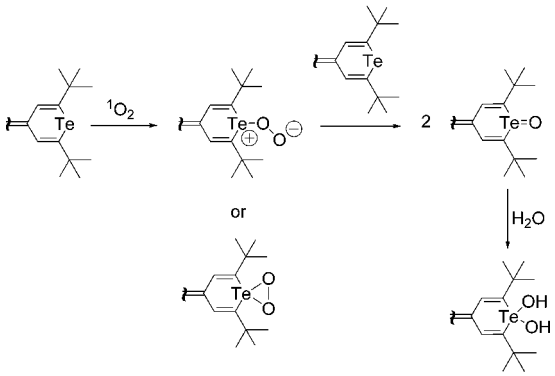
The calculated cyclization barriers for X−O−O into $XO_2$ dioxirane (X = RN, $R_2Si$, $R_2S$, and S) can be compared with the ∼19 kcal/mol cyclization barrier for carbonyl oxides to dioxiranes (Table 38).[273] Computational data is not available

**Scheme 44. Photooxidation of Tellurium-, Selenium-, and Oxygen-Containing Dyes**



(ref. 271)

| Structure | X | Y | Z |
|---|---|---|---|
| **114** | Te | Te | $BF_4^-$ |
| **115** | Te | Se | $ClO_4^-$ |
| **116** | Te | O | $ClO_4^-$ |
| **117** | Se | O | $ClO_4^-$ |
| **118** | O | O | $ClO_4^-$ |




for the acyclic X−O−O to cyclic $XO_2$ conversion (where X = $R_3P$, $R_2Se$, $R_2Ge$, $R_2Sn$, $R_2Pb$, $R_2Te$, and Se). Not for all $XO_2$ dioxiranes has an acyclic XOO counterpart been computationally found. For example, $R_3P$ appears to be such a case, for which many theoretical methods conclude that the acyclic $R_3POO$ species does not intervene in reactions of $R_3P$ with $^1O_2$. Sawaki has conducted B3LYP/6-31G(d) calculations of the reaction enthalpies and activation energies for the cyclization of X−O−O to cyclic $XO_2$ (where X = O, HN, $H_2C$, S, HP, $H_2Si$, Se, HAs, and $H_2Ge$).[3] A lower

**Table 37. Relative Energetics of the Heteroatom Dioxiranes Compared to Their Corresponding O−X−O Acyclic Counterparts[a]**

| entry | $XO_2$ cyclic structure | O−X−O acyclic structure | method and basis set | $\Delta E_{A\rightarrow B}$ | ref |
|---|---|---|---|---|---|
| 1 | $PhNO_2$ dioxaziridine | $PhNO_2$ nitrobenzene | B3LYP/6-31G(d) | −80.7 | 7 |
| 2 | $HNO_2$ dioxaziridine | $HNO_2$ nitro compound | B3LYP/6-31G(d) | −74.0 | 7 |
| 3 | $SO_2$ cyclic | O=S=O | B3LYP/cc-pVTZ | −99.8 | 111 |
| 4 | $HPO_2$ dioxaphosphirane | $HP(=O)_2$ | SCF-CEPA-1 | −79.6 | 165 |
| 5 | $Me_2SO_2$ dioxathiirane | $Me_2S(=O)_2$ sulfone | B3LYP/6-31+G(d) | −87.6 | 212 |
| 6 | $MeSi(O)_2Ph$ dioxasilirane | MeSi(=O)OPh ester | B3LYP/6-311++G(d,p) | −61.7 | 51 |
| 7 | $H_2SiO_2$ dioxasilirane | HSi(=O)OH acid | B3LYP/TZ2P-ECP | −81.0 | 90 |
| 8 | $H_2GeO_2$ dioxagermirane | HGe(=O)OH acid | B3LYP/TZ2P-ECP | −74.9 | 90 |
| 9 | $H_2SnO_2$ dioxastannirane | HSn(=O)OH acid | B3LYP/TZ2P-ECP | −70.6 | 90 |
| 10 | $H_2PbO_2$ dioxastilbirane | HPb(=O)OH acid | B3LYP/TZ2P-ECP | −71.8 | 90 |
| 11 | $H_2CO_2$ dioxirane | HC(=O)OH acid | B3LYP/TZ2P | −94.6 | 90 |

[a] Energies in kilocalories per mole.

**Table 38. Calculated Cyclization Barriers for the Reaction of Acyclic X−O−O to the Corresponding $XO_2$ Dioxiranes[a]**

| X−O−O acyclic structure | $XO_2$ cyclic structure | method and basis set | $\Delta E_{A\rightarrow B}$ | TS barrier | ref |
|---|---|---|---|---|---|
| trans HNOO nitroso oxide | $HNO_2$ dioxaziridine | SFC/6-31G+p | 4.2 | 43.8 | 44 |
| MeSi(OO)Ph silanone *O*-oxide | $MeSi(O_2)H$ dioxasilirane | B3LYP/6-311++G(d,p) | −49.6 | 0.8 | 51 |
| SOO acyclic | $SO_2$ cyclic | B3LYP/cc-pVTZ | −7.5 | | 111 |
| $Me_2SOO$ peroxysulfoxide | $Me_2SO_2$ dioxathiirane | MP2/6-31G(d) | −3.0 | 19.0 | 176 |
| $H_2COO$ carbonyl oxide | $H_2CO_2$ dioxirane | MP2/6-31G(d) | −28.6 | 19.1 | 273a |

[a] Energies in kilocalories per mole.

activation energy was predicted for the cyclization of X−O−O in higher-row elements, for example, $H_2Si$ < $H_2Ge$ < HP < $H_2C$ ∼ $H_2S$ < HN < O. The second-row elements have more prominent 1,3-dipoles and enhanced double bond character in the X−O bond, whereas the higher-row elements have less double bond character.[3] It has also been suggested that a larger difference in the electronegativity between the X and O atoms results in a lower rotation barrier of X−O−O, which facilitates cyclization to the dioxirane.[143b]

## 4.4. Intermolecular Reactions

Carbon-based dioxiranes may donate an oxygen atom to acceptor molecules, such as alkenes, phosphines, sulfides, and in some cases even saturated hydrocarbons.[4,6,274−276] Since $R_2CO_2$ dioxiranes have low strain energies (∼11 kcal/mol for R = Me; ∼16 kcal/mol for R = H), their enhanced oxidative reactivity[277] does not derive from the strain release in the oxygen-transfer process.[89,278−280] Instead, it is a result of the weak peroxide bond.[89,278−280] Some heteroatom-substituted $XO_2$ dioxiranes are able to transfer an oxygen atom to acceptor molecules (Table 39), but the literature is limited in comparison to $R_2CO_2$ dioxiranes.[4,6] An oxygen-transfer reaction of dioxaziridine $RNO_2$ or dioxasiliranes $R_2SiO_2$ has not yet been established. Oxygen-transfer studies of other $XO_2$ dioxiranes (X = $R_2Se$, $R_2Ge$, $R_2Sn$, $R_2Pb$, $R_2Te$, S, and Se) have also not been done.

**Alkenes.** Dioxaphosphirane $(o\text{-}MeOC_6H_4)_3PO_2$ has been used to convert alkenes to epoxides.[99] This alkene epoxidation appears to be a nonradical process. The mechanism of deoxygenation of $(o\text{-}MeOC_6H_4)_3PO_2$ does not involve a unimolecular fragmentation of an oxygen atom.[137] A dioxaphosphirane derived from 1-methyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane reacts supposedly with norbornene to give norbornene oxide.[154,155a] There are no data available that demonstrates an intermolecular oxygen transfer from an intermediary dioxaziridine to an alkene. A problem is that the alkene, e.g., 2,3-dimethyl-2-butene reacts with the ground state triplet nitrene to form an aziridine instead of a reaction with dioxaziridine to give the epoxide. An oxygen-substituted nitrene reaction exemplifies this, in which the triplet nitrene $CH_3ON$ (**119**) reacts with 2,3-dimethyl-2-butene to produce the aziridine **120** (Scheme 45).[10,23f] Acyclic nitroso oxides have been proposed to convert alkenes to epoxides **121**.[3] Nitroso oxide (e.g., PhNOO) and dioxaziridine (e.g., $PhNO_2$) will also rapidly oxidize additional triplet nitrene, since the reaction of nitrene with $^3O_2$ is slower.[39b] The highly reactive $PhN^{\bullet}OO^{\bullet}$ transfers an oxygen atom to toluene and anisole. At present, there is not sufficient data available for comparing possible oxygen-transfer reactions of dioxaziridines and nitroso oxides.

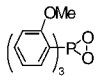
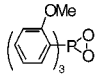
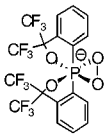
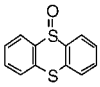
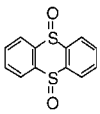
**Phosphorus- and Sulfur-Containing Reactants.** Dioxaphosphiranes are capable of delivering an oxygen atom to phosphines, sulfides, and sulfoxides.[136−140,142,143,154,155] Also, dioxathiiranes, e.g., $PhMeSO_2$ and $Bu_2SO_2$ (generated from sulfide radical cation−superoxide reactions), react presumably with phenyl sulfide to give phenyl sulfoxide.[184,185]

## 4.5. Synthetic Prospectives

Disappointingly, heteroatom-containing dioxiranes have not yet been found useful as oxidant alternatives for the popularly used carbon-based dioxiranes. Except for dioxaphosphirane, the $XO_2$ dioxiranes have only been of mechanistic interest, but their synthetic versatility remains still to be established; whereas the mechanistic aspects of $XO_2$ dioxiranes (X = $R_3P$, RN, $R_2Si$, and $R_2S$) are becoming better understood, little or no experimental evidence confirms the existence of the remaining $XO_2$ dioxiranes (X = $R_2Se$, $R_2Ge$, $R_2Sn$, $R_2Pb$, $R_2Te$, S, and Se).

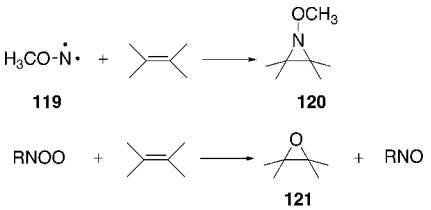
Early research on $R_2CO_2$ dioxiranes showed that they were formed in carbene−$O_2$ reactions under conditions (e.g., low-temperature matrix, combustion, etc.) that proved of little use in synthetic applications. The versatility of $R_2CO_2$ dioxiranes in synthetic organic chemistry emerged after the discovery of their generation from aqueous oxone−ketone reactions.[4,6] The use of oxone to generate dioxiranes from ketones was an important discovery. $R_2CO_2$ dioxiranes are generated from ketones in other ways, including the reaction with arenesulfonic peracids [generated from (arenesulfonyl)-imidazole/$H_2O_2$/NaOH],[272] peroxyimidic acid MeC(=NH)-

**Table 39. Bimolecular Reaction of $XO_2$ Dioxiranes**

| Year | Structure | Trap | Product | Ref. | Comments |
|---|---|---|---|---|---|
| 2006, 2003 |  | alkenes | epoxides[a] | 137 | |
| 2004 |  | $CH_2{=}CH_2$ |  | 63-73 | Tentative assignment of a silica gel-attached dioxasilirane |
| 2003 |  | $Ph_2S$ | $Ph_2SO$ | 184 | |
| 2001 |  | $Ar_3P$ | $Ar_3PO$ | 140 | |
| 1999 |  | $Ph_3P$ | $Ph_3PO$ | 136 | |
| 1993 |  | $Ph_2SO$ | $Ph_2SO_2$ (sulfone) | 143a | |
| 1993 |  | $Ar_2S$ | $Ar_2SO$ | 143a | |
| |  | $Ar_2SO$ | $Ar_2SO_2$ (sulfone) | 143a | |
| 1993 |  | norbornene | norbornene oxide | 154 | |
| |  |  |  (major product) | 154 | |
| |  | $Ph_2S$ | $Ph_2SO$ | | |
| |  | $Ph_2S$ | $Ph_2SO$ | | |

[a] Corresponding epoxides from norbornene, *cis*-stilbene, cyclohexene, and 1-octene.

**Scheme 45. Reaction of a Nitrene or Nitroso Oxide with an Alkene**




(refs. 8 and 10)

OOH (thought to be generated from $MeCN/H_2O_2$),[274] and possibly peroxynitrite.[275,276] Overcoming obstacles in generating experimentally useful concentrations of $R_2CO_2$ dioxiranes and in developing catalytic processes for their production was essential for synthetic applications to be realized.

No $XO_2$ dioxiranes have yet been generated from their corresponding X═O precursors, analogous to the preparation of $R_2CO_2$ dioxiranes from ketones. Attempts in this regard have been sparsely reported. For example, generating dioxaphosphirane $Ph_3PO_2$ by the oxidation of $Ph_3P{=}O$ with MCPBA or $H_2O_2$−trifluoroacetic acid−trifluoroacetic anhydride was unsuccessful.[2] A reaction of $^{18}O$-labeled dimethylsulfoxide with oxone failed to generate the $Me_2SO_2$ dioxathiirane.[1] In view of their considerable instability and tendency to form polymers, the reaction of oxone with $R_2Si{=}O$ silanones has not been explored, in an attempt to generate dioxasilirane.

## 5. Summary

Progress has been made in regard to the direct experimental evidence for the generation of $R_3PO_2$, $RNO_2$, and $R_2SiO_2$ dioxiranes. The $R_2SO_2$ and $R_2TeO_2$ dioxiranes are tentatively assigned based on indirect experimental methods; however, experimental evidence is lacking for the homologue dioxiranes $R_2SeO_2$, $R_2GeO_2$, $R_2SnO_2$, $R_2PbO_2$, $SO_2$, and $SeO_2$. Theoretical calculations predict that the $XO_2$ dioxiranes should persist under a variety of reaction conditions, but no computations have as yet been reported on the cyclic $SeO_2$.

The chemistry of $XO_2$ dioxiranes is still not well understood, and it is far less developed compared to that of $R_2CO_2$ dioxiranes,[4,6] a serious shortcoming for the effective use of $XO_2$ dioxiranes in synthetic chemistry. In this regard, the dioxaphosphiranes are the only $XO_2$ dioxiranes that

display synthetic utility in intermolecular (oxygen-transfer) reactions.

Challenging problems that await exploration include the following: (i) the discovery of methods to generate $XO_2$ dioxiranes from their corresponding X=O (monoxide) precursors, (ii) the development of asymmetric $XO_2$ oxygen-transfer reactions (precursors or catalysts bearing chiral substituents on X), (iii) the discovery of a possible synthetic advantage of $XO_2$ over $R_2CO_2$ in cases where X itself is a chiral center, (iv) the design of heterogeneous reactions to tether $XO_2$ dioxiranes onto solid surfaces to minimize unwanted bimolecular reactions, (v) the creation of "persistent" or at least sufficiently long-lived $XO_2$ dioxiranes to enable their isolation under the more common laboratory conditions by stabilizing the dioxiranes kinetically (e.g., utilizing sterically bulky substituents to shield the peroxide center or by caging dioxiranes in host molecules such as carcerands or dendrimers) or thermodynamically (e.g., electronic substituent effects to reduce the energy difference between reactants and intermediate), and (vi) assessment of the nucleophilic or ambiphilic oxidation character of the $XO_2$ dioxirane oxygen atoms.

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