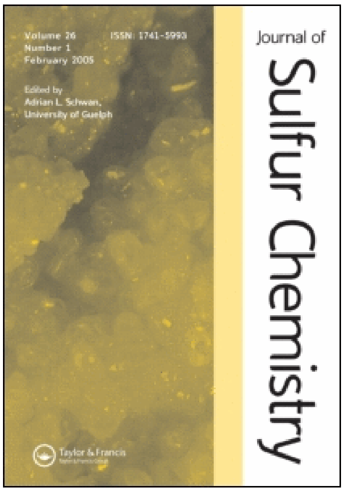

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Episulfoxides: Synthesis and Chemistry

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EPISULFOXIDES: SYNTHESIS AND CHEMISTRY

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This review summarizes recent publications on episulfoxides including aspects of their methods of preparation and chemistry. Special attention has been paid to a class of hindered episulfoxides which smoothly deliver sulfur monoxide which can be trapped by dienes.

Keywords: Episulfoxides, thiirane 1-oxide, sulfur monoxide, 1,3-dienes, trapping of SO

CONTENTS

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*Corresponding author.

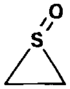
1. BACKGROUND ON EPISULFOXIDES

To our knowledge, there are two previous review articles on episulfoxides: one by Maccagnani[1] and another, in Japanese, by Kondo.[2] The most recent of these[1] appears to cover the literature up to 1980. Our work draws on references up to March, 1996 by CAS on-line researches.

In general, hetero three-membered ring compounds are highly reactive. This is because these compounds have high molecular strain and consequently, the hetero atom-carbon bond, which has a relatively low bonding energy, is easily cleaved. This principle has been applied to many organic transformations, such as reactions to extend a carbon chain by the means of an epoxide,[3] the synthesis of compounds which have two functional groups on the β-position using ring-opening of aziridine or episulfides[4] and ring-opening polymerization.[5]

Thiirane 1-oxide **1**, thiirane 1,1-dioxide **2** as well as the unusual compounds thiirene 1-oxide **3** and thiirene 1,1-dioxide **4** exist. In these compounds, the oxygen atom is not in the plane of the three-membered ring. Therefore, they show new reactivity which is totally different from that of an epoxide and they are expected to react quite differently.

In this series of compounds, **2** is well-known; it was synthesized by treatment of diazo compounds with sulfur dioxide.[6] Later, this functionality



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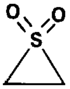

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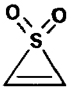


4

received attention as an intermediate in the Ramberg-Bäcklund reaction.[7] Compound **3** was first reported by Carpino,[8] in addition, compound **4** was synthesized by the same group.[9]

The synthesis of compound **1** has been also attempted by several groups. However, oxidation could not be stopped at **1** or **2** and only sulfonic acid derivatives[10] or polyethylene sulfone[11] resulted. The first synthesis of **1** appeared in a patent in 1955.[12] In 1965, Dittmer and Levy[13] reported the synthesis of dibenzoylstilbene episulfoxide. In the next year, Hartzell and Paige[14] reported the oxidation of ethylene episulfide by sodium periodate.

2. STRUCTURE OF EPISULFOXIDES

Ethylene sulfoxide (ESO) has received considerable attention with respect to its characterization because of its simple structure and symmetry. Microwave spectroscopic analysis,[15] NMR, IR and Raman spectra[16] have been reported. The structural parameters of ESO are shown in Table 1 with a comparison to dimethyl sulfoxide (DMSO).[17]

In ESO, the CSC angle is about half of that of DMSO because it is a part of the three-membered ring. The CSO bond angles in the case of DMSO is 45° and in the case of ESO is 67° as shown in Figure 1.

TABLE 1 Molecular Structures of ESO and DMSO

	ESO	*DMSO*
S-O	1.483 Å	1.477 Å
C-S	1.822 Å	1.810 Å
C-C	1.504 Å	—
O-S-C	111°01′	106°43′
C-S-C	48°46′	96°23′
C-C-S	65°77′	—
μ	3.72 D	3.96 D

FIGURE 1 CSO Bond Angles of ESO and DMSO.

In addition, Table 2 lists bond lengths and angles for the parent episulfoxide as well as data for the analogous episulfide, oxirane, episulfone, aziridine and phosphorane.

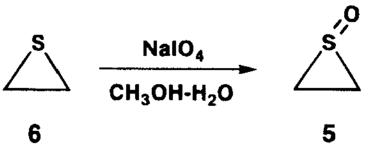
The sharp difference between the strain energy of cyclopropane and its heteroatom analogs is indicative of the higher degree of stabilization of the heterocyclic compounds by the π-electrons of the heteroatom. The above data shows that the bonding parameters of the three-membered ring of the episulfoxide is almost the same as that for the corresponding episulfide.

3. METHODS OF PREPARATION

3.1. Oxidation of Episulfides

3.1.1. With sodium periodate

The first clearly described episulfoxide was ethylene episulfoxide **5** obtained in 1966 by Hatzell and Paige[14] through periodate oxidation of the well-known episulfide **6** (Scheme 1).



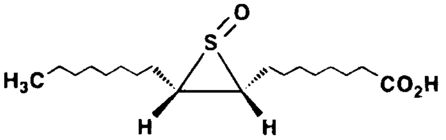
SCHEME 1

It is a low-yield reaction because the use of methanol as a solvent makes the extraction difficult. In addition, certain kinds of substituted episulfoxides are so unstable that they cannot be isolated. Furthermore, the sulfides of *cis*- and *trans*-9,10-octadecenoic acid and that of *cis*-13,14-docosenoic

TABLE 2 Bond Lengths (Å) and Bond Angles for the Three-Membered Ring Heterocycles

	X					
	O[18]	NH[19]	P[20]	S[18]	SO[15]	SO_2[21]
C-C	1.472	1.480	1.502	1.492	1.504	1.590
C-X	1.436	1.488	1.807	1.819	1.822	1.731
C-X-C	61°24′	—	47°24′	48°26′	48°26′	54°40′
C-C-X	59°18′	—	66°18′	65°48′	65°48′	62°40′

acid have been oxidized to the episulfoxides **7**, **8**, and **9**, respectively, with sodium periodate at room temperature.[22] As a result, this method may be considered as convenient for the preparation of long-chain fatty acid episulfoxides. Literature reports on the oxidation of short-chain episulfoxides reveal the use of only very low temperatures for such reactions.[14,23]



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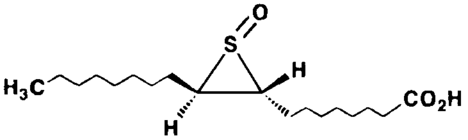

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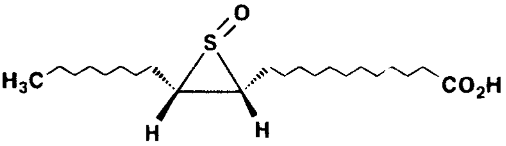

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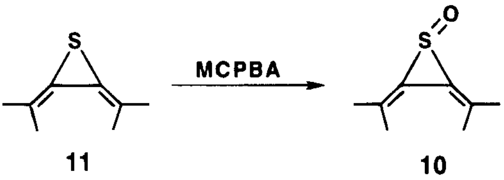
3.1.2. *With hydrogen peroxide*

Hardy and[24] reported that the H_2O_2-V_2O_5-*t*-BuOH system can be used as an oxidizing reagent; however, this method is not good for unstable episulfoxides. In addition, Dittmer and Levy[13] reported that the oxidation of dibenzoylstilbene sulfide with hydrogen peroxide in acetic acid gave the corresponding episulfoxide in good yield.

3.1.3. *With peroxy- or m-chloroperoxybenzoic acid*

Kondo and coworkers[25] reported a more general method of oxidation of episulfides; they performed the oxidation with the more versatile peroxybenzoic acid. Moreover, they[26] prepared and characterized several episulfoxides whose stereochemistry was assigned. In addition, they noticed that the stereochemical course of the oxidation is very sensitive to steric factors. For instance, the oxidation of *cis*-stilbene and styrene sulfide afforded exclusively the corresponding *anti*-episulfoxides with no trace of the *syn*.

Other authors,[27] found that in the reaction with propylene episulfide, peroxy- or *m*-chloroperoxybenzoic acid is the best oxidizing reagent and methylene chloride the best solvent. 2,3-Diisopropylidenethiirane 1-oxide **10** was also obtained from the oxidation of episulfide **11** with *m*-chloroperoxybenzoic acid (Scheme 2).[28]



SCHEME 2

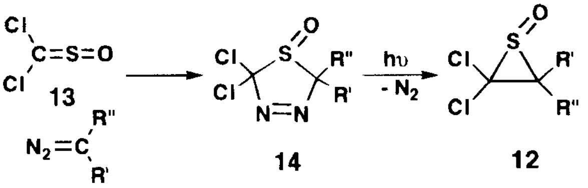
3.1.4. *With 3,3-dimethyldioxirane*

Recently, it was reported[29] that *cis*- and *trans*-2,3-di(*p*-methoxyphenyl)-2,3-diphenylethene sulfoxide were obtained from the corresponding episulfides upon oxidation with 3,3-dimethyldioxirane. Although the products could not be isolated and purified, they could be characterized spectroscopically.

3.2. Cycloaddition Reaction with Diazo Compounds

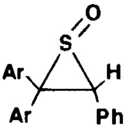
3.2.1. *With sulfines*

The possibility of a [2 + 3] cycloaddition of sulfines was first suggested by Zwanenburg and coworkers.[30] They obtained relatively stable dichloro episulfoxides **12** from the reaction of sulfine **13** with diazo compounds and proposed that they arise from the initially formed cycloaddition products **14** by nitrogen elimination (Scheme 3).



SCHEME 3

Treatment of diarylsulfines with aryldiazomethanes smoothly produces episulfoxides **15** in good yields.[31] The formation of **15** takes place by a nucleophilic attack of the diazo carbon at the sulfine sulfur providing a zwitterionic diazonium intermediate **16**, *via* an internal 1,3-elimination of nitrogen.



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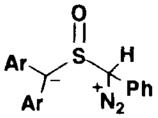
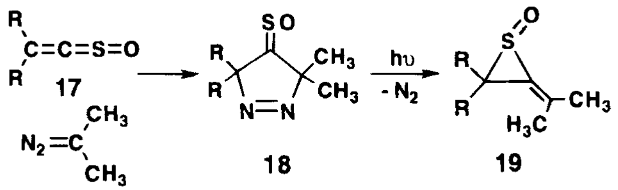


16

This proposed mechanism bears some analogy with the one that explains the formation of epioxides from ketones and diazo compounds. The mechanism in Scheme 3 was also substantiated,[32] however, the formation of **15** *via* the thiadiazoline 1-oxide intermediate **14** cannot be excluded.

3.2.2. With thioketene 1-oxides

Thioketene 1-oxides **17** react nicely with diazopropane to give good yields of adduct **18** resulting from the [2 + 3] cycloaddition across the carbon-carbon double bond of the heterocumulene. The photolysis of this adduct in benzene or carbon tetrachloride results in rapid elimination of nitrogen and formation of episulfoxide **19** (Scheme 4).[33]

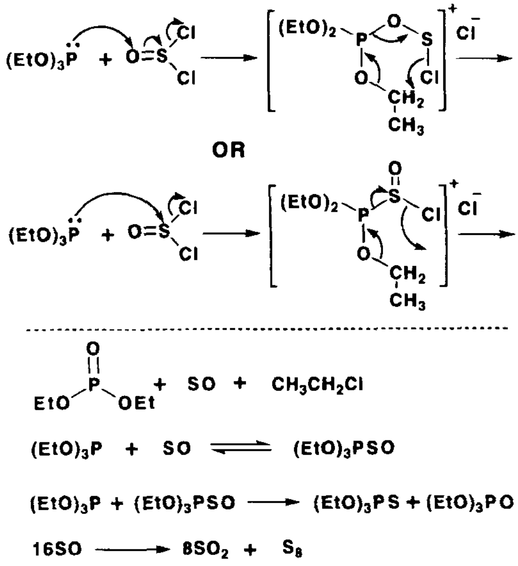


SCHEME 4

4. REACTIONS OF EPISULFOXIDES

4.1. Generation of Sulfur Monoxide

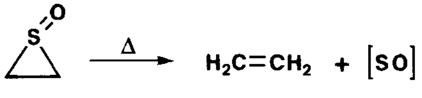
Sulfur monoxide has been postulated as a transient intermediate in several cases. The reaction of thionyl chloride with dimethyl sulfide,[34] 1,1-diarylethylenes,[35] or phenylacetylene[35] yield monochlorodimethyl sulfide, 1,1-diaryl-2-chloroethylenes, and 1-phenyl-1,2-dichloroethylene, respectively. Sulfur monoxide was suggested as a product; however, there was no evidence presented. Sulfur monoxide was speculated to be a primary reaction intermediate in the reaction of trialkyl phosphites with thionyl chloride (Scheme 5).[36] Formally the mechanism can be shown with either



SCHEME 5

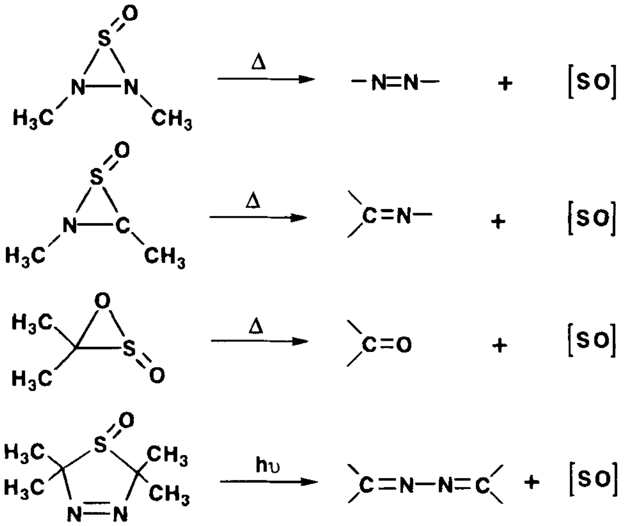
attack of phosphite on the oxygen *or* the sulfur. In either case the products (including S=O) logically follow *via* the mechanism shown.

Hartzell and Paige[14] showed that the pyrolysis of episulfoxides at temperatures over 100 °C delivers the corresponding olefins (Scheme 6). Sulfur monoxide was assumed to be a product and the whole process was followed using mass spectrometry.



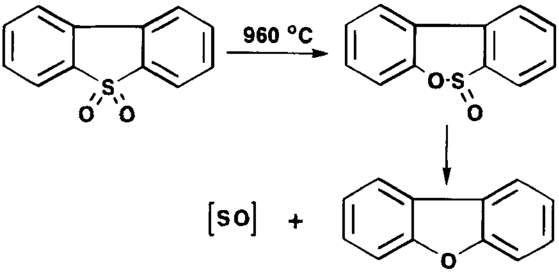
SCHEME 6

Saito[37] has suggested that sulfur monoxide is generated in the $^3\Sigma^-$ state in this decomposition, but his evidence was not convincing. Maccagnani and coworkers[38] found that in contrast to ethylene episulfoxide and alkyl substituted episulfoxides, the aryl substituted sulfoxides liberate sulfur monoxide at lower temperatures, with respect to ethylene episulfoxide, yielding almost quantitatively and stereospecifically the corresponding π-bonded molecules. In addition, they[39] demonstrated the transient formation of sulfur monoxide (Scheme 7).



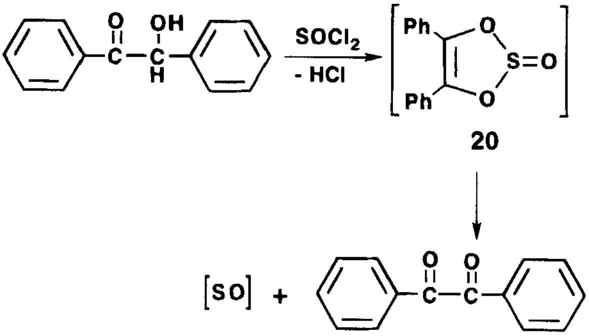
SCHEME 7

In the pyrolysis of dibenzothiophene 5,5-dioxide (resulting in dibenzofuran) a rearrangement with loss of sulfur monoxide was reported (Scheme 8).[40]



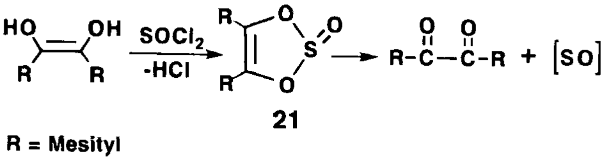
SCHEME 8

Also, sulfur monoxide was observed in the roasting of a rare earth sulfide in a nitrogen atmosphere at 300–800 °C.[41] Fieser and Okumura[42] suggested that sulfur monoxide is a product of the reaction of benzoin with thionyl chloride at room temperature giving benzil *via* the cyclic sulfite **20** (Scheme 9).



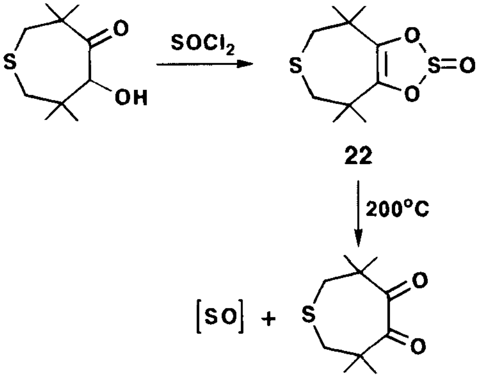
SCHEME 9

Moreover, the closely-related cyclic sulfite **21**[43] has been isolated and found to decompose to give benzil and sulfur monoxide (Scheme 10).



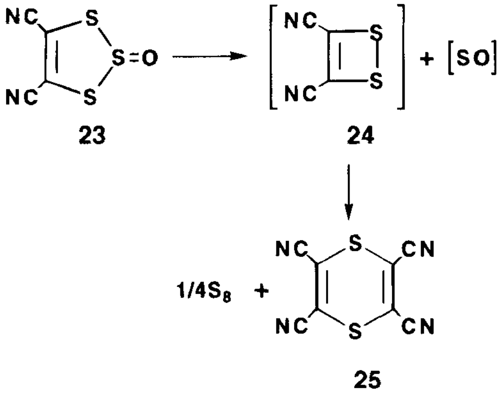
SCHEME 10

De Groot and coworkers[44] isolated sulfite **22** as a stable solid; subsequently, pyrolysis at 200 °C gave the diketone and presumably sulfur monoxide (Scheme 11).



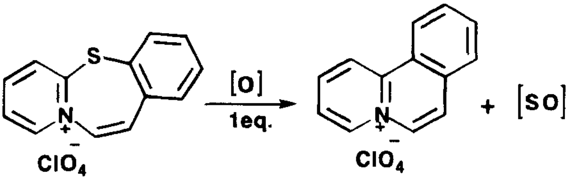
SCHEME 11

In addition, DeJongh and Van Fossen[45] reported that the predominant fragmentation pathway of *o*-phenylene sulfide is the loss of sulfur monoxide on either gas phase pyrolysis or electron impact. The kinetics of the decomposition of the trithiole 2-oxide **23** were carefully studied.[46] The generation of sulfur monoxide was postulated and the unstable intermediate dicyano-1,2-dithiete **24** led to the formation of dithiin **25** (Scheme 12).



SCHEME 12

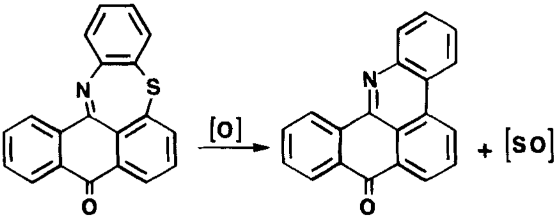
Oxidation of various thiazepinium salts **26**[47] with peroxyacetic acid led to the formation of phenanthridizinium salts **27** and sulfur monoxide (Scheme 13).



26 **27**

SCHEME 13

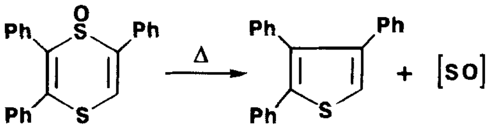
Similarly, Galt and coworkers[48] have also oxidized thiazepine **28** to obtain 8-oxodibenzo[*c,mn*]acridine (**29**) and presumably sulfur monoxide (Scheme 14).



28 **29**

SCHEME 14

The monosulfoxide of 2,3,5-triphenyldithiin **30** is unstable at 90 °C in toluene giving 2,3,4-triphenylthiophene and sulfur monoxide (Scheme 15).[49]



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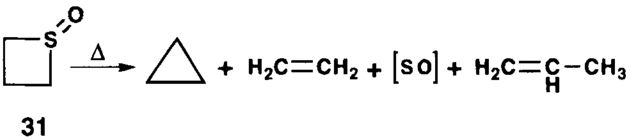
SCHEME 15

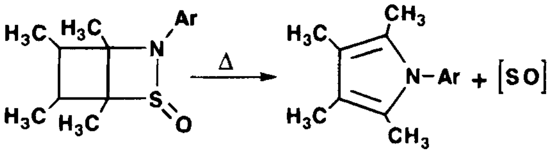
Dorer and Salomon[50] studied the photolysis of sulfoxide **31** resulting in formation of ethylene, propylene, cyclopropane and presumably sulfur monoxide (Scheme 16).



31

SCHEME 16

Sulfinamide **32** is thermally unstable at room temperature and readily loses sulfur monoxide, yielding quantitatively the corresponding pyrrole **33** (Scheme 17).[51]



32 **33**

Ar = *p*-nitrophenyl; 2,6-dimethylphenyl; phenyl

SCHEME 17

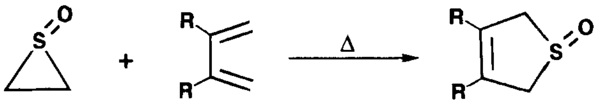
Recently, Glass and Jung[52] reported that thermal decomposition of *cis*- and *trans*-2,3-di(*p*-methoxyphenyl)-2,3-diphenylethene sulfoxide gave the corresponding olefin with moderate stereospecificity and presumably sulfur monoxide. It was also convincingly demonstrated[53] that sulfur monoxide is an intermediate species in the dechlorination of thionyl chloride with metals.

In addition, the isolation of simple derivatives of sulfur monoxide has been reported in the literature. Meuwsen and Gebhardt[54] isolated a compound which was probably the "diethyl acetal of sulfur monoxide". Goehring and Messner[55] reported that the material they isolated is the oxime of sulfur monoxide and a compound which is isomeric with it. The isolated compounds are unstable and decompose to a brown material thought to be a polymer. Garcia-Fernandez[56] prepared some inorganic selenium and tellurium compounds which may contain sulfur monoxide as a ligand.

4.2. With Dienes and Polyenes

There are many reactions in which hetero three-membered ring compounds are converted into olefins by thermal elimination.[57] Episulfoxide compounds also can be decomposed by heat and give sulfur monoxide and an olefin. The electronic ground state of sulfur monoxide has been shown to be a triplet by microwave optical analysis.[58] The sulfur monoxide molecule can be regarded as an analog of oxygen,[59] its half-life is so short that few reactions are known in which it has been detected.

Dodson and Sauers[60] were the first to show that sulfur monoxide, generated *in situ* by the thermolysis of episulfoxide **5**, could be trapped by the 1,3-dienes **34** and **35** to give 2,5-dihydrothiophene 1-oxides **36** and **37** (Scheme 18), (Table 3).



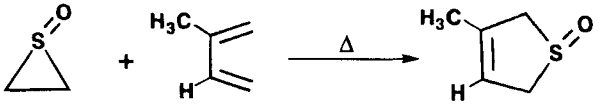
5

34 ; R = CH_3
35 ; R = C_6H_5

36 ; R = CH_3
37 ; R = C_6H_5

SCHEME 18

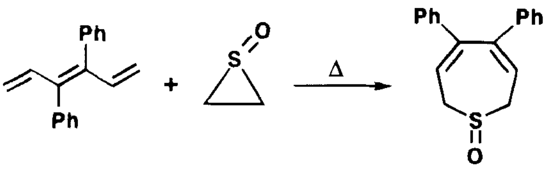
Equimolar amounts of isoprene **38** and episulfoxide **5** in refluxing toluene gave 2,5-dihydro-3-methylthiolene 1-oxide **39**,[61] in moderate yield (Scheme 19), (Table 3).



5 **38** **39**

SCHEME 19

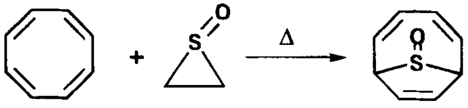
A low yield of 2,7-dihydro-4,5-diphenylthiepin 1-oxide **40** was observed when 3,4-diphenyl-1,3,5-hexatriene **41** reacted with episulfoxide **5** (Scheme 20), (Table 3).[62]



41 **5** **40**

SCHEME 20

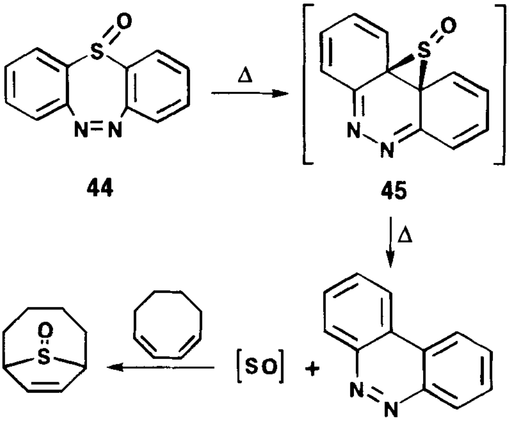
The thermal reaction of cyclooctatetraene **42** and episulfoxide **5** in boiling xylene resulted in the formation of the cycloadduct **43** to which the *anti*-configuration was assigned (Scheme 21), (Table 3).[63]



42 **5** **43**

SCHEME 21

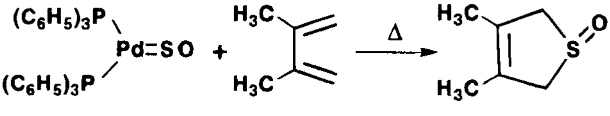
Sulfur monoxide was extruded from dibenzo[*b*,*f*][1,4,6]thiadiazepin 1-oxide (**44**) in refluxing chloroform and trapped with 1,3-dienes to give 2,5-dihydrothiophene 1-oxides (Scheme 22), (Table 3).[64] The same authors[64]



SCHEME 22

suggested that episulfoxide **45** could be a logical intermediate from the thermal decomposition of the sulfoxide **44** as shown in Scheme 22 below.

Recently, Heyke and coworkers[65] reported that the bis(triphenylphosphine)sulfur monoxide palladium complex **46** can be used as an SO source for the formation of 2,5-dihydro-3,4-dimethylthiophene 1-oxide **36** from 2,3-dimethyl-1,3-butadiene **34** (Scheme 23), (Table 3).



46 **34** **36**

SCHEME 23

A summary of the trapping experiments is presented in Table 3.

TABLE 3 Reaction of Conjugated Dienes with Sulfur Monoxide (SO)

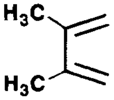
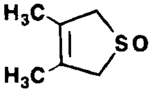
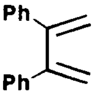
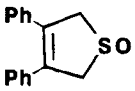
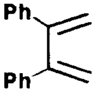
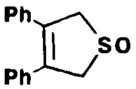
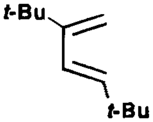
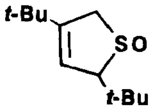
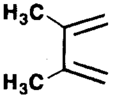
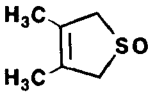
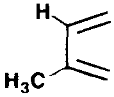
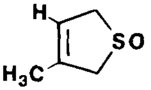
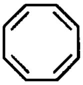
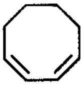
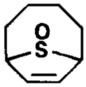
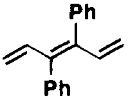
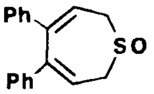
conjugated diene	*origin of SO*	*solvent*	*temp. (°C)*	*product*	*yield (%)*	*ref.*
	a	toluene	110		21	60
	a	toluene	110		25	60
	b	benzene	80		30	64
	a	toluene	110		40	60
	c	THF	65		25	65

TABLE 3 (*Continued*)

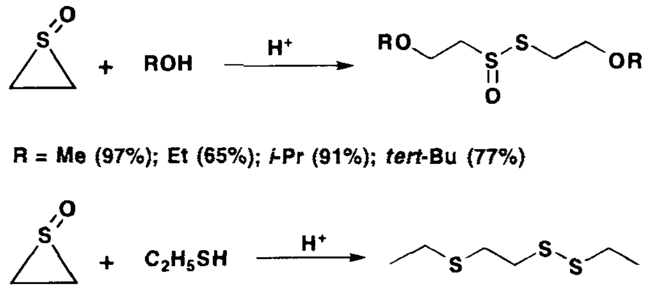
conjugated diene	*origin of SO*	*solvent*	*temp. (°C)*	*product*	*yield (%)*	*ref.*
	a	toluene	110		72	61
	a	xylene	140		30	63
	b	benzene	80		19	64
	a	*toluene*	110		35	62

a. ethylene episulfo[illegible] *b,f*][1,4,6]thiadiazepin 1-oxide (44); c. bis(triphenylphosphine) sulfur monoxide palladium (46).

4.3. With Alcohols and Thiols

4.3.1. In the presence of a catalyst

Episulfoxides react (acid catalyst)[66] through activation by protonation of the sulfoxide, followed by nucleophilic attack on a ring carbon. The sulfinic acid product is unstable and condenses to form various S-S bonded compounds (Scheme 24).

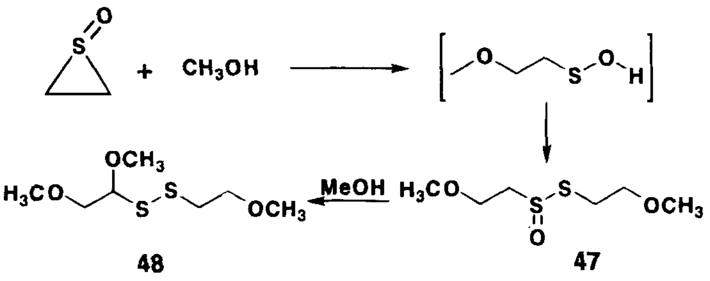


R = Me (97%); Et (65%); *i*-Pr (91%); *tert*-Bu (77%)

SCHEME 24

4.3.2. Without a catalyst

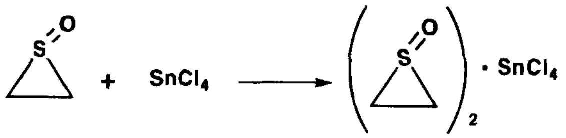
In 1974, Kondo and Negishi[67] discovered that the thermal reaction of ethylene sulfoxide in methanol without an acidic catalyst afforded thiosulfinate **47** as a primary product; this rearranged into disulfide **48** as a final product (Scheme 25).



SCHEME 25

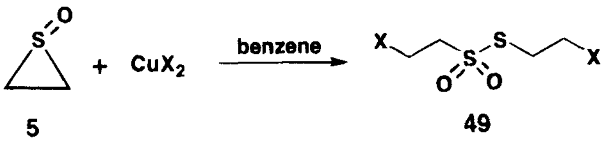
4.4. With Copper(II) Halides[68]

In general, sulfoxides form stable complexes with heavy-metal salts or transition metal complexes. However, the only complexation known for ethylene sulfoxide is a 2:1 addition adduct with tin(IV) chloride (quantitative yield) (Scheme 26).



SCHEME 26

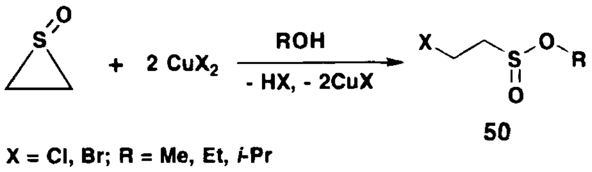
When ethylene sulfoxide **5** is added to a suspension of a copper(II) halide in benzene solution, the thiosulfonate **49** is obtained in good yield (Scheme 27).



X = Cl (66%); X = Br (65%)

SCHEME 27

When the reaction was carried out in methylene chloride containing a trace amount of methanol, methyl β-haloethanesulfinate **50** was obtained as the sole product, in good yield (Scheme 28).

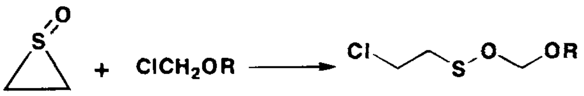


50

SCHEME 28

4.5. With α-Halo Ethers

Vilsmaier and Hloch[69] reported that the reaction of ethylene sulfoxide **5** with α-halo ethers gave only the sulfenate **51** (Scheme 29).

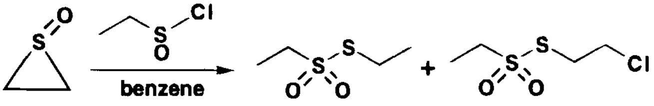


5 **51**

SCHEME 29

4.6. With Sulfinyl Halides

The reaction of ethylene sulfoxide **5** with ethanesulfenyl chloride in benzene was undertaken.[68a] The resulting product was a mixture of the thiosulfonates **52** (20%) and **53** (80%) (Scheme 30).

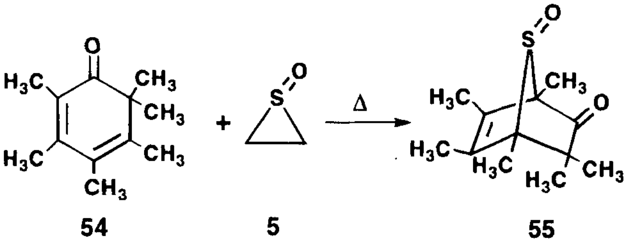


5 **52** **53**

SCHEME 30

4.7. With Dienones

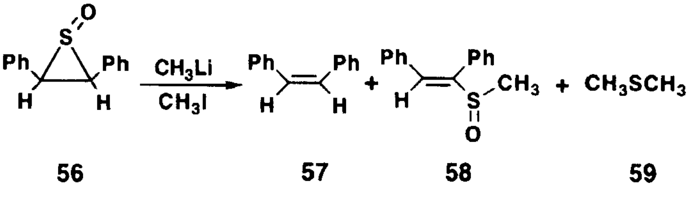
Murray and coworkers[70] reported that the reaction of ethylene sulfoxide **5** with an equimolar amount of 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone **54** afforded a good yield of 2,3,4,5,6,6-hexamethyl-7-thiabicyclo[2.2.1]hept-5-en-2-one 7-*anti*-oxide **55** (Scheme 31).



SCHEME 31

4.8. With Organolithium Compounds

The reaction of episulfoxides with organolithium compounds has been studied.[71] For example, the reaction of methyllithium with stilbene sulfoxide **56** in the presence of methyl iodide leads to the formation of stilbene **57** (with complete retention of configuration at the carbon skeleton) the methyl vinyl sulfoxide **58** and dimethyl sulfide **59** (Scheme 32).

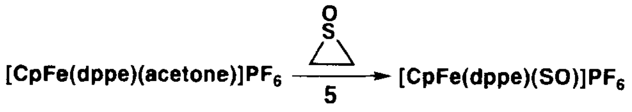


SCHEME 32

4.9. With Organometallic Compounds

Schenk and Müssig[72] reported that 1,2-bis(diphenylphosphinoethane)-η^5-cyclopentadienyl acetone iron(II) hexafluorophosphate **60** reacted with ethylene episulfoxide **5** to give 1,2-bis(diphenylphosphinoethane)-η^5-

cyclopentadienyl sulfur monoxide iron(II) hexafluorophosphate **61** in 63% yield (Scheme 33).

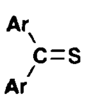


60 **61**

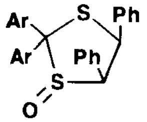
SCHEME 33

4.10. With Thioketones

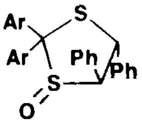
Thermolysis of stilbene sulfoxide **56** in the presence of a thioketone **62** resulted in the formation of the dithiolane 1-oxides **63** and **64** in good yield.[73]



62



63

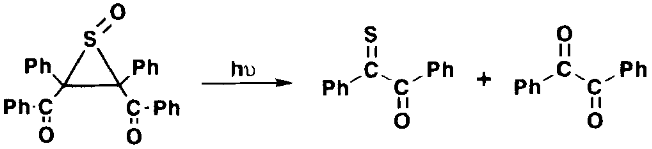


64

On the other hand, thermal decomposition of an alkyl substituted episulfoxide took place easily at room temperature to give a sulfinic acid ester through the formation of the sulfinic acid intermediates.[26]

4.11. Other Methods

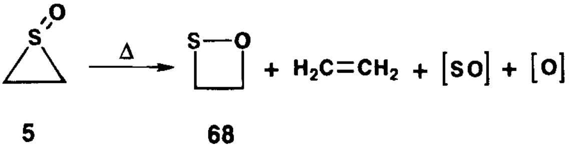
It was reported[74] that pyridine *N*-oxide can be deoxygenated by episulfoxides to give the corresponding pyridine, the alkene and sulfur dioxide. Dittmer and coworkers[75] studied the photolysis and pyrolysis of dibenzoylstilbene sulfoxide **65**. They found that benzil **66** and monothiobenzil **67** can be formed (Scheme 34).



65 **66** **67**

SCHEME 34

In addition, thermolysis of ethylene sulfoxide **5** has been studied[76] by flash vacuum thermolysis field ionization mass spectrometry[77] in the temperature range 1043–1404K (Scheme 35).



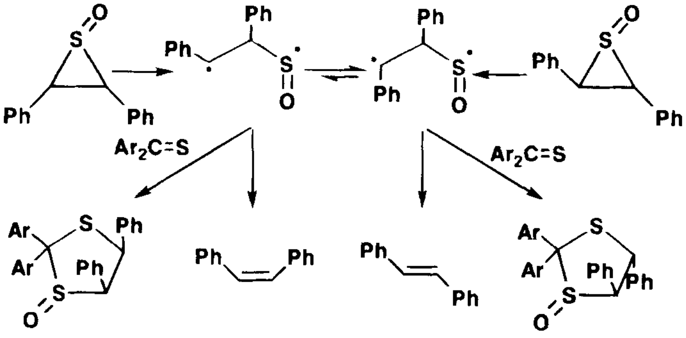
SCHEME 35

Evidence was presented that the ring enlargement product 1,2-oxathietane **68**, is formed alongside atomic oxygen extrusion and sulfur monoxide elimination. The extrusion of atomic oxygen from organic sulfoxides has been previously reported.[78]

5. MECHANISM OF THERMAL DECOMPOSITION OF EPISULFOXIDES

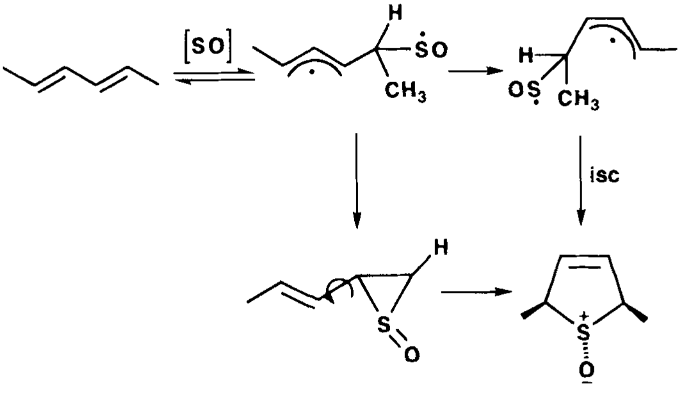
Hartzell and Paige[14] favor a two-step mechanism in which a dipolar intermediate loses its stereochemical integrity prior to decomposing into sulfur monoxide and an olefin. In contrast, Baldwin and coworkers[79] observed that the stereochemistry of the decomposition decreases with increasing temperature and favored a biradical intermediate in the decomposition. Other authors[80] also observed that the temperature of decomposition has a strong influence on the stereochemical course of the elimination of the sulfur monoxide. Kondo and coworkers[73] concluded that the thermal fragmentation of episulfoxides to afford an olefin and sulfur monoxide proceeds stepwise through a biradical intermediate (Scheme 36).

Finally, Lemal and Chao[81] examined the stereochemistry of sulfur monoxide addition to the three isomeric 2,4-hexadienes. With each of the dienes, a mixture of isomeric thiophenes was obtained with a high degree of stereoselectivity and regiospecificity. The authors[81] ruled out a direct attack of episulfoxide on the diene because they noticed that the rate of decomposition of episulfoxide is not increased by raising the diene concen-



SCHEME 36

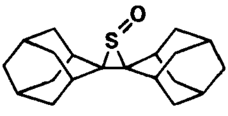
tration. Because the reaction proceeds at essentially the same rate in acetonitrile as in toluene, the authors favored a biradical mechanism of extrusion of sulfur monoxide (Scheme 37).



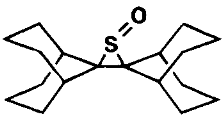
SCHEME 37

In the above Scheme, rotation about the partial double bond C-3 and C-4 and intersystem crossing (isc) must occur before a product can form. They suggested that the stereoselectivity in these reactions may result from the torsional stiffness of the C-2, C-3 bond (estimated 6–10 kcal mole^{-1} barrier) due to the interaction between the C-3 p-orbital and the sulfur monoxide group. Such interaction, whether direct[14,79] or indirect, may lower the torsional barrier for the C-3, C-4 bond. All in all, the literature results generally support a biradical mechanism of extrusion of sulfur monoxide.

We have reported on some improved methods to deliver sulfur monoxide by way of episulfoxide **69**[82] and episulfoxide **70**.[83] In general, the results reveal that these hindered episulfoxides are most effective as S=O transfer agents.

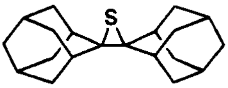


69

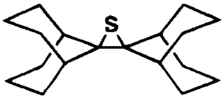


70

Episulfoxides **69** and **70** can be prepared by oxidation of the episulfides **71** and **72**, respectively, with *m*-CPBA in high isolated yield (92%).



71



72

The episulfides **71** and **72** can be synthesized by reaction of triphenylmethanesulfenyl chloride **73** (or its thio **74** and dithio **75** homolog) with the corresponding olefins in an average yield of 90%. The structures of the episulfides **71** and **72** were established by ^{1}H and ^{13}C NMR as well as by mass spectrometry.

$(C_6H_5)_3C{-}S{-}Cl$ **73**

$(C_6H_5)_3C{-}S{-}S{-}Cl$ **74**

$(C_6H_5)_3C{-}S{-}S{-}S{-}Cl$ **75**

Episulfides **71** and **72** prepared in this manner can be stored at room temperature for months with no apparent decomposition or loss in yields during their oxidation to the corresponding episulfoxides. Thermal decomposition of episulfides **71** and **72** in refluxing ethyl acetate for 15 h under a nitrogen atmosphere afforded the corresponding olefins in a yield of 98% along with elemental sulfur (68%). In addition, **71** and **72** were completely decomposed when the mixture was refluxed for 2 h in toluene solution.

When the above reactions were carried out in the presence of 2,3-dimethyl-1,3-butadiene **34**, the same products were obtained (elemental sulfur and olefin). No evidence was found for the trapping of diatomic sulfur by diene **34**. It would appear that the concatenation mechanism of sulfur loss from episulfides is operative.[84]

6. SYNTHESIS OF EPISULFOXIDE 69

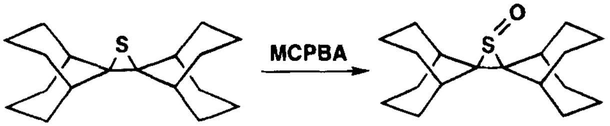
Episulfoxide **69** was prepared by *m*-CPBA oxidation of episulfide **70** in methylene chloride solution under a nitrogen atmosphere at –78 °C. Recrystallization from *n*-pentane gave a pure product of episulfoxide **69** in an isolated yield of 99% (Scheme 38).

71 **69**

SCHEME 38

7. SYNTHESIS OF EPISULFOXIDE 70

Episulfoxide **70** was prepared in the same way as **69**. The episulfide **72** was treated with *m*-CPBA in methylene chloride solution at –78 °C under a nitrogen atmosphere to give the episulfoxide **70** in high isolated yield (98%) (Scheme 39).



72 **70**

SCHEME 39

The structure of the episulfoxides **69** and **70** was established by ^{1}H and ^{13}C NMR as well as by mass spectrometry. In addition, the X-ray crystallography of episulfoxide **69** was reported[82] for the first time.

In the literature there are only three reaction systems reported which generate and trap sulfur monoxide in the presence of 1,3-dienes; the yields are generally low. Moreover, these methods have some limitations. The major problem in the case of the Dodson,[60,62] Lemal,[61] Chao[63] and Heyke[65] procedures is that ethylene episulfoxide **5** is unstable at room temperature, has a vile odor and causes burns on contact with the skin.

In the case of the procedure of Chow[64] the most important limitation is in the preparation of sulfoxide **44**; in addition, the authors could not isolate episulfoxide **45** which they thought could have been obtained from the thermolysis of sulfoxide **44** (Scheme 22). The yield of the trapped adduct was low in each case. It is noteworthy to mention that *trans*-2,3-diphenylethene episulfoxide has been shown to transfer sulfur monoxide to ylides in low (11–19%) yield.[85]

However, the episulfoxides **69** and **70** are very stable even if they are exposed to the atmospheric moisture for several days; they are crystalline and easy to prepare. In addition, we found that sulfur monoxide can be easily generated and trapped smoothly in very good isolated yields to form 2,5-dihydrothiophene 1-oxide through thermal decomposition of **69** and **70** in the presence of 1,3-dienes.

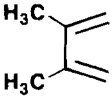
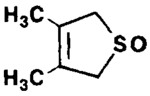
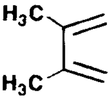
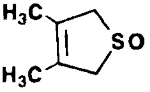
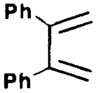
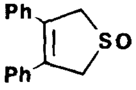
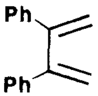
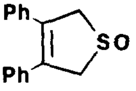
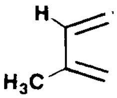
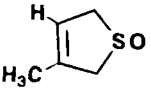
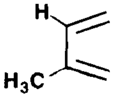
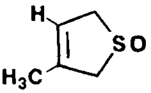
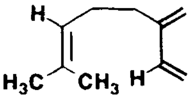
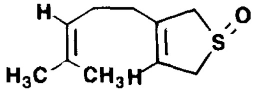
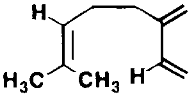
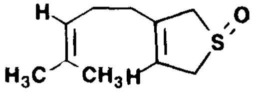
The general procedure used for the reaction of episulfoxides **69** and **70** with 1,3-dienes (2,3-dimethyl-1,3-butadiene **34**, 2,3-diphenyl-1,3-butadiene **35**, isoprene **38** or myrcene **76** is as follows: a solution of the diene and the episulfoxide in an appropriate solvent is refluxed for a certain time under a nitrogen atmosphere. The reaction can be followed by thin layer chromatography using 15 to 25% ethyl acetate in hexane as eluent.

The first fraction is isolated in near quantitative yield with the same eluent and identified as the corresponding olefin. By elution with methanol the second fraction is isolated and identified as the corresponding 2,5-dihydrothiophene 1-oxides as oily, pure products. The isolated yields (Table 4) are quite high compared to those in the literature for the decomposition of other episulfoxides.

Acknowledgments

We thank the Natural Sciences and Engineering Research Council of Canada and F. C. A. R. (Québec) for financial support of this work.

TABLE 4 Reactions of Episulfoxides **69** and **70** with 1,3-Dienes

conjugated diene	*origin of SO*	*solvent*	*temp. (°C)*	*product*	*yield (%)*
	a	toluene	110		80
	b	toluene	110		82
	a	toluene	110		70
	b	toluene	110		73
	a	toluene	110		69
	b	toluene	110		72
	a	toluene	110		52
	b	toluene	110		55

a = episulfoxide **69**
b = episulfoxide **70**

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