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The Sulfur Diatomics: Generation and Trapping Chemistry

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Aspects of the generation and trapping of diatomic sulfur (S_2) and sulfur monoxide (SO) are reviewed with special emphasis on recent work.

INTRODUCTION

The major, symmetric diatomic molecules (H_2 , N_2 , O_2) have been known for over 200 years.¹ While Cl_2 was produced in 1630, the other halogen diatomics are discoveries of the 19th century. The unsymmetrical diatomics are many in number, with the oldest being muriatic acid (HCl) which dates from as far back as A.D. 900, with clear references to it as *aqua regia* by the year 1200; the discovery of HF even predates that of N_2 .¹

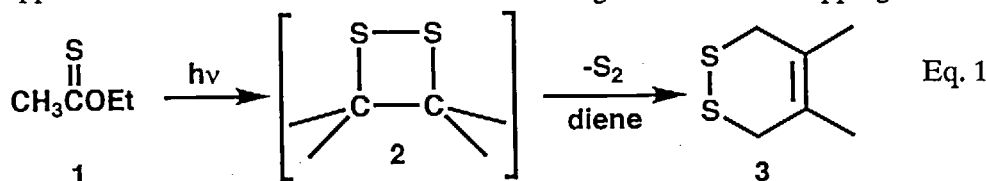
One of the most interesting mixed diatomics in recent years has been nitric oxide (NO) which is responsible for numerous biological effects as a neurotransmitter and likely has roles in memory and learning.² Over 3500 papers were published on this molecule in 1995 alone. Considerable research has been carried out on S-nitrosothiols as transporters of NO .^{2c}

DIATOMIC SULFUR

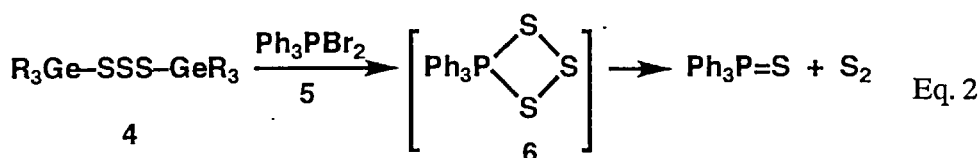
For the past several years, we have been interested in finding methods to generate and study the chemistry of the two main sulfur diatomics, S_2 and SO. Diatomic sulfur has been known for about half a century,³ its electronic structure explored⁴ and the dissociation energy determined (101.7 kcal/m)⁵. It is the predominant sulfur allotrope above 720 °C and the main component of the vapor above FeS_2 at 850 °C. The stability of this gas at high temperature is considerable and the ground state of the molecule is a triplet.¹

Recently, S_2 was detected by the Hubble telescope in Jupiter's dark spot resulting from the impact of the G fragment of the Comet Shoemaker-Levy 9.⁶ One unusual invention apparently involving diatomic sulfur, is a device called "The Sulfur Lamp" which produces bright white light by exposing a small amount of sulfur to microwave radiation.⁷

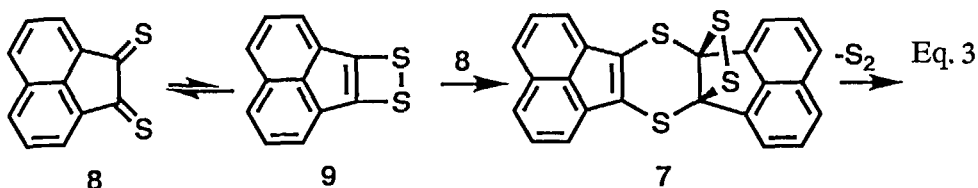
In 1975, Jahn and Schmidt⁸ reported a photolysis reaction of thione ester 1, portraying S_2 as being lost from a probable intermediate 2. There was a variety of sulfurated products formed in this reaction and the yield of trapped disulfide 3 was only 2% (Eq. 1). It is not fully clear whether this was a clean trapping of the elusive S_2 , or a result of some other process. Nonetheless, it appears to be the first record of diatomic sulfur generation *and* trapping.



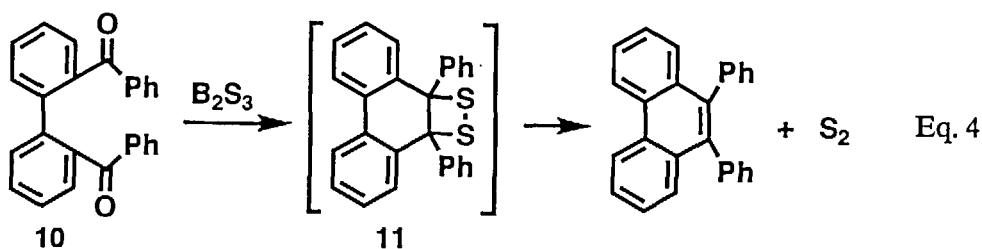
In spite of many synthetic explorations concerning this molecule,⁹ relatively little was accomplished in terms of its formation and general synthetic utility until the work of Steliou in 1984.¹⁰ His method of delivery of S_2 parallels a procedure for the generation of singlet oxygen. When germanium trisulfide 4 is treated with phosphine derivative 5, a trithiazozonide 6 intermediate is likely produced which apparently decomposes into stable products and delivers S_2 (Eq. 2); this reactive species is trapped by a variety of dienes in good, overall yield.



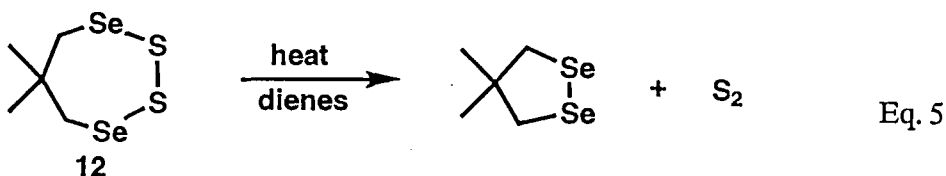
Since this seminal discovery, a variety of groups have reported methods to deliver S_2 ; of considerable interest are the varied molecules that have served as precursors. In 1985, Cava reported¹¹ that S_2 was lost from the decomposition of a possible transient 1,2-dithietane 7 likely formed from a Diels-Alder addition of dithione 8 *via* its 1,2-dithiete tautomer 9 (Eq. 3); trapping experiments were not carried out.



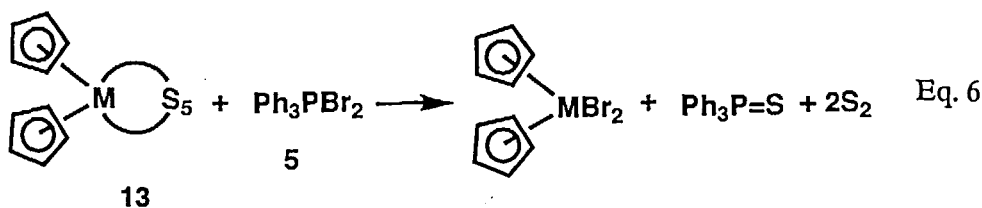
A very inventive approach is also due to Steliou¹² who showed in 1987 that biphenyl derivative **10**, when sulfurated with B_2S_3 (generated *in situ*), effectively delivers S_2 to dienes likely *via* dithietane intermediate **11** (Eq. 4). He was able to trap diatomic sulfur with four dienes in yields of *ca.* 75%.



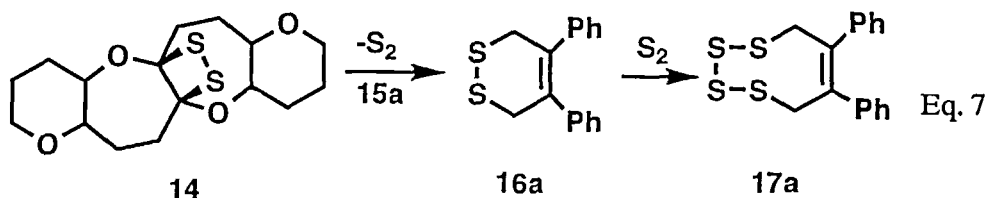
Also in 1987, Schmidt reported¹³ the decomposition of tetrachalcogenide **12** which delivered S_2 to several dienes in *ca.* 50% isolated yield (Eq. 5). In addition, Ando¹⁴ prepared a precursor to anthracene endodisulfide and was successful in obtaining diene trapping.



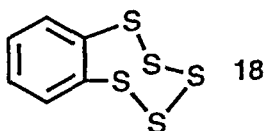
Using different metallocene pentasulfides **13** in combination with dibromide **5**, our group showed¹⁵ that diatomic sulfur could be trapped in low to moderate yield (Eq. 6). This form of decomposition is a parallel process with the one in the first Steliou paper.¹⁰



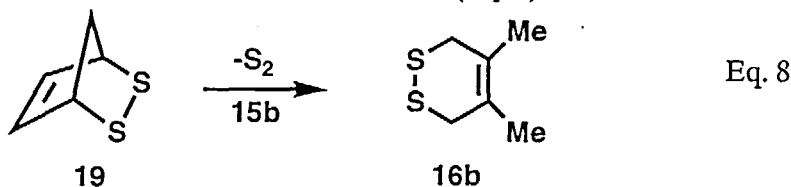
One interesting compound which delivers S_2 was reported by Nicolaou.¹⁶ Dithiatopazine (**14**) possesses (crystal structure/theoretical calculations) a stable 1,2-dithietane ring which, when heated with 2,3-diphenyl-1,3-butadiene (**15a**), delivers one S_2 unit to **15a** affording disulfide **16a** in 25% yield; apparently **16a** adds another S_2 fragment giving cyclic tetrasulfide **17a** in an isolated yield of 28% (Eq. 7).



A cyclic polysulfide **18** was used to transfer S_2 to dienes in yields averaging 55%.¹⁷ There have been a number of related molecules synthesized by several groups¹⁸ which appear to have potential to serve as sources of S_2 ; however, trapping experiments were not carried out.

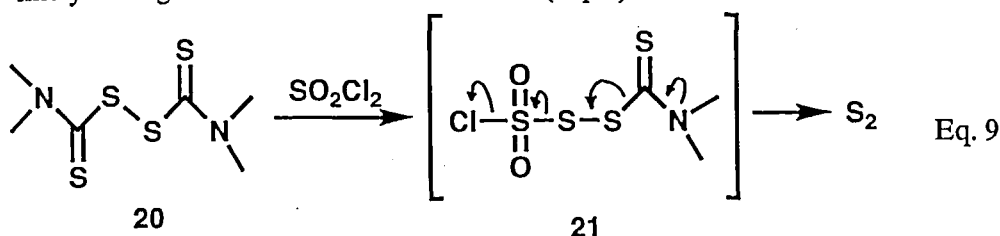


In 1992, Gilchrist reported a Diels-Alder reversion of bicyclic disulfide **19**. This molecule was independently prepared by a dithiol oxidation; it is formally the Diels-Alder adduct of cyclopentadiene and S_2 . Structure **19** undergoes a cycloreversion to transfer S_2 to diene **15b** (2,3-dimethyl-1,3-butadiene) in low yield giving cyclic disulfide **16b** and tetrasulfide **17b** (Eq. 8).¹⁹

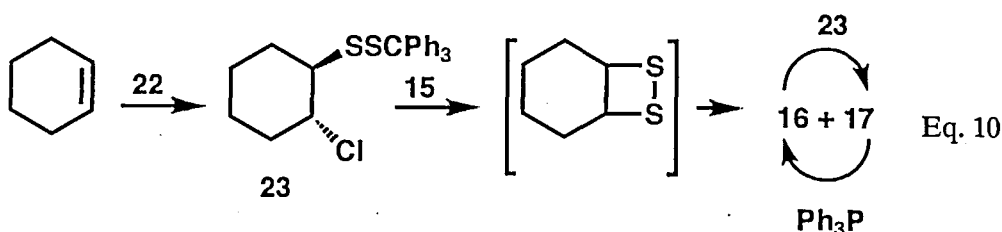


We have been able to generate a variety of diatomic sulfur precursors of quite diverse structure. Thiuram disulfide **20** was observed by Cava²⁰ to lose sulfur (apparently by a diatomic fragment) upon chlorination with SO_2Cl_2 . We

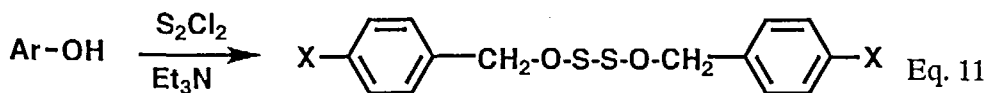
repeated this chemistry with appropriate diene traps and found evidence of diatomic sulfur loss (however, a low yield of trapped products) from the reaction, likely through chlorinated intermediate 21 (Eq. 9).²¹



A potentially useful precursor has recently been discovered, involving an opportunity to access 1,2-dithietanes. We have found²² when triphenylmethanethiosulfonyl chloride 22 is added to a variety of alkenes, *trans*-1,2 adduct 23 is formed in high yield. When 23 is warmed in the presence of a diene trap, cyclic di- and tetrasulfides 16 and 17 are formed. The tetrasulfide is the dominant S₂ addition product, but can be conveniently converted to the disulfide (*vide infra*) by treatment with triphenylphosphine, (Eq. 10). In addition, when trapped product 16 is warmed with adduct 23, tetrasulfide 17 results.



The most recent example of diatomic sulfur transfer reagents are the alkoxy disulfides 24.²³ These molecules have been known for over 100 years²⁴ but have been given relatively little attention since the work of Thompson in 1965.²⁵ We have prepared a series of them by a modified procedure (Eq. 11) in isolated yields of *ca.* 85% (Table 1).



Ar = *p*-x-C₆H₄

24

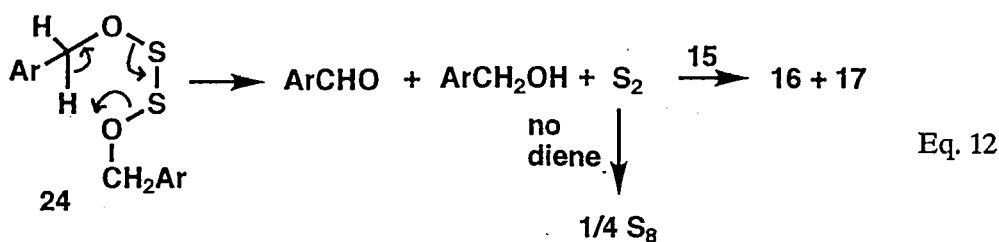
These compounds can be stored for months at *ca.* -15 °C with no measurable decomposition. The nitro derivative **24b** is stable in solution to *ca.* 70 °C at which point it begins to decompose forming elemental sulfur, *p*-nitrobenzyl alcohol and *p*-nitrobenzaldehyde in high yield.

Table 1

ROSSOR 24	X	yield ^a	mp °C
a	H	88	50-51
b	NO ₂	90	92-93
c	Cl	86	45-47
d	OMe	62 ^b	34-36
e	Me	82	liquid

^a Isolated yields after flash chromatography/recrystallization; **6d** was unstable on silica gel.

The most likely thermal decomposition mode is displayed in Eq. 12 and strongly suggests the loss of ¹S₂. By using an excess of reagent **24** (usually **24b**), yields of over 75% of trapped disulfide **16a,b** are ultimately isolated.^{23,26} Under the conditions of this reaction, (toluene, 100-105 °C) when dienes are heated with elemental sulfur, neither adducts **16** or **17** are detected. This experiment demonstrates that the trapped products are not likely the result of a transfer of sulfur fragments by "activated sulfur".²⁷



Overall, this technique of S₂ transfer appears to be effective and relatively easy to carry out. Our future work in this area is directed towards finding other alkoxy disulfides which will decompose at lower temperatures in order to extend the scope of this chemistry.

Of special interest is the structure of this class of compound **24**. Steudel reported^{25b} the first detailed analysis of this class by executing a gas-phase structure of dimethoxydisulfide (dimethoxydisulfane), **25** by electron diffraction.

We have carried out an x-ray structure analysis of **24b** and **24c**.²⁸ A few of the relevant bonding parameters are collected in Table 2; structure **24b** is displayed below.

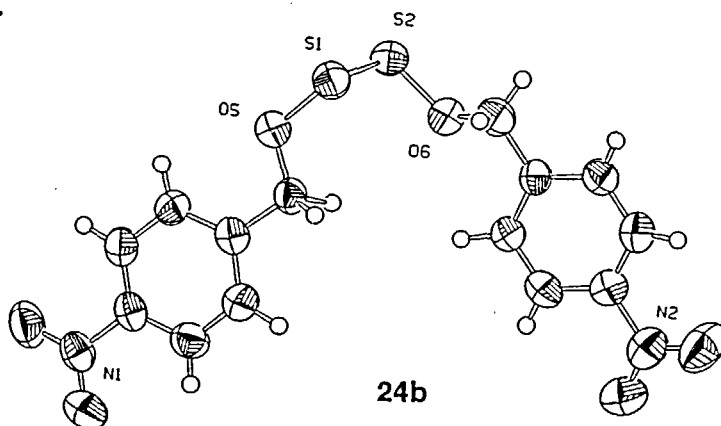


Table 2			
ROSSOR	S-S Å	O-S-S °	O-S-S °
24b ²⁸	1.968	85.6	107.3, 107.8
24c ²⁸	1.932	76.8	108.9
25 ^{25b}	1.960	91	108.2
25 ^{25c}	1.972	81.5	108.2

Of note is the short sulfur-sulfur bond length in these molecules (1.93 - 1.97 Å).²⁸ This is to be compared to the length of a typical disulfide bond of 2.02-2.06 Å.²⁹ The S-S bond in diatomic sulfur is 1.89 Å³⁰ with the shortest known S-S length of 1.86 Å in F₂S=S.³¹ Comment is warranted on this "branch-bonded" form of sulfur-sulfur linkage.

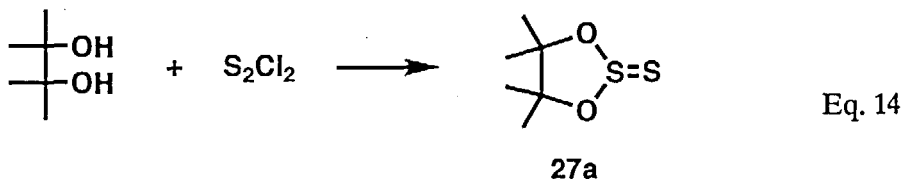
This structure of difluorodisulfane (**26**) is a curious and uncommon anomaly since the clarification by Kuczkowski³¹ over 30 years ago in that two structural forms exist for "sulfur monofluoride" with the more stable form being the unusual "branch-bonded" isomer **26b** (Eq. 13).



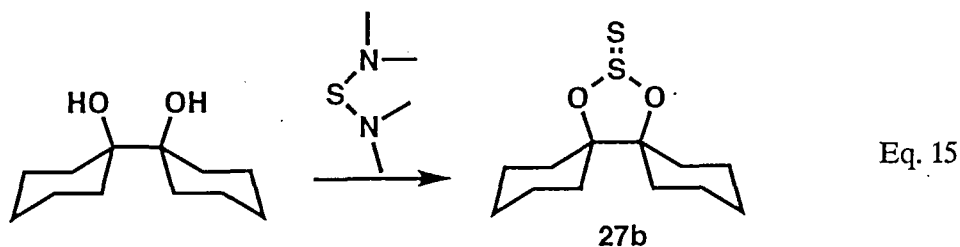
Eq. 13

This finding has been amply confirmed by other researchers.³² These isomers appear to have an appreciable barrier of conversion (23-46 kcal/mol)³³ which is sufficient to rationalize their independent existence. A barrier for the corresponding dichlorodisulfane (ClS-S-Cl/Cl₂S=S) rearrangement has been calculated to be only *ca.* 3 kcal/mol.³³

While there is some evidence for the existence of the branch-bonded isomer of dichlorodisulfane,³⁴ this species has not been clearly confirmed. Some evidence for the existence of branch-bonding in sulfur monochloride is found in the report by Thompson³⁵ in that the reaction of S₂Cl₂ with 1,2 diols appears to give thionosulfites **27a** as opposed to the linear alkoxydisulfide isomer (Eq. 14).



The structure of these compounds were strongly inferred by their ¹H NMR spectrum suggesting the presence of the thiono functionality. In 1980,³⁶ we prepared the only confirmed thionosulfite **27b** by a curious reaction with a monosulfur transfer reagent (Eq. 15). Here, the X-ray crystal structure shows the S-S bond length to be quite short at 1.901 Å (see Table 2).

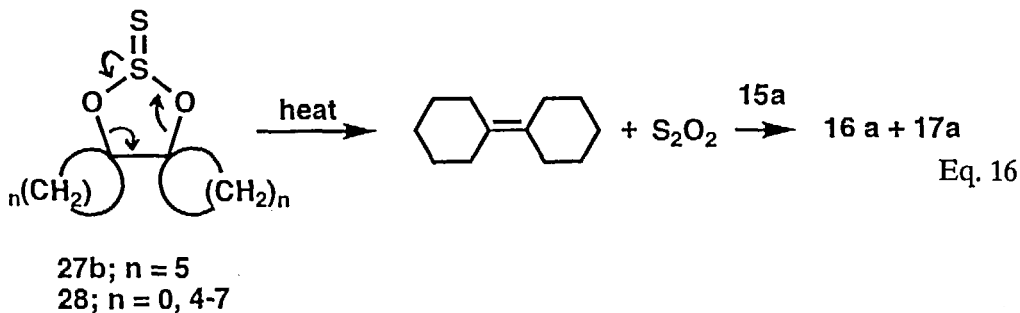


It appears that the tetrachalcogenide linkage prefers to bond as the thiono isomer (-O-(S=S)-O) when it has an opportunity to be in a 5-membered ring. The "linear" structure (-O-S-S-O-) appears to be preferred in open-chain molecules, *e.g.* **24** and **25**. To date, there are no examples of a thionosulfite that is not cyclic.³⁵ Two theoretical investigations on this interesting question as to "open-chain" vs. "branch-bonded" isomerization have recently been published.^{37a,b}

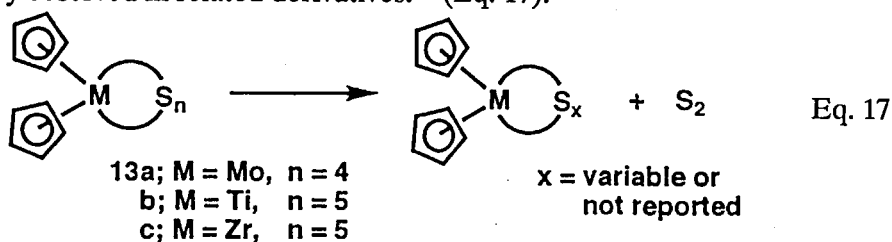
A puzzling feature of the ^1H NMR spectrum of each of the alkoxy disulfide derivatives **24**, is the presence of a sharp AB quartet. This signal is unchanged from *ca.* -70°C to the decomposition point (*e.g.* for **24b** at *ca.* 70°C). There is no clear precedent for a structure such as **24b** to exhibit hindered rotation; in addition, we have no evidence that there is any equilibrium between the linear and branched structures. *Ab initio* calculations have been carried out³⁸ which suggest that a significant rotational barrier is introduced as the S-S bond is shortened from values of 2.06 \AA ^{29,39} down to the known values for the alkoxy disulfides of *ca.* 1.95 \AA .^{25b,c,28}

This finding would appear to explain the clean AB quartet for **24** at temperatures of *ca.* 70°C which requires a rotational barrier of *at least* 20 kcal/mol .

We have investigated some of the chemistry of the branch-bonded molecule **27b** to see if it might also serve as a diatomic sulfur transfer species. When **27b** is heated above its melting point ($100\text{--}101^\circ\text{C}$) to *ca.* 150°C , an acidic gas is evolved.³⁶ Preliminary analysis of the residue shows that elemental sulfur and a variety of olefinic products are formed. In the presence of diene **15a**, trapped disulfide **16a** is formed along with a minor amount of tetrasulfide **17a**.⁴⁰ These data suggest that the decomposition mode is as depicted in Eq. 16. It appears that the relatively rare sulfur oxide S_2O_2 is formed and disproportionates to sulfur (*via* S_2) and sulfur dioxide. At present, a variety of symmetrical and unsymmetrical thionosulfites **28** have been prepared in order to study the scope of this interesting decomposition reaction.⁴¹



Several years ago we were able to show that diatomic sulfur could be transferred from metallocene pentasulfides **13** by the action of phosphorus derivative **5**.¹⁵ Recent results in our lab have shown that diatomic sulfur can be effectively generated from several other related compounds by simply heating in DMSO, chlorobenzene or DMF.⁴² This is perhaps not so surprising in that the products of these reactions are smaller, stable, sulfur-ring metallocene systems frequently observed in related derivatives.⁴³ (Eq. 17).



The reactions appear to involve a simple extrusion of a diatomic sulfur fragment. While there is variation depending on the metallocene polysulfide, reasonable yields of trapped product (*ca.* 25-50%) (Table 3) are achieved with diene **15a** as a trap. Given the ease of preparation of the metallocenes **13 b,c**, it suggests that these reagents could be effective for delivering diatomic sulfur. In control experiments, when elemental sulfur is used as the possible transfer reagent, no trapping is observed unless the temperatures are high and the solvents are DMSO or DMF (*vide infra*).

Table 3

13	Solvent	-SS-% ^a	-SSSS-% ^a
a	DMSO	29	3
a	DMF	-	-
a	C ₆ H ₅ Cl	27	2
b	DMSO ^b	9	1
b	DMF	30	6
b	C ₆ H ₅ Cl	38	4
c	DMSO ^c	-	-
c	DMF	-	-
c	C ₆ H ₅ Cl	49	7

^a Most values are NMR yields with an internal standard; ^b **13b** decomposes rapidly at 125 °C; ^c **13c** decomposes at room temperature after *ca.* 30 min.

Given the long history of "activated sulfur"⁴⁴ and the ability of the element to become attached to carbon fragments in the vulcanization of rubber,⁴⁴ we have become interested in determining if there was a way to simply use S₈ (or easily made allotropes S₆ or S₁₀)⁴⁵ as a reagent, with minimal or no chemical "activation" in order to effect a two-sulfur transfer.

It has been reported that cyclic disulfide 16a can be prepared (69% yield) by heating dienes 15a with elemental sulfur in DMF;⁴⁶ the authors made no speculation as to how this process takes place. We have carried out a wide variety of experiments using various solvents/temperatures with diene 15a in the presence of elemental sulfur using no "base-activation".⁴² The results are summarized in Table 4

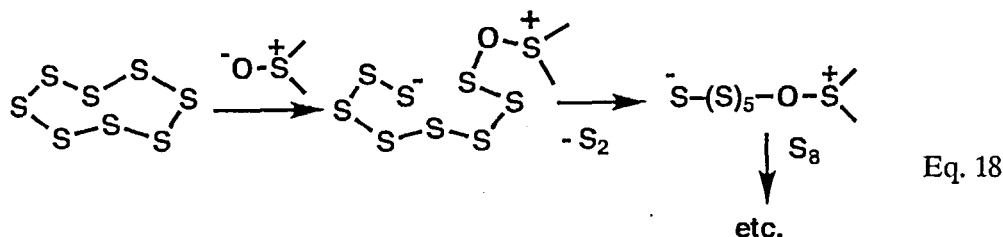
Table 4

	solvent ^a	-SS-% ^a (16a)	-SSSS-% ^a (17a)
15a	DMSO	70	15
15a	DMF	54	26
15a	C ₆ H ₅ Cl	16	16
15a	(EtO) ₂ CH ₂	22	7
15a	Toluene	<2	<2

^a Values are NMR yields with an internal standard.

It is clear that this method of diatomic sulfur transfer can be quite effective resulting in yields of over 80%²⁶ for the net, two-sulfur transfer. It is not clear why the amount of trapped product (tetrasulfide 17) varies in the way that it does, but it should not represent a problem for the preparation of cyclic disulfides from a synthetic point of view. It is likely that a number of cyclic disulfides of a generic structure such as 16, have significant biological activity.²⁷

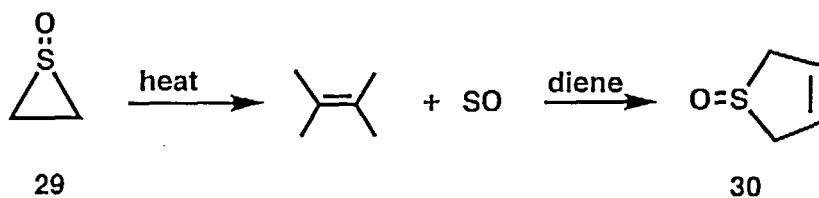
A possible mechanistic interpretation to explain this transfer is posed in Eq. 18. This mechanism (or one similar) may make it be possible to explain at least some of the many diverse reactions involving elemental sulfur, (particularly those in polar solvents) that abound in the literature.



At the present time, there are over a dozen reagents (including elemental sulfur itself) that will deliver diatomic sulfur to a diene. The remarkably different structural types of molecules that perform this transformation suggest that there will be many more discovered in the future. In addition, previous experiments in our laboratory have suggested the possibility of the transfer of diatomic selenium;^{37d} this is presently being explored.⁴⁷

SULFUR MONOXIDE

The other simple, diatomic molecule containing sulfur is sulfur monoxide.⁴⁸ Much less work has been accomplished in this area⁴⁹ as compared with diatomic sulfur. Sulfur monoxide was first identified by its UV spectrum in 1929 but is not thermodynamically stable, decomposing in the gas phase.¹ The main method of generation of S=O has been by the pyrolysis of ethylene episulfoxide (29) at *ca.* 100 °C.⁵⁰ (Eq. 19) There are other methods of S=O production involving diverse structures⁵¹; di- tri- and tetraene trapping experiments have been carried out by a number of workers.⁵² Yields of trapped product (sulfoxide 30) are usually *ca.* 30% and frequently lower.



Eq. 19

These hindered episulfoxides are easily prepared by *m*-CPBA oxidation of the corresponding episulfides (33, 34) in high isolated yield (92%). These episulfides in turn, are prepared in over 90% yield by simply treating the corresponding olefins with triphenylmethanesulfonyl chloride (35)^{22c} (Eq. 20). The episulfoxides are shelf-stable molecules; the crystal structures of 31-34 have been determined.^{55,56}



The decomposition of the episulfoxides is simple and the trapping effective. Dienes such as **15a,b** are added to a solution of episulfoxide in toluene (3:1 excess of episulfoxide). After refluxing for 24 h under nitrogen, the solvent is evaporated and the mixture chromatographed using 20% EtOAc in hexanes. The

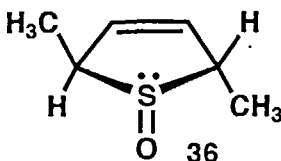
first fraction is the alkene (98% recovery) and the second, the trapped sulfoxide (ca. 70-80% yield). A variety of dienes, solvents and temperatures were used to optimize the yields. A selected summary of the results are presented in Table 5.

Table 5

(episulfoxide)	solvent	diene	sulfoxide% ^a
31	toluene	15a	70
31	xylene	15a	27
32	toluene	15a	73
32	xylene	15a	38
31	toluene	15b	80
31	toluene	15b ^b	N.R.
32	toluene	15b	82
32	EtOAc	15b ^c	N.R.
32	toluene	15b ^d	70

^a 3:1 ratio of episulfoxide to diene; refluxing solvent for 8-24 hr; isolated yields after flash chromatography; ^b 1:1 ratio of episulfoxide to diene; 80 °C, 10 days; ^c 1:1 ratio of episulfoxide to diene; 77 °C, 7 days; ^d 1:3 ratio of episulfoxide to diene; reflux, 12 hr; yield based on episulfoxide.

The mechanism of S=O loss appears to be a diradical process which has been suggested by virtually all of the mechanistic studies already carried out, especially those by Baldwin,⁵⁷ Lemal⁵³ and Glass.⁵⁴ In an experiment similar to that of Lemal,⁵³ we reacted episulfoxide 31 with a mixture of 2,4-hexadiene isomers (c,c; c,t; t,t); an 85% yield of trapped sulfoxide (t,t) 36 was obtained. This is in contrast to the results of Lemal in that they observed each of the three possible sulfoxides. However, by *ab initio* calculations,⁵⁸ the t,t isomer 36 appears to be the most stable of the three possible sulfoxide products. The formation of this product would still be consistent with a long-lived, triplet, biradical intermediate which gives *full* isomerization of the products under our specific set of reaction conditions. This reaction has been reported to be sensitive to temperature,^{54b,c,57} possibly explaining this lack of specificity in our experiment.



ACKNOWLEDGEMENTS

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