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Recent Chemistry of the Chalcogen Diatomics

Sylvie L. Tardif, Andrzej Z. Rys, Charles B. Abrams, Imad A. Abu-Yousef,
Pierre B. F. Lesté-Lasserre, Erwin K. V. Schultz, and David N. Harpp*

Department of Chemistry, McGill University, Montreal, Canada H3A 2K6

Abstract: The chemistry of the generation and trapping of diatomic sulfur (S_2) and sulfur monoxide (SO) are reviewed with special emphasis on recent work, including initial efforts to detect and trap diatomic selenium (Se_2).

INTRODUCTION

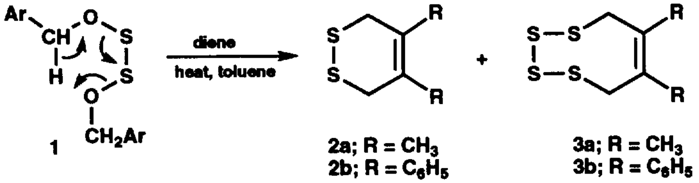
Symmetric diatomic molecules have been extensively researched as to structure and chemistry.[1] While chlorine was prepared over 300 years ago, other members of this family have only been known since the 1800s. Mixed diatomics such as HCl have had a long history[1] yet, one of the most researched molecules in recent years is nitric oxide (N=O); it has been shown to have a very wide variety of important biological effects.[2]

DIATOMIC SULFUR

Since the initial discovery by Steliou in 1984[3] of the rational generation of diatomic sulfur and its successful transfer to dienes, a number of groups have focussed on this and related problems. Our first account in this area was published in 1988[4b]; since that time research has expanded to include sulfur monoxide (SO).[5]

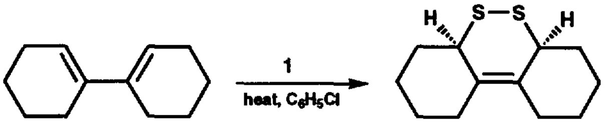
The structure of diatomic sulfur has been known for many years. Details on this as well as a summary of published research on the generation of diatomic sulfur have been recently summarized.[6]

The purpose of this report is to summarize our current work in this area. A significant breakthrough for the effective generation of diatomic sulfur involves the chemistry of alkoxydisulfides **1**. We have shown that members of this class of compound decompose near 75° C to permit the transfer of diatomic sulfur to dienes to give cyclic disulfides **2** in overall isolated yields of *ca.* 75%[7a] (Eq. 1).



Eq. 1

The tetrasulfide adduct **3** is also formed in these trapping reactions; recent control experiments have shown that only very small amounts of the disulfide adduct **2** are converted to the tetrasulfide **3** upon heating.[8] The disulfide **2** is however, a competitive entity with regard to the diene for trapping S_2. Interestingly, a series of experiments performed in the presence of 1,1'-bicyclohexene **4** show *no* traces of the corresponding tetrasulfide adduct (Eq. 2).[3,8,9]

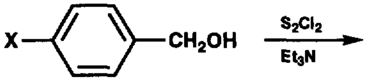


4

61%

Eq. 2

Alkoxydisulfides have been known for over 100 years[10] but have been given relatively little attention since the work of Thompson in 1965.[11a] The efforts of Steudel[11b,c,f] in this area are a notable exception. We have prepared a series of them in isolated yields of *ca.* 85% (Eq. 3, Table 1).



1

1a; X = H
1b; X = NO_2
1c; X = Cl
1d; X = OCH_3
1e; X = CH_3

Eq. 3

Table 1- Synthesis of Alkoxydisulfides **1**

ROSSOR 1	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 and recrystallization;
[b] **1d** was unstable on silica gel.

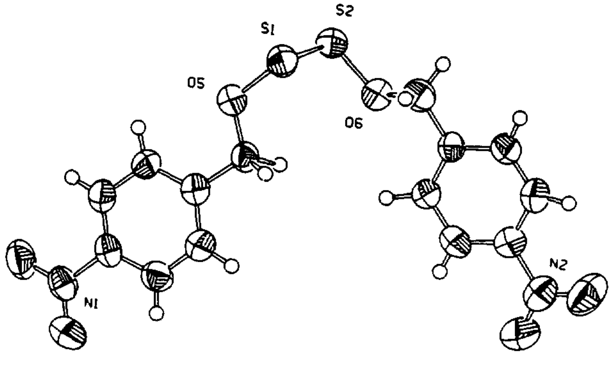
Each of these molecules transfers a diatomic sulfur unit to a diene, however the temperatures of decomposition vary somewhat as do the stabilities of **1**. In general, those structures with electron-withdrawing substitutents in the para position of the aromatic ring are the most stable, while those with electron-donating ones suffer decomposition at room temperature in 1-2 days; all of them survive well when refrigerated.

Of special interest is the structure of the -OSSO- moiety. Steudel reported[11b,c] the first detailed information in this area in the gas-phase as well as a low-temperature crystal structure analysis of dimethoxydisulfide (**5**). We have completed an X-ray structure determination of **1b** and **1c**.[8a] Of interest is the short sulfur-sulfur bond in these molecules (1.93-1.97 Å) (Table 2). The normal length for a typical sulfur-sulfur bond ranges from 2.02-2.06 Å.[12] The shortest known S-S bond is that of the branch-bonded version of S_2F_2[13] with a value of 1.86 Å.

Table 2- Structural features of 1.

ROSSOR	S-S Å	O-S-S-O °	O-S-S °
1b[8]	1.968	85.6	107.3, 107.8
1c[8]	1.932[a]	76.8	108.9
5[11b]	1.960	91	108.2
5[11c]	1.972	81.5	108.2

[a] This value appears unusually short and is being reinvestigated.

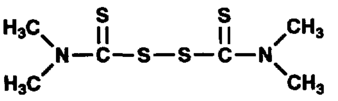


Ortep diagram of alkoxydisulfide **1b**.

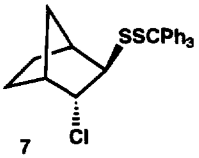
A fascinating feature of the ^1H NMR spectrum of each of the alkoxydisulfide derivatives **1** is the presence of a sharp AB quartet. This signal is constant from *ca.* -70° C to the decomposition point (*e.g.* for **1b** at *ca.* 70° C). There is no clear literature precedent for a structure such as **1b** to exhibit hindered rotation. Further, we have no evidence that there is an equilibrium between the linear and branched structures.

Ab initio calculations have been carried out[14] which suggest a significant and unprecedented rotational barrier is introduced when the S-S bond is shortened from *ca.* 2.06 Å[12,15] to the actual values for the alkoxydisulfides of *ca.* 1.96 Å.[8a,11b,c] This experiment nicely rationalizes the clean AB quartet for **1** at temperatures of *ca.* 70° C which requires a rotational barrier of *at least* 18-20 kcal/mol.

In addition to alkoxydisulfides **1**, we have been able to generate a variety of diatomic sulfur precursors of quite varied structure. These include thiuram disulfide **6**[16] and adduct **7**[17]. While the yields of transfer are not high, the results have stimulated us to investigate an even wider variety of potential precursors.

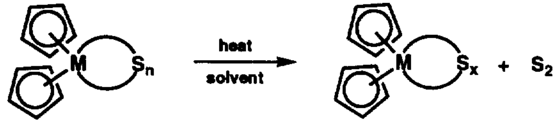


6



7

Some time ago, we showed that diatomic sulfur could be transferred from metallocene pentasulfides **8** by the action of triphenylphosphine dibromide (**9**).[4,18] Recently, we have shown that diatomic sulfur can be generated from **8** by simply heating in DMSO, chlorobenzene or DMF.[19] (Eq. 4).



Eq. 4

8a; M = Mo, n = 4
b; M = Ti, n = 5
c; M = Zr, n = 5

x = variable or
not reported

These reactions may involve a simple diatomic sulfur extrusion. Reasonable yields of trapped product (*ca.* 25-50%, Table 3) are obtained. In control experiments, when elemental sulfur is used as the transfer reagent, no trapping is observed unless the solvents are DMSO or DMF or the temperatures are high.

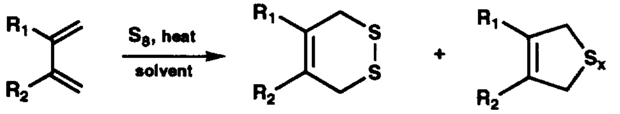
Table 3- Yields of S_2 and "S_4" Transfer from **8**.

8	Solvent	(**2b**)[a]	(**3b**)[a]
a	DMSO	29	3
a	DMF	-	-
a	C_6H_5Cl	27	2
b	DMSO[b]	9	1
b	DMF	30	6
b	C_6H_5Cl	38	4
c	DMSO[c]	-	-
c	DMF	-	-
c	C_6H_5Cl	49	7

[a] Most values are NMR yields with an internal standard;
[b] **8b** decomposes rapidly at 125° C; [c] **8c** decomposes at room temperature after *ca.* 30 min.

Given the long history of "activated sulfur",[20a] we have become interested in finding a way to simply use S_8 (or easily made allotropes S_6 or S_{10}) as a reagent (*vide infra*), with minimal or no chemical "activation" in order to effect a two-sulfur transfer.

We have found that elemental sulfur[20b] shows a variable level of activity towards dienes. Cyclic disulfides **2** form along with some polysulfides (Eq. 5). The final yield of disulfides **2** (after conversion of the polysulfides with triphenylphosphine) ranges from 45% to over 80% depending on the nature of the diene. The results are summarized in Table 4.



Eq. 5

2 polysulfides

10a (R_1, R_2 = CH_3); **b** (R_1, R_2 = C_6H_5); **c** (R_1 = H, R_2 = $(CH_2)_2CH{=}(CH_3)_2$
solvent = DMSO, DMF, C_6H_5Cl, $C_6H_5CH_3$, $(CH_2OEt)_2$; x = 3,4 and higher

Table 4

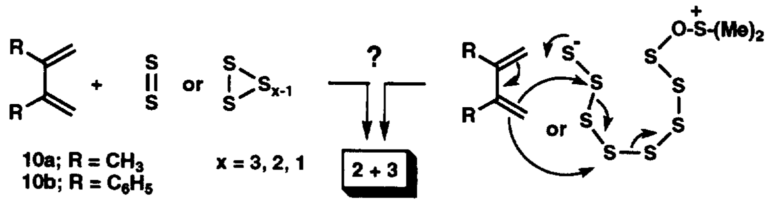
diene[a]	solvent	2b%[a]	3b%[a]
10b	DMSO	70	15
10b	DMF	54	26
10b	C_6H_5Cl	16	16
10b	$(EtO)_2CH_2$	22	7
10b	Toluene	<2	<2

[a] Values are NMR yields with an internal standard.

This method of diatomic sulfur transfer can be very effective, resulting in yields of over 80% for the net, two-sulfur transfer. It is unclear why the amount of trapped product (tetrasulfide **3b**) varies, but it does not pose a problem for the preparation of cyclic disulfides. Some cyclic disulfides of a general structure such as **2**, have biological activity.[7b,e]

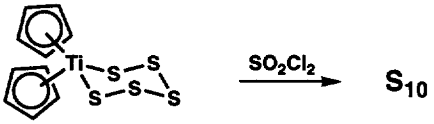
When pure disulfides **2** were heated with elemental sulfur in DMSO, only a fraction of tetrasulfides **3** were formed as was observed in the reactions with dienes under identical conditions. We also examined the possibility that tetrasulfides were formed first in a sulfuration reaction and were then equilibrated to disulfides with elemental sulfur. This postulate was not confirmed as only 8% of **3b** (R = C_6H_5) was converted to **2b** when heated with an excess of S_8 in DMSO solvent. These experiments suggest that neither insertion nor equilibration effectively determines the composition of the sulfuration products and that formation of both di- and polysulfides occurs in a single step.

It is possible that the octasulfur ring is opened by solvent and the ionic intermediate could generate discrete sulfur units S_n with n = 2, 3, 4 or 5 reacting with dienes. The existence of S_3, S_4 or S_5 has been proposed on the basis of molecular orbital calculations.[21] A possible mechanistic hypothesis to explain this multiple sulfur transfer is posed in Eq. 6. This mechanism may permit an explanation of at least some of the many diverse reactions involving elemental sulfur, (particularly those in polar solvents) that abound in the literature.



Eq. 6

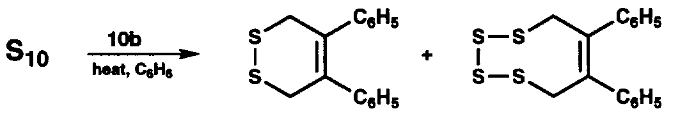
We have also examined other sulfur allotropes as potential diatomic sulfur precursors. Warming hexasulfur (S_6) with diene **10b** in toluene transfers diatomic sulfur, but only in modest (5-6%) yield. We believed that S_{10} appeared to be a better candidate for S_2 transfer in that a loss of S_2 could afford the stable S_8 allotrope. S_{10} is prepared by treating titanocene pentasulfide (**8b**) with sulfuryl chloride (Eq. 7).[22]



Eq. 7

8b

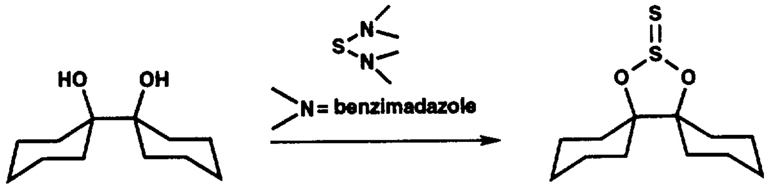
Preliminary trapping experiments have been carried out with S_{10} under mild conditions (refluxing benzene). Using 2,3-diphenyl-1,3-butadiene (**10b**), disulfide adduct **2b** and the corresponding tetrasulfide derivative **3b** have been identified as the only trapped products of the reaction when *equimolar* amounts of the diene and S_{10} are used.[23] The overall yield of disulfide **2b** is 25% along with 2% of the tetrasulfide **3b** (Eq. 8). Elemental sulfur is formed in this process thus showing a reasonable efficiency of competitive trapping by the diene since diatomic sulfur eventually oligomerizes to octasulfur. Initially, we found some inconsistency in the reproducibility of reactions because S_{10} appears quite sensitive to traces of base.



Eq. 8

2b (25%) **3b (2%)**

Another interesting structure which could potentially deliver diatomic sulfur is the only confirmed thionosulfite **11a** formed by an unusual reaction with a *mono*sulfur transfer reagent (Eq. 9).[24] Here, the X-ray crystal structure shows the S-S bond length to be quite short at 1.901 Å (see Table 2 for related structures).



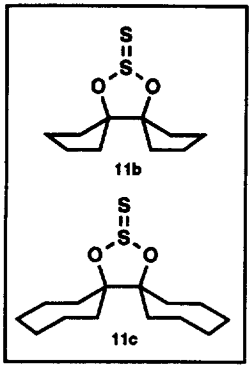
Eq. 9

11a

It appears that the tetrachalcogenide linkage prefers to bond as the thiono isomer (-O-(S=S)-O) when it is present in a 5-membered ring. The "linear" structure (-O-S-S-O-) is adopted in open-chain molecules, *e.g.* 1 and 5. To date, there are no examples of a thionosulfite that is not cyclic.[24,25] A number of theoretical investigations on this interesting question as to "open-chain" *vs.* "branch-bonded" isomerization (including S_2F_2) and related derivatives have been published.[26]

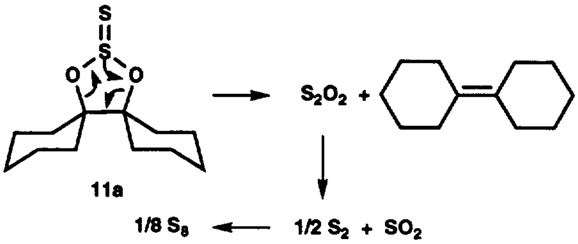
We have investigated some of the chemistry of thionosulfite **11a** to discover its capacity to also serve as a diatomic sulfur transfer species. When **11a** is heated above its melting point (100-101° C) to *ca.* 150° C, an acidic gas is evolved.[24] Preliminary analysis of the products shows that elemental sulfur and a variety of olefinic materials are formed. In the presence of diene **10b**, a small amount of trapped disulfide **2b** is formed (^{1}H NMR).[27]

The mass spectra of **11a** suggest that the decomposition mode is as shown in Eq. 10. It appears that the relatively unusual sulfur oxide S_2O_2 is formed and disproportionates to sulfur (*via* S_2) and sulfur dioxide. A variety of other thionosulfites (*e. g.* **11b,c**) have been prepared in order to study the scope of this interesting decomposition reaction.[28]



11b

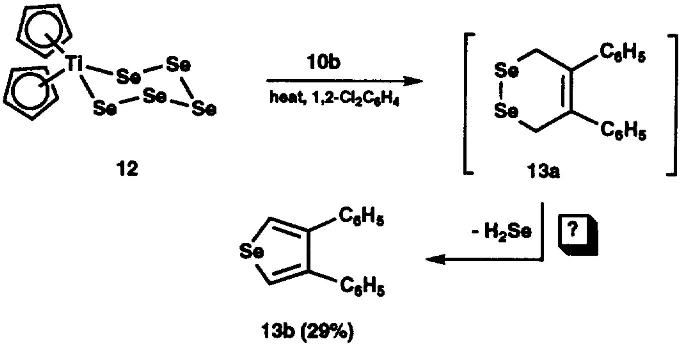
11c



Eq. 10

Presently, there are over a dozen reagents (including elemental sulfur itself) that will deliver diatomic sulfur to a diene. The different structural types of molecules that perform this transformation suggest that there will be many more discovered in the future.[29]

In addition, previous experiments in our laboratory have suggested the possibility of the transfer of diatomic selenium;[30] this is presently being explored.[31] When compound **12**, the selenide analog of titanocene pentasulfide (**8b**) was warmed with 2,3-diphenyl-1,3-butadiene (**10b**) in *o*-dichlorobenzene, one trapped product (selenophene **13b**) was isolated in 29% yield (Eq. 11). It could have resulted from the loss of H_2Se from intermediate **13a** (diselenium being trapped by diene **10b**). The structure of **13b** was determined by X-ray crystallography.[31]



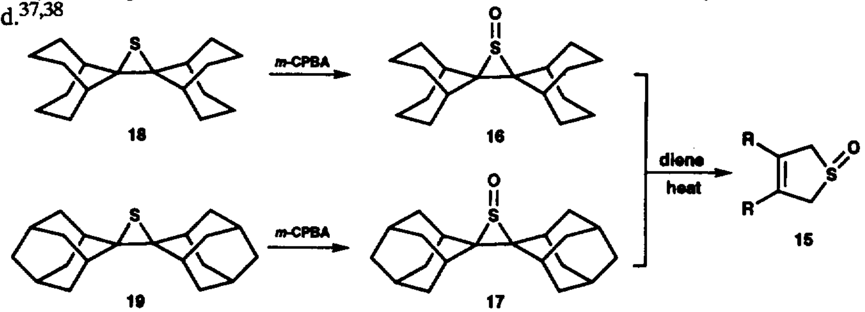
Eq. 11

SULFUR MONOXIDE

Another sulfur-containing diatomic molecule is sulfur monoxide.[32] Considerably less attention has been paid to this chemistry[5,33] as compared to diatomic sulfur. Sulfur monoxide was first identified in 1929 but is thermodynamically unstable, decomposing in the gas phase.[1] The common method of generating S=O has been by the pyrolysis of ethylene episulfoxide (**14**) at *ca.* 100° C.[34] Yields of trapped product (sulfoxide **15**) are usually *ca.* 30% and frequently lower.

Work by Lemal[35] was primarily directed towards elucidating the mechanistic features of this process although one trapping experiment with isoprene gave a synthetically significant 72% isolated yield of the corresponding sulfoxide. A recent paper by Glass[36] examined the decomposition of an episulfoxide which decomposed to the olefin with the likely extrusion of S=O.

We have found that the hindered episulfoxides, adamantylideneadamantane thiirane-1-oxide (**16**) and analog **17**,[37,38] deliver S=O to dienes in isolated yields averaging 75%. These hindered episulfoxides are prepared by *m*-CPBA oxidation of the corresponding episulfides (**18**, **19**) in high isolated yield (92%). The episulfoxides (**16**, **17**) are shelf-stable molecules; their crystal structures have been determined.[37,38]



Dienes such as **10a,b** are added to a solution of episulfoxide in toluene (3:1 excess of episulfoxide). After refluxing for 24 h under nitrogen followed by work-up, the alkene (98% recovery) is isolated along with the trapped sulfoxide (*ca.* 70-80% yield). A variety of dienes, solvents and temperatures were employed to optimize the yields. A selected summary of the results are shown in Table 5.

Table 5

(episulfoxide)	solvent	diene[a]	sulfoxide%[a]
16	toluene	**10a**	70
16	xylene	**10a**	27
17	toluene	**10a**	73
17	xylene	**10a**	38
16	toluene	**10b**	80
16	toluene	**10b**[b]	N.R.[e]
17	toluene	**10b**	82
17	EtOAc	**10b**[c]	N.R.[e]
17	toluene	**10b**[d]	70

[a] 3:1 ratio of episulfoxide to diene; refluxing solvent for 8-24 hrs except where noted; 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 hrs; yield based on episulfoxide; [e] no reaction

The mechanism of S=O loss appears to be a diradical event which has been suggested by virtually all of the mechanistic studies already carried out, especially those by Baldwin,[39] Lemal[35] and Glass.[36]

SUMMARY

This area of small molecule chemistry has grown impressively over the past 13 years from the first reagents to deliver diatomic sulfur. With further research it may be possible to prepare virtually any cyclic disulfide in good-excellent yield by the use of elemental sulfur itself.

In a parallel fashion, an even more complex problem will be to master these heterocyclic manipulations with selenium. At present, the transfer of sulfur monoxide is reasonably effective, however yet another challenge will be the possible generation of small molecules mixing sulfur with oxygen, phosphorus and nitrogen which should also follow the Diels-Alder trapping chemistry outlined above.

EXPERIMENTAL

Trapping of Diatomic Sulfur by Alkoxydisulfide 1.- Alkoxydisulfide **1b** (900 mg., 2.5 mmol) and diene **4** (114 mg, 0.7 mmol) were added to 7 mL of chlorobenzene. In addition, 2.5 mmol (99 mg) of MgO is also added to the the flask. The reaction was immersed in an oil bath held at 135-140° C and stirred for 2 hrs. Most of the solvent is evaporated under reduced pressure and the residue is triturated in hexanes (3 x 10 mL) and filtered each time. Evaporation of the hexanes provides a residue that was dissolved in CCl_4 and chromatographed on silica gel (10% CS_2 in CCl_4). The major fractions were recombined and rechromatographed using CCl_4. The disulfide adduct (61%, combined yield) is a clear, yellow oil characterized by ^{13}C NMR ($CDCl_3$): δ 26.62, 27.96, 31.95, 34.52, 44.55, 132.44 ppm.

Sulfuration of Dienes with Elemental Sulfur.- A typical procedure is as follows. The reagents (1 mmol of diene and a 4-fold excess of sulfur) are added to 4 mL of solvent. The reaction mixture is refluxed for 3-12 h. An excess (3 mmol) of PPh_3 is added to the still hot solution. The mixture is stirred at room temperature for about 30 min. An excess of elemental sulfur (1.5 mmol) dissolved in a small amount of CS_2 is added and the solution stirred for an additional 10 min. After the solvent is removed, the residue is triturated with hexanes. Precipitated $PPh_3=S$ is washed 5 times with hexanes to ensure removal of the organic disulfide. The solvent is evaporated and the residue introduced at the top of a chromatographic column with a minimal amount of CS_2. Elution is carried out first with hexanes and then with a mixture of hexanes/ether (100:1). The product is obtained in 45-82% isolated yield. There was no trace of the tetrasulfide, or other polysulfide. Sometimes another impurity was observed in small amounts (*ca.* 5%) in the case of **10a**. Its ^1H NMR spectrum was consistent with the Diels-Alder dimer of the diene as reported above. When the sulfuration of **10a** was carried out on a 10X scale, after distillation a 67% yield of **2a** was obtained.

Trapping of Diatomic Sulfur by S_{10}.- Recrystallized S_{10} (31.2 mg, 0.097 mmol) was refluxed with diene **10b** (20.0 mg, 0.097 mmol) in 2 mL of benzene-d_6 under a nitrogen atmosphere. An internal standard of 1,3,5-tri-*t*-butylbenzene was added (18.0 mg, 0.071 mmol). The yields reported are from this internal comparison.

Thermolysis of Thionosulfite 11a.-Pre-distilled DMF (4 mL) was added to a mixture of diene (**10b**) (0.021 g, 0.10 mmol) and thionosulfite **11a** (0.025 g, 0.095 mmol) in a round-bottomed flask under a nitrogen atomsphere. This was immersed in an oil bath maintained at 150-160° C. The reaction progress was monitored by tlc and stopped when **11a** was depleted. The solvent was removed and analysis was carried out by ^1H NMR.

Attempted Trapping of Diselenium.- A solution of pentaselenide **12** (0.229 g, 0.4 mmol) and diene **10b** (0.365 g, 1.77 mmol) in 5 mL of *o*-dichlorobenzene was refluxed for 6 days. The solvent was removed under reduced pressure. The reaction flask was extracted with pentane and the solution filtered through a cotton plug in a pipette. The resulting red/orange solution was concentrated; the crude material was purified by column chromatography on silica using hexane as eluent. The yield of **13b** (white crystals, mp 106-108° C) was 33 mg (29%); ^{1}H NMR ($CDCl_3$) δ: 7.94 (s, 2H), 7.11-7.24 (m, 10H); ^{77}Se NMR (Me_2Se) δ: 584.

Sulfur Monoxide Trapping from the Decomposition of Adamantylideneadamantane Thiirane-1-Oxide (16) with Diene 10a.- 2,3-Dimethyl-1,3-butadiene (**10a**) (0.0513 g, 0.625 mmol) was added to **16** (0.593 g, 1.875 mmol) in 30 mL of dry toluene. The solution was refluxed for 12 h under a nitrogen atmosphere. The reaction was followed by tlc using 15% EtOAc in hexane as eluent. After evaporating the solvent under reduced pressure, the first fraction was isolated by column chromatography using the same eluent and was identified as adamantylideneadamantane (99%). Elution with methanol provided sulfoxide **15a** (0.065 g, 80%) as an oil. ^{1}H-NMR ($CDCl_3$) δ: 3.83 (d, $2H_a$), 3.48 (d, $2H_b$) and 1.77 (s, 6H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 14.46, 64.32 and 126.07 ppm; MS (m/z, rel. int., assignment): 130, 100%, $M^{+\cdot}$; 82, 30%, $M^{+\cdot}$ -SO: 67, 61%, $M^{+\cdot}$ -$SOCH_3$.

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3. Steliou, K.; Gareau, Y.; Harpp, D. N. *J. Am. Chem. Soc.* **1984**, *106*, 799; our own unsuccessful efforts in this area date to the early 1970s. It should be noted that impressive efforts towards the generation of diatomic sulfur were carried out in a Ph.D. thesis in 1976 by D. L. Smith (University of Arizona, Professor Richard Glass, supervisor), University Microfilms, Ann Arbor, MI, 77-11,451.
4. a) Our initial, unsuccessful efforts in this area date to the early 1970s with organic bicyclic disulfides, Harpp, D. N.; Snyder, J. P; Montecalvo, D. unpublished results; b) Harpp, D. N.; MacDonald, J. G. *J. Org. Chem.* **1988**, *53*, 3812.
5. a) Abu-Yousef, I. A.; Harpp, D. N. *Tetrahedron Lett.* **1995**, *36*, 201; b) in addition, we have published a review on this topic, see Abu-Yousef, I. A.; Harpp, D. N. *Sulfur Reports* **1997**, *in press*.
6. Harpp, D. N. *Phosphorus, Sulfur and Silicon* **1997**, 51, 0000, *in press*.
7. a) Tardif, S. L.; Williams, C. R.; Harpp, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 9067. It should be mentioned that in virtually all reactions where diatomic sulfur is transferred, moderate amounts of polysulfide (almost always tetrasulfides 3) are formed. These polysulfides are treated with triphenylphosphine and converted back to the disulfide adduct in nearly 100% isolated yield.

Under the conditions of this reaction, (toluene, 100-105 °C) when dienes are heated with elemental sulfur, neither di- nor tetrasulfide adducts are detected. This demonstrates that the trapped products are not likely the result of a transfer of sulfur fragments by "activated sulfur". For further comments on this as well as background on diatomic sulfur transfer see b-d: b) Steliou, K.; *Acc. Chem. Res.* **1991**, *24*, 341; c) Steliou, K.; Gareau, Y.; Milot, G.; Salama, P. *Phosphorus, Sulfur and Silicon* **1989**, *43*, 209; d) another paper by Steliou addresses the issue of diatomic sulfur as a free species; see Steliou, K.; Salama, P.; Yu, X. *J. Am. Chem. Soc.* **1992**, *114*, 1456; e) Freeman, F.; Kim, D. S. H. L.; Rodriguez, E. *Sulfur Reports* **1989**, *9*, 207.

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9. Unreacted diene, elemental sulfur, the corresponding alcohol and aldehyde are the other products detected and isolated.
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