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Sulfenyl Chloride Chemistry. New Precursors for Diatomic Sulfur Transfer

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When triphenylmethanesulfenyl chloride (**1**) (or its thio homologue **2**) are treated with various bicycles, norbornene **(5)**, or bicyclo[2.2.2]octene **(6)**, dithio adducts **7** and **8** were produced in good isolated yields. Final products were obtained via an episulfide intermediate. The stereochemistry of addition has been determined by X-ray analysis. Treatment of thiosulfenyl chloride **2** (or its dithio homologue **3**) with other olefins, cyclopentene **(10)**, cyclohexene **(11)**, or 1,4-dioxene **(12)**, leads to the formation of disulfides (**13**−**15** from **2**) and trisulfides **(16** and **17** from **3)** in high isolated yields (ca. 92%). The structures of **7**, **8**, and **13**−**17** were established by ^{1}H and ^{13}C NMR and elemental analysis as well as by X-ray determination. When these adducts are warmed with a 1,3-diene **42**, they deliver diatomic sulfur-trapped derivatives, cyclic di-**49** and tetrasulfide adducts **46**. A variety of solvents, temperatures, times, and concentrations were employed to optimize the yield of **46** and **49**. The tetrasulfide adduct **46** is quantitatively converted to disulfide **49** with triphenylphosphine; this affords cyclic disulfides in >50% isolated yield from the diene. In addition, evidence has been obtained implicating dithietane intermediate **4**.

Introduction

The chemistry of sulfenyl halides has been extensively studied.[1] The reaction of sulfenyl halides with olefins has been interpreted mechanistically in terms of the formation of an episulfonium ion intermediate[2] that is intercepted by a halide ion to form a β-halo thioether. The chemistry of triphenylmethanesulfenyl chloride **(1)** and its thio (**2**) and dithio (**3**) homologues is much less examined.[3]

$(C_6H_5)_3C{-}S{-}Cl$ **1**

$(C_6H_5)_3C{-}S{-}S{-}Cl$ **2**

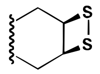
$(C_6H_5)_3C{-}S{-}S{-}S{-}Cl$ **3**

The reaction of triphenylmethanesulfenyl chloride **(1)** with norbornene has been investigated previously.[4] Indeed, other similar types of sulfenyl halides have been shown to add to carbon−carbon double bonds; this has resulted in preparative methods for episulfides.[5]

In the case of the reaction of sulfenyl chloride **1** with norbornene, a number of products were reported,[4] but details were lacking, and neither their stereochemistry nor the mechanism of the reaction was demonstrated.

Recently, we[6] investigated an interesting reaction of triphenylmethanesulfenyl chloride **(1)** where its sulfur atom is extruded quantitatively and catalytically by a reaction with thioketones. In another study,[7] the reaction of triphenylmethanethiosulfenyl chloride **(2)** with 1,3-dienes affords a 1,4-addition product, which subsequently produces cyclic di- and tetrasulfides in good overall yield. The net effect of the latter transformation is to deliver a 2- and 4-sulfur fragment to the diene.

We have initiated a study of some of the chemistry of this type of addition for the preparation of a new series of di- and trisulfides hoping that these reagents can be used to develop a useful pathway to dithietanes **4** as potentially stable intermediates and/or diatomic sulfur precursors.



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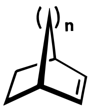
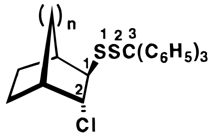
Results and Discussion

An equimolar amount of triphenylmethanesulfenyl chloride **(1)** was reacted with bicyclo[2.2.1]heptene **(5)** or bicyclo[2.2.2]octene **(6)** at room temperature under a nitrogen atmosphere. *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane **(7)** and *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane **(8)** were produced, respectively, in good isolated yields (ca. 47%). Dithio adducts **7** and **8** where obtained in a high yield (ca. 92%) when 2 mol ratio of sulfenyl chloride **1** was used.



5; n = 1
6; n = 2



7; n = 1
8; n = 2

The identity of these adducts **7** and **8** was confirmed by ^{1}H and ^{13}C NMR and elemental analysis as well as by X-ray analysis. The X-ray crystallographic structures

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[1] Gundermann, K. D. *Angew Chem., Int. Ed. Engl.* **1963**, *2*, 674. Harstaff, W. R.; Langler; R. F. *Sulfur in Organic and Inorganic Chemistry*; Senning, A., Ed.; Marcel Dekker: New York, 1982; Vol. 4, p 193. Schmit, G. H.; Garrat, D. G. *The Chemistry of the Double Bonded Functional Groups*; Patai, S., Ed.; John Wiley & Sons: New York, 1982, Chapter 9.

[2] Kühle, E. *Synthesis* **1970**, 561.

[3] Harpp, D. N.; Ash, D. K. *Int. J. Sulfur Chem., A* **1971**, *1*, 211.

[4] Majewski, J. M.; Zakrzewski, J. *Tetrahedron Lett.* **1981**, *22*, 3659.

[5] (a) Fujisawa, T.; Kobori, T. *Chem. Lett.* **1972**, 1065. (b) Fujisawa, T.; Kobori, T. *Chem. Lett.* **1972**, 935. (c) Bombala, M. U.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3013.

[6] Williams, C. R.; Harpp, D. N. *Tetrahedron Lett.* **1991**, *32*, 7633.

[7] Williams, C. R.; Harpp, D. N. *Tetrahedron Lett.* **1991**, *32*, 7651.

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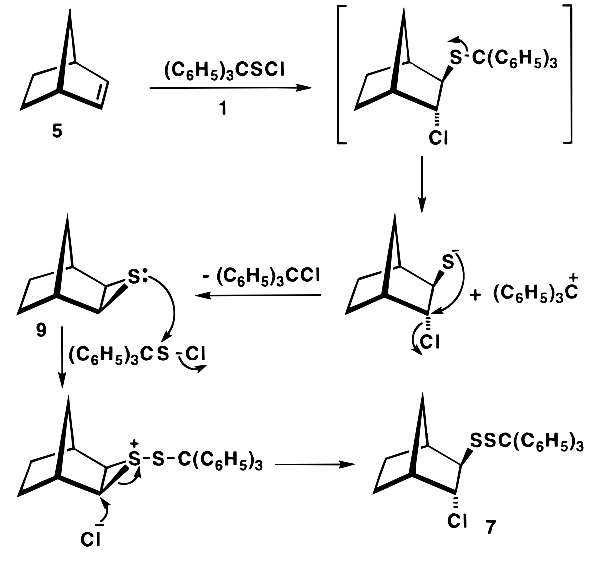
Scheme 1

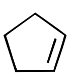


of **7** and **8** were reported[8] for the first time. Selected bond lengths and angles are shown in Table 1 of the Supporting Information.[9]

The analysis revealed that the regiochemistry of **7** and the symmetry of **8** permits only one isomer. The addition products **7** and **8** contained two sulfur atoms rather than one. A plausible mechanism showing the explanation for the presence of the second sulfur atom is indicated by the pathway in Scheme 1.

To demonstrate the likelihood of this mechanism, we independently prepared *exo*-episulfide **9**[5c] and treated it with triphenylmethanesulfenyl chloride **(1)**. Dithio **7** was isolated in 90% yield; this gives clear support to pathway displayed in Scheme 1.

In the same manner, we found that triphenylmethanethiosulfenyl chloride **(2)** reacted with bicyclo[2.2.1]heptene **(5)**, bicyclo[2.2.2]octene **(6)**, cyclopentene**(10)**, cyclohexene **(11)**, and 1,4-dioxene **(12)** at room temperature under a nitrogen atmosphere. Dithio adducts **7** and **8** and *trans*-2-chloro-1-(triphenylmethyldithio)cyclopentane **(13)**, *trans*-2-chloro-1-(triphenylmethyldithio)cyclohexane **(14)**, and *trans*-2-chloro-3-(triphenylmethyldithio)-1,4-dioxane **(15)** were formed, respectively, in high isolated yields (ca. 92%).



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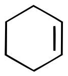

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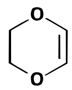

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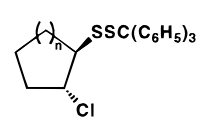
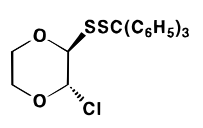
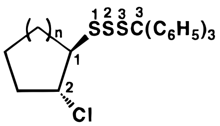


13; n = 1
14; n = 2



15

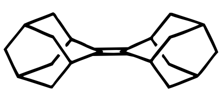
The structures of these adducts were established by ^{1}H and ^{13}C NMR as well as by elemental analysis. The assignments of relevant ^{13}C NMR chemical shifts relative to tetramethylsilane of the disulfide adducts are reported in Table 2 of the Supporting Information.We also found that treatment of cyclopentene **(10)** and cyclohexene **(11)** with triphenylmethanedithiosulfenyl chloride **(3)** at room temperature under a nitrogen atmosphere leads to the formation of *trans*-2-chloro-1-(triphenylmethyltrithio)cyclopentane **(16)** and *trans*-2-chloro-1-(triphenylmethyltrithio)cyclohexane **(17)**, respectively, in high isolated yields (ca. 94%).



16; n = 1
17; n = 2

The identity of trisulfides **16** and **17** was confirmed by ^{1}H and ^{13}C NMR and elemental analysis as well as by X-ray determination. The X-ray crystallographic structures of **16** and **17** were reported[10] for the first time. Selected bond lengths and angles are shown in Table 3 of the Supporting Information.[9]

The assignments of relevant ^{13}C NMR chemical shifts relative to tetramethylsilane of trithio adducts are reported in Table 4 of the Supporting Information. In addition, we investigated the reaction of triphenylmethanesulfenyl chloride **(1)** and its thio (**2**) and dithio (**3**) homologues with more hindered olefins such as adamantylideneadamantane **(18)** and bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane **(19)**.



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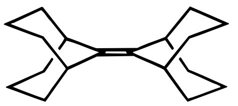

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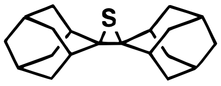
1,2-Addition products such as **7** and **8** were not isolated; instead, cyclization takes place forming the corresponding episulfides adamantylideneadamantanethiirane **(20)**[11] and bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonanethiirane **(21)**,[11b,12] respectively.



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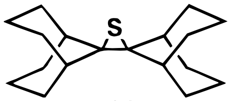

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We also studied the reaction of triphenylmethanesulfenyl chloride **(1)** and its thio (**2**) and dithio (**3**) homologues with another series of olefins. Cyclic olefins such as 1,2-diphenylcyclohexene **(22)**, 1,2-diphenylcyclobutene **(23)**, 1,4-dimethylcyclohexene **(24)**, (1*R*)-(+)-α-pinene **(25)**, (1*S*)-(−)-*β*-pinene **(26)**, 3-carene **(27)**, 2-carene **(28)**, camphene **(29)**, 3,4-dihydro-2H-pyran **(30)**, 2,5-dihydrofuran **(31)**, and 2,5-dimethoxy-2,5-dihydrofuran **(32)** did not react with the series of sulfenyl chlorides, **1**−**3**.

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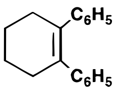
(8) Abu-Yousef, I. A.; Hynes, R. C.; Harpp, D. N. *Tetrahedron Lett.* **1993**, *34*, 4289.

(9) Johnson, C. K. *ORTEP-A Fortran Thermal Ellipsoid Plot Program*; Technical Report ORNL-5138; Oak Ridge National Laboratories: Oak Ridge, TN, 1976.

(10) Abu-Yousef, I. A.; Hynes, R. C.; Harpp, D. N. *Tetrahedron Lett.* **1993**, *34*, 7167.

(11) (a) Abu-Yousef, I. A.; Harpp, D. N. *Tetrahedron Lett.* **1995**, *36*, 201. (b) Abu-Yousef, I. A.; Harpp, D. N. *Sulfur Rep.* **1997**, *20*, 1.

(12) Abu-Yousef, I. A.; Harpp, D. N. *New Sulfenyl Chloride Chemistry. Stable Precursors For Sulfur Monoxide Transfer*; 25th Canadian Chemical Conference, Guelph, Ontario, Canada, June, 1995.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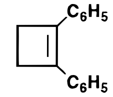
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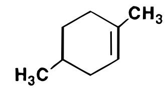
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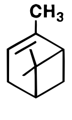
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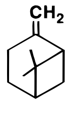
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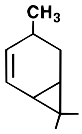
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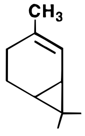
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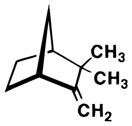
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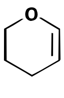
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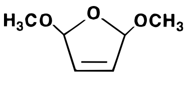
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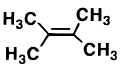
In addition, acyclic olefins such as 1,1,2,2-tetramethylethylene **(33)**, 1,1,2,2-tetraphenylethylene **(34)**, 1,1,2,2-tetracyanoethylene **(35)**, *trans*-stilbene **(36)**, *cis*-stilbene **(37)**, 1-bromo-2-methylpropene **(38)**, styrene **(39)**, bromostyrene **(40)**, and vinylcyclohexane **(41)** were also tried.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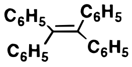
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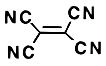
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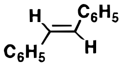
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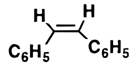
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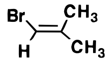
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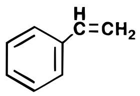
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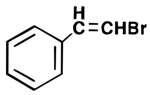
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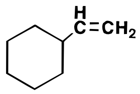

41

We discovered that olefins **22**−**41** remained unaffected even if the reactions were carried out over a few weeks. This behavior can be explained by the fact that the reaction must take place at room temperature because sulfenyl chlorides **1**−**3** decomposed upon heating, and most of the olefins are stable to addition chemistry, either due to conjugation or because they are vinyl halides.

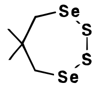
Trapping of Diatomic Sulfur (S_2). We found that when each of the 1,2-addition products **7**, **8**, or **13**−**17** were decomposed in the presence of 2,3-dimethyl-1,3-butadiene **(42)**, evidence was obtained of the trapping of diatomic sulfur.

In the literature, there are several reaction systems reported that successfully generate diatomic sulfur in synthetically useful yields.[13] These methods have certain limitations. For example, since triphenylphosphine dibromide **(43)** is light and moisture sensitive as well as reactive toward a wide variety of functionalities, the two procedures[13a,d] that require the use of compound **43** are difficult. In addition, the triarylmetal trisulfides **44**[13a] are not easy to prepare.

$R_3MSSSMR_3$
44
M = Si, Ge; R = Ph, *p*- $CH_3C_6H_4$

Ph_3PBr_2
43

The major limitation in case of the procedure of Steliou[13c] is that it must be conducted in the absence of most functionalities. The major sulfurating reagent, hexamethyldisilthiane, which was used in his procedure[14] to produce S_2, uses a method for the conversion of ketones to thioketones. The disilthiane readily reacts with moisture to produce hydrogen sulfide (H_2S). In addition, boron trichloride is a strong Lewis acid and readily complexes with oxygen or other donor atoms to hamper S_2 formation. In the case of the procedure of Schmidt and Görl,[13b] the major limitation is the difficulty in the preparation of 5,5-dimethyl-1,2-dithia-3,7-diselenacycloheptane **(45)**. The production of the cyclic tetrasulfide adduct 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(46)** from the reaction of S_2 with dienes has been indicated in several instances.[13d,e,f,15,17a]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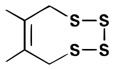
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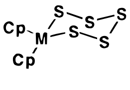
Nicolaou[15] isolated the corresponding cyclic tetrasulfide in the reaction of dithiatopazine **47** with 2,3-diphenyl-1,3-butadiene.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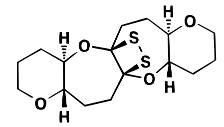
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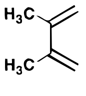
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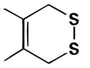
Most recently, Harpp and co-workers[13e] isolated cyclic di- and tetrasulfide adducts **46** and **49** from the thermal decomposition of alkoxydisulfide **50** with **42** in good yield.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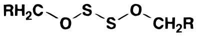
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One important theme of this work was to try to trap S_2 in the thermal decomposition of di- and trithio adducts **7**, **8**, and **13**−**17**. These in turn might decompose to species such as dithietane intermediate **4**, which should then transfer S_2 directly to dienes or lose S_2, which is then captured by dienes.

The successful identification of trapped S_2 was realized by ^1H NMR in the observation of cyclic disulfide **49** and tetrasulfide **46**. This took place when the decomposition of the 1,2-addition products **7**, **8**, and **13**−**17** was conducted in the presence of 2,3-dimethyl-1,3-butadiene **(42)**. Once these adducts were identified, the reaction conditions were modified so that the yield of the trapped adducts **49** and **46** was maximized.

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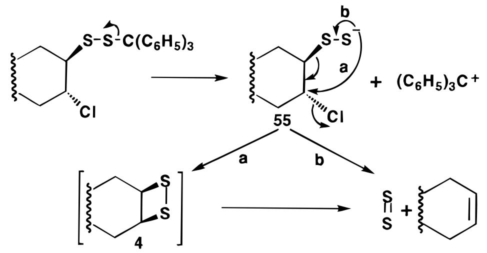
[13] (a) Steliou, K.; Gareau, Y.; Harpp, D. N. *J. Am. Chem. Soc.* **1984**, *106*, 799. (b) Schmidt, M.; Görl, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 887. (c) Steliou, K.; Salama, P.; Brodeur, D.; Gareau, Y *J. Am. Chem. Soc.* **1987**, *109*, 926. (d) Harpp, D. N.; McDonald, J. G. *J. Org. Chem.* **1988**, *53*, 3812. (e) Tardif, S.; Williams, C. R.; Harpp, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 9067. (f) These methods as well as others are summarized in the following articles: Harpp, D. N. The Sulfur Diatomics. *Phosphorus, Sulfur and Silicon* **1997**, *120 & 121*, 41−59. Tardif, S. L.; Rys, A. Z.; Abrams, C. B.; Abu-Yousef, I. A.; Leste-Lasserre, P. B. F.; Schultz, E. K. V.; Harpp, D. N. *Tetrahedron* **1997**, *53*, 12225−12236.

[14] Steliou, K.; Mrani, M. *J. Am. Chem. Soc.* **1982**, *104*, 3104.

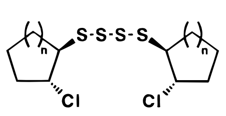
[15] Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Carroll, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 3801.

Scheme 2

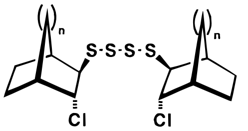


The general procedure used for the reaction of **7**, **8**, and **13**−**17** with 2,3-dimethyl-1,3-butadiene **(42)** is as follows. A solution of diene **42** and **7**, **8**, and **13**−**17** in an appropriate solvent was refluxed for a certain time under a nitrogen atmosphere. The reaction was followed by thin-layer chromatography using 15−25% chloroform in hexane as the eluent. In each case, cyclic disulfide **49** was detected by ^{1}H NMR in low yield and cyclic tetrasulfide adduct **46** was isolated in good yield. Their identities were confirmed by ^{1}H and ^{13}C NMR as well as by mass spectrometry.

Byproducts, the acyclic tetrasulfide adducts **51**−**54**, chlorotriphenylmethane, and starting material along with triphenylmethanethiol and elemental sulfur were isolated in low yields. In addition, the corresponding olefin was also detected by ^{1}H NMR. The identity of sulfide adducts **51**−**54** was confirmed by ^{1}H and ^{13}C NMR as well as by elemenal analysis.



51; n = 1
52; n = 2



53; n = 1
54; n = 2

In each case, there are two possible ways olefin could form. Scheme 2, path a, shows the possible formation of dithietane intermediate **4**. Scheme 2, path b, displays a concerted fragmentation producing diatomic sulfur and olefin directly from intermediate **55**. At present, it is not clear which mechanism is followed.

When 3 equiv of **7** were heated in ethyl acetate with 1 equiv of a standard diatomic sulfur trap, both cyclic disulfide adduct **49** and cyclic tetrasulfide adduct **46** were detected by ^{1}H NMR.

Eventually, tetrasulfide **46** was isolated in 24% yield. It is possible that intermediate **4** either transfers its two sulfur atoms to the diene trap to form **49** or gives up S_2, which is then trapped (Scheme 3). As has been noted by ourselves[13d,e,16] and in other labs,[17] a likely second trap of a two-sulfur unit takes place, forming tetrasulfide **46**.

The major product of the reaction is formed by an intermolecular pathway when **7** is heated in ethyl acetate, eventually giving the corresponding tetrasulfide **53** in 59% yield.

A possible pathway to explain this result is suggested in Scheme 3. In addition, starting material (16%) was isolated along with triphenylmethanethiol (27%), chlorotriphenylmethane (19%), and elemental sulfur (17%). Bicyclo[2.2.1]heptene **(5)** was detected by ^{1}H NMR (ca. 8%).

Scheme 3

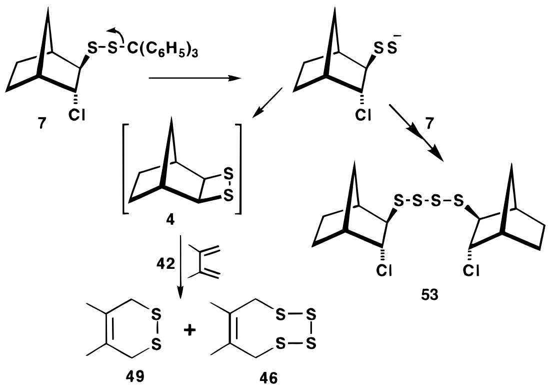


Table 1. Summary of Diatomic Sulfur-Trapping Experiments of 1,3-Diene 42 with Dithio Adducts 13 and 14

entry no.	R^a	solvent	temp (°C)	time (h)	% yield **46**^{b} from dithio		% yield^b of adducts	
					13	**14**	**51**	**52**
1	1:3	EtOAc	77	12	12	27	55	41
2	1:1	EtOAc	77	12	18	35	54	34
3	3:1	EtOAc^c	77	10	50	58	24	16
4	3:1	EtOAc^d	77	10	47	54	27	19
5	5:1	EtOAc	77	10	49	57	28	15
6	3:1	CH_2Cl_2	36	15	7	10	61	62
7	3:1	$CHCl_3$	36	15	10	15	59	58
8	1:1	$CHCl_3$	61	15	10	20	57	51
9	3:1	$CHCl_3$	61	15	11	26	56	42
10	1:1	C_6H_5Cl	132	2	16	31	55	36
11	3:1	C_6H_5Cl^{c}	132	2	30	48	40	20
12	3:1	C_6H_5Cl^{d}	132	2	29	47	39	18
13	3:1	C_6H_5Cl	132	10	30	49	37	20
14	5:1	C_6H_5Cl	132	2	32	50	36	18

^{a} Refers to the molar ratio of disulfides **13** and **14** to 1,3-diene **42**. ^{b} isolated yields after flash chromatography. ^{c} 50 mL of the solvent was used. ^{d} 15 mL of the solvent was used.

Recently, we reported[8] that stable 1,2-addition products **7** and **8** are formed when the reaction of triphenylmethanesulfenyl chloride **1** (or its thio (**2**) and dithio (**3**) homologue) were treated with bicyclo[2.2.1]heptene **(5)** and bicyclo[2.2.2]octene **(6)**. While diatomic sulfur transfers took place from them to a diene acceptor **42**, the yield of the final products was quite low. We tried to synthesize a new series of 1,2-addition products such as **13**−**17** in order to obtain better yields of **49** and **46**. Olefins such as cyclohexene **(11)** and cyclopentene **(10)** were used for this purpose.

In contrast, we discovered that the addition products (**13** and **14** from **2**; **16** and **17** from **3**) are effective in transferring two sulfur units to a diene trap when each of the di- and trithio adducts **13**, **14**, **16**, or **17** was heated in the presence of diene **42**. The decomposition was further investigated by varying the reaction conditions in an effort to maximize the yield of the trapped di-**49** and tetracyclic adducts **46**. A variety of solvents, temperatures, times, and concentrations were employed to optimize the yields of the trapped adducts. A summary of the results is shown in Table 1 (disulfides **13** and **14**). Acyclic tetrasulfide adducts **51** and **52** were formed by an intermolecular pathway as one of the minor products (Tables 1). The same results were obtained in the case of trisulfides **16** and **17** as shown in Table 5 of the

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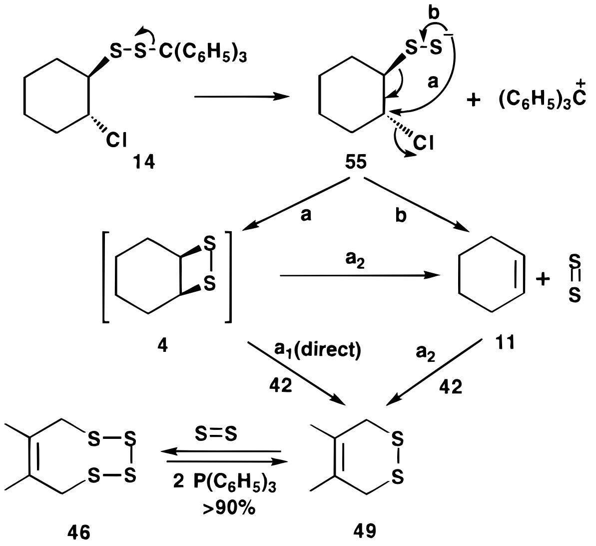
(16) Chew, W.; Harpp, D. N. *Sulfur Lett.* **1993**, *15*, 247.

(17) (a) Gilchrist, T. L.; Wood, J. R. *J. Chem. Soc., Chem. Commun.* **1992**, 1460. (b) Nicolaou, K. C.; DeFrees, S. A.; Hwang, C.-K.; Stylianides, N. A.; Carroll, P. J.; Snyder, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 3029.

Scheme 4



Supporting Information. Other minor products such as triphenylmethanethiol (ca. 29%) were also isolated along with chlorotriphenylmethane (ca.17%), starting material (ca. 9%), and elemental sulfur (ca. 24%). In addition, cyclopentene **(10)** and cyclohexene **(11)** were detected by ^{1}H NMR (ca. 7%). It is noteworthy to mention that an independent experiment showed that cyclohexene and elemental sulfur were produced upon the thermal decomposition of cyclohexenesulfide with ethyl acetate (*T* = 77 °C), with chlorobenzene (*T* = 132 °C), and with chloroform (*T* = 61 °C).

Also, it should be mentioned that an independent experiment showed that only about 40% of the theoretical amount of chlorotriphenylmethane emerges from silica gel chromatography; the trityl group is likely retained by reaction with the siloxy functions in the silica gel. By elution with methanol the trityl group was obtained (ca. 54%) in the form of triphenylmethanecarbinol (total recovery ca. 94%).

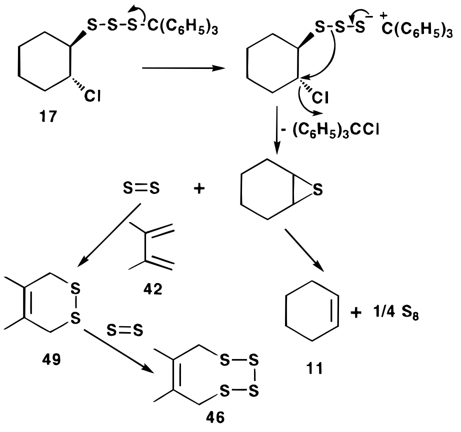
In these experiments, low yields of triphenylmethanethiol and elemental sulfur were obtained. To explain this, an independent experiment was carried out in which a solution with known amounts of triphenylmethanethiol and elemental sulfur was passed through the used column under the same conditions. Only 50−55% of these materials were isolated. It was necessary to use a column with a particular eluent (10−20% chloroform in hexane), since it was the only one that resulted in efficient separation of our major product.

The assignments of relevant ^{13}C NMR chemical shifts relative to tetramethylsilane of acyclic tetrasulfide adducts are reported in Table 7 of the Supporting Information. In the case of dithio reagent **14**, two decomposition avenues are likely (Scheme 4).

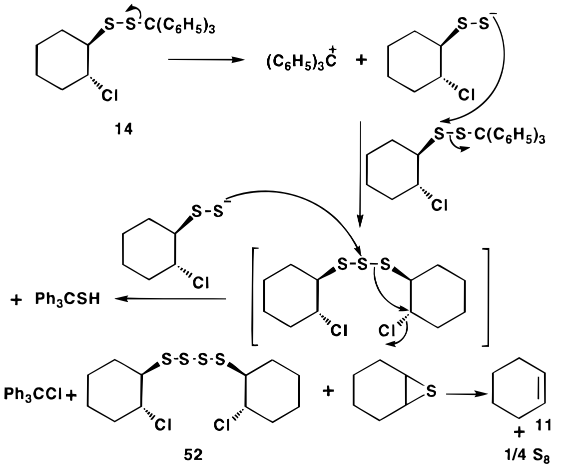
Dithietane intermediate **4**[15] (Scheme 4, path a) either directly transfers its two sulfur atoms to the diene trap to form **49** (Scheme 4, path a$_1$) or undergoes a cycloreversion to cyclohexene and $^1S_2$, which is then trapped (Scheme 4, path a$_2$). Conversely, intermediate **55** could fragment (Scheme 4, path b) directly to deliver $^1S_2$ which is then trapped (Scheme 4, path a$_2$).

In addition, we found cyclohexene **(11)** in the crude mixture; it is difficult to rationalize the presence of this molecule except by the decomposition of dithietane intermediate **4** or by a concerted expulsion of $^1S_2$ from intermediate **55** (Scheme 4). A second capture of a two-sulfur unit apparently takes place, which results in cyclic tetrasulfide adduct **46** as the major product. When an excess amount of precursors **13**, **14**, **16**, or **17** was employed, there was a significant production of tetrasulfide adduct **46** from disulfide **49**.

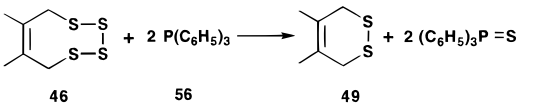
Scheme 5



Scheme 6



We found that cyclic tetrasulfide **46** can be converted quantitatively to a disulfide adduct **49** by an in situ treatment with triphenylphosphine **(56)** (eq 1).[13e] As a result, this methodology serves to transfer a two-sulfur unit to a diene in over 50% overall isolated yield.



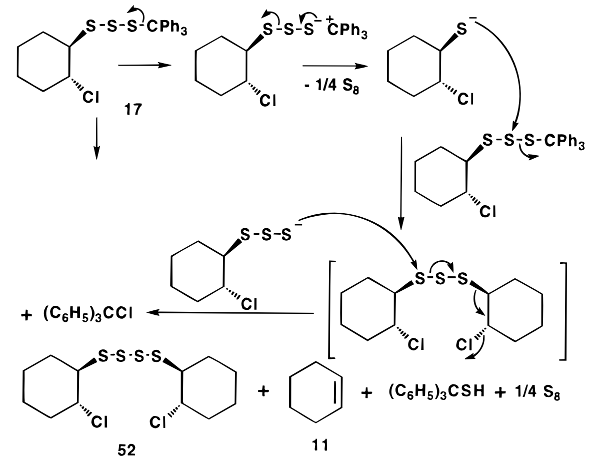
(1)

The most probable mechanism for the formation of cyclic tetrasulfide **46** from the thermal decomposition of dithio reagent **14** in the presence of **42** is shown in Scheme 4 above. A parallel path for the formation of **46** from **17** and **42** is shown in Scheme 5.

The formation of tetrasulfide **52** from **14** is rationalized in Scheme 6; a parallel path for the formation of **52** from trithio **17** is shown in Scheme 7.

In sum, the stable sulfenyl chlorides **1**−**3** each add to five different olefins to give stable adducts. These adducts deliver a net two-sulfur transfer to various dienes in overall isolated yields of up to 60%.

Scheme 7



Experimental Section

Reaction of Triphenylmethanesulfenyl Chloride (1) with Bicyclo[2.2.1]heptene (5). A typical procedure is illustrated; the same general procedure follows for **6**. A solution of triphenylmethanesulfenyl chloride[18,19] **(1)** (1.97 g, 12.5 mmol) in 25 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo[2.2.1]heptene **(5)** (1.177 g, 12.5 mmol) in 25 mL of dry CH_2Cl_2 under a nitrogen atmosphere at room temperature. The mixture was stirred for 20 h. Removal of the solvent under reduced pressure and chromatography[20] of the residue on silica gel with 10% chloroform in hexane afforded an oily product, which solidified upon treatment with 35−60 °C petroleum ether. Recrystallization from *n*-pentane gave 47% yield of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane **(7)**: mp 114−115 °C; ^{1}H NMR ($CDCl_3$) δ 0.94−1.60 (m, 7H), 2.01−2.04 (m, 1H), 2.28−2.30 (m, 1H), 3.62−3.64 (m, 1H), and 7.19−7.46 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$) δ 21.8, 28.3, 35.13, 42.6, 44.8, 58.8, 66.4, 71.3, 126.9, 127.9, 130.2, and 143.7 ppm. Anal. Calcd for $C_{26}H_{25}ClS_2$: C, 71.50; H, 5.73; S, 14.67. Found: C, 71.81; H, 5.82; S, 14.88. The X-ray crystallographic structure of dithio **7** was reported for the first time.[8]

In the case of **6**, compound **8** was formed in 43% yield: mp 118−119 °C; ^{1}H NMR ($CDCl_3$) δ 1.92−1.21 (m, 11H), 3.60 (m, 1H), and 7.20−7.55 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$) δ 18.6, 18.8, 25.0, 25.3, 28.7, 34.0, 55.9, 65.0, 71.2, 127.4, 128.3, 130.2, and 143.8 ppm. Anal. Calcd for $C_{27}H_{27}ClS_2$: C, 71.94; H, 5.99; S, 14.21. Found: C, 71.85; H, 6.12; S, 14.32. The X-ray crystallographic structure of dithio **8** was reported for the first time.[8]

Reaction of Triphenylmethanethiosulfenyl Chloride (2) with Bicyclo[2.2.1]heptene (5). By using thiosulfenyl chloride **2**,[20] in a similar preparation, a 93% yield of **7** was obtained, which had identical spectral properties to the product prepared using **1**: mp 114−115 °C. ^{1}H and ^{13}C NMR data were consistent with the structure of **7**, which was prepared via **1**.

Reaction of Triphenylmethanethiosulfenyl Chloride (2) with Bicyclo[2.2.2]octene (6). By using thiosulfenyl chloride **2**,[20] in a similar preparation, a 87% yield of **8** was obtained, which had identical spectral properties to the product prepared using **1**: mp 118−119 °C. Spectral data were consistent with the previous preparation of **8**.

Reaction of Triphenylmethanethiosulfenyl Chloride (2) with Cyclopentene (10). A typical procedure is illustrated; the same general procedure follows for **11** and **12**. A solution of triphenylmethanethiosulfenyl chloride **(2)**[20] (2.143 g, 6.25 mmol) in 20 mL of dry methylene chloride was added dropwise to a stirred solution of cyclopentene **(10)** (0.426 g, 6.25 mmol) in 25 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 7 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 15% chloroform in hexane afforded an oily product, which solidified under vacuum overnight. Recrystallization from *n*-pentane gave 2.25 g (88%) of *trans*-2-chloro-1-(triphenylmethyldithio)-cyclopentane **(13)**: mp 99−101 °C; ^{1}H NMR ($CDCl_3$) δ 1.27−2.40 (m, 7H), 4.30−4.40 (m 1H), and 7.21−7.70 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$) δ 22.0, 28.9, 33.7, 55.3, 65.8, 71.4, 127.0, 127.9, 130.0, and 143.6. Anal. Calcd for $C_{24}H_{23}Cl_2S_2$: C, 70.18; H, 5.60; S, 15.59. Found: C, 70.65; H, 5.60; S, 16.02.

Table 2. Preparation of Starting Materials

				product		% yield[b]	
alkene	**1**, **2**, or **3**	R^a	time (h)	dithio	trithio	dithio	trithio
5	**1**	1:1	20	**7**		**46**	
5	**1**	1:2	11	**7**		**93**	
6	**1**	1:1	22	**8**		**43**	
6	**1**	1:2	13	**8**		**90**	
5	**2**	1:1	15	**7**		**93**	
6	**2**	1:1	15	**8**		**87**	
10	**2**	1:1	9	**13**		**88**	
11	**2**	1:1	5	**14**		**90**	
12	**2**	1:1	8	**15**		**78**	
10	**3**	1:1	4		**16**		**93**
11	**3**	1:1	3		**17**		**94**

[a] Refers to the molar ratio of alkene to sulfenyl chloride **1**, **2**, or **3**. [b] CH_2Cl_2 was used as a solvent in each case.

In the case of **11**, compound **14** was formed in 90% yield: mp 103−104 °C; ^{1}H NMR ($CDCl_3$) δ 0.85−2.11 (m, 9H), 3.70−3.85 (m, 1H), and 7.15−7.55 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$) δ 22.5, 22.8, 28.6, 32.8, 52.8, 62.3, 71.4, 127.0, 128.0, 130.2, and 143.8 ppm. Anal. Calcd for $C_{25}H_{25}ClS_2$: C, 70.69; H, 5.89; S, 15.08. Found: C, 70.35; H, 6.08; S, 15.09.

For 1,4-dioxene **(12)**,[21] compound **15** was isolated as an oily product in a yield of 78%: ^{1}H NMR ($CDCl_3$) δ 3.38−3.50 (m, 2H), 3.58−3.61 (m, 1H), 4.11−4.20 (m, 2H), 5.31−5.36 (m, 1H), and 7.45−7.18 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$) δ 59.1, 59.7, 71.92, 88.2, 90.0, 127.7, 128.0, 130.0, and 143.2 ppm. Anal. Calcd for $C_{23}H_{21}ClO_2S_2$: C, 64.40; H, 4.93; S, 14.95. Found: C, 64.41; H, 4.94; S, 14.99.

Reaction of Triphenylmethanedithiosulfenyl Chloride (3) with Cyclopentene (10). By using dithiosulfenyl chloride **3**,[20] in a similar way as for thiosulfenyl chloride **2**, a 93% yield of **16** was obtained: mp 73−74 °C; ^{1}H NMR ($CDCl_3$) δ 1.52−2.25 (m, 6H), 3.30−3.41 (m, 1H), 4.40−4.42 (m, 1H), and 7.22−7.43 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$) δ 22.0, 29.7, 34.3, 59.4, 65.1, 73.3, 127.2, 128.0, 130.3, and 143.2 ppm. Anal. Calcd for $C_{24}H_{23}ClS_3$: C, 65.11; H, 5.19; S, 21.71. Found: C, 65.32; H, 5.10; S, 21.99. The X-ray crystallographic structure of trithio **16** has been reported.[10]

In the case of **11**, compound **17** was formed in 94% yield: mp 138−139 °C; ^{1}H NMR ($CDCl_3$) δ 1.30−1.71 (m, 6H), 2.11−2.21 (m, 2H), 2.83−2.85 (m, 1H), 3.99−4.03 (m, 1H), and 7.17−7.37 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$) δ 23.51, 23.88, 30.33, 34.30, 56.49, 61.51, 73.42, 127.14, 127.91, 130.37, and 143.33 ppm. Anal. Calcd for $C_{25}H_{25}ClS_3$: C, 65.74; H, 5.48; S, 21.04. Found: C, 65.66; H, 5.72; S, 20.70. The X-ray crystallographic structure of trithio **17** was reported for the first time.[10]

All of the experiments shown above are summarized in Table 2.

Thermal Chemistry of Dithio Adduct 7. A representative procedure is illustrated for **7**. The same was carried out for **8**, **13**, **14**, **16**, and **17**. The summary of these experiments is shown in Table 3. A solution of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane **(7)** (0.6 g, 1.48 mmol) in 20 mL of dry ethyl acetate was refluxed for 40 h under a nitrogen atmosphere. The reaction was followed by thin-layer chromatography using 20% $CHCl_3$ in hexane as

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(18) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley & Sons: New York, 1967; Vol. 1, p 1121.

(19) Williams, C. R.; Britten, J. F.; Harpp, D. N. *J. Org. Chem.* **1994**, *59*, 806.

(20) Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(21) Moss, R. D.; Paige, J. *J. Chem. Eng. Data* **1967**, *12*, 452.

Table 3. Thermal Chemistry of Adducts

adduct	reflux (h)	% yield tetrasulfide	% Ph_3CSH	% Ph_3CCl	% S_8	% olefin	% starting material
7	40	**53** (68)	21	19	18	7	15
8	42	**54** (60)	25	21	15	6	15
13	8	**51** (65)	24	20	26	8	12
14	13	**52** (69)	26	23	18	9	15
16	10	**51** (67)	27	19	23	6	10
17	15	**52** (65)	28	21	23	8	13

Table 4. Trapping Experiments with 2,3-Dimethyl-1,3-butadiene (42)

adduct	reflux (h)	% yield tetrasulfide	% yield		% Ph_3CSH	% Ph_3CCl	% S_8	% olefin	% starting material
			46	**49**					
7	36	**53** (59)	24	6	25	23	14	5	10
8	36	**54** (51)	19	5	23	21	18	7	14
13	8	**51** (24)	50	8	26	21	18	9	12
14	10	**52** (16)	58	10	28	18	17	8	10
15	13		45	7	24	20	12	6	14
16	24	**51** (22)	60	9	30	20	25	6	8
17	15	**52** (12)	63	8	29	17	24	7	9

eluent. After the solvent was evaporated under reduced pressure, the products were separated by column chromatography using the same eluent (20% $CHCl_3$ in hexane), in which the first fraction was isolated in a yield of 68% as an oily product and identified as di[(2-chloro)-1-norbornyl] tetrasulfide **(53)**: ^1H NMR ($CDCl_3$) δ 1.22−2.09 (m, 6H), 2.51 (m, 2H), 3.15 (m, 1H), and 4.15 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$) δ 21.87, 28.90, 35.84, 43.50, 44.75, 62.59 and 66.77 ppm. Anal. Calcd for $C_{14}H_{20}Cl_2S_4$: C, 43.44; H, 5.17; S, 33.10. Found: C, 43.58; H, 4.92; S, 33.04.

In the case of **8**, compound **54** was formed in 60% yield, respectively: ^1H NMR ($CDCl_3$) δ 1.20−2.15 (m, 10H), 3.58 (m, 1H), and 4.02 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$) δ 19.27, 19.48, 25.36, 26.17, 30.61, 34.48, 61.55, and 64.96 ppm. Anal. Calcd for $C_{16}H_{24}Cl_2S_4$: C, 46.29; H, 5.79; S, 30.86. Found: C, 46.10; H, 5.65; S, 30.63.

For **13** and **16**,compound **51** was isolated in yields of 65% and 67%, respectively: ^1H NMR ($CDCl_3$) δ 1.56−2.09 (m, 4H), 2.26−2.58 (m, 2H), 3.73−3.88 (m, 1H), and 4.51−4.69 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$) δ 22.59, 30.23, 34.79, 59.59, and 65.36 ppm. Anal. Calcd for $C_{10}H_{16}Cl_2S_4$: C, 35.85; H, 4.78; S, 38.24. Found: C, 35.50; H, 4.49; S, 38.35.

In the case of **14** and **17**, compound **52** was formed in 69% and 65% yields, respectively: ^1H NMR ($CDCl_3$) δ 1.29−1.95 (m, 6H), 2.19−2.41 (m, 2H), 3.18−3.33 (m, 1H), and 4.19−4.25 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$) δ 23.88, 24.29, 30.61, 35.07, 56.99, and 61.70 ppm. Anal. Calcd for $C_{12}H_{20}Cl_2S_4$: C, 39.70; H, 5.51; S, 35.29. Found: C, 40.08; H, 5.33; S, 35.00.

Trapping of Diatomic Sulfur from the Decomposition of Dithio Adduct 7 with 2,3-Dimethyl-1,3-butadiene (42). A sample procedure is as follows. 2,3-Dimethyl-1,3-butadiene **(42)** (0.0125 g, 0.153 mmol) was added to a mixture of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane **(7)** (0.20 g, 0.458 mmol) in 35 mL of dry ethyl acetate. The solution was refluxed for 36 h under a nitrogen atmosphere. The reaction was followed by thin-layer chromatography using 25% $CHCl_3$ in hexane as the eluent. After the solvent was evaporated under reduced pressure, the products were separated by column chromatography using the same eluent (25% $CHCl_3$ in hexane), in which the first fraction was isolated in a yield of 59% as an oily product and identified as the acyclic di[(2-chloro)-1-norbornyl]tetrasulfide **(53)**. Spectral data were consistent with the previous isolation of **53**. The second fraction was isolated and identified as the cyclic tetrasulfide adduct **(46)** (24%): ^1H NMR ($CDCl_3$) δ 3.63 (s, 4H) and 1.79 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 18.12 (CH_3), 42.76 (CH_2) and 130.33 ($C{=}C$) ppm. MS (*m/z*, rel int., assignment) 210, 8%, $M^{+\bullet}$; 146, 45%, $M^{+\bullet} - S_2$; 82, 90%, $M^{+\bullet} - S_4$; 67, 100%, $M^{+\bullet} - CH_3S_4$. Cyclic disulfide **49** was detected by ^1H NMR in low yield (ca. 6%).The same experiments were conducted for the decomposition of dithio adducts **8** and **13**−**17** with 2,3-dimethyl-1,3-butadiene **(42)**. The full summary is found in Table 4.

Thermal Chemistry of Cyclic Tetrasulfide 46 in the Presence of Triphenylphosphine (56). Triphenylphosphine **(56)** (0.142 g, 0.542 mmol) was added to a mixture of cyclic tetrasulfide **46** (0.057 g, 0.271 mmol) in 40 mL of dry diethyl ether. The solution was refluxed for 3 h under a nitrogen atmosphere. The reaction was followed by thin-layer chromatography using 15% $CHCl_3$ in hexane as the eluent. After the solvent was evaporated under reduced pressure, the products were isolated by column chromatography using the same eluent (15% $CHCl_3$ in hexane), which afforded cyclic disulfide **49** as an oily product in a yield of 98%: ^1H NMR ($CDCl_3$) δ 1.74 (s, 6H) and 3.19 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$) δ 20.81, 34.15, and125.15 ppm. MS (*m/z*, rel int., assignment) 146, 75%, $M^{+\bullet}$; 82, 100%, $M^{+\bullet} - S_2$; 67, 82%, $M^{+\bullet} - CH_3S_2$. In addition, triphenylphosphine sulfide was isolated in a yield of 98%.

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Supporting Information Available: Copies of the ^1H and ^{13}C spectra of compounds **7**, **8**, **13**−**17**, and **51**−**54** and tables of bond length data for **7**, **8**, **16**, and **17** and other relevant ^{13}C NMR data (27 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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