PRECURSORS FOR DIATOMIC SULFUR ($^1S_2$) AND SULFUR MONOXIDE (SO) FORMATION

A THESIS SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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بسم الله الرحمن الرحيم

وعلمك ما لم تكن تعلم وكان
فضل الله عليك عظيما

صدق الله العظيم

"AND TAUGHT THEE WHAT THOU KNEWEST NOT

AND GREAT IS THE GRACE OF GOD UNTO THEE"

To My Parents And

To Leena and Waila

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BY

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ABSTRACT

The electrophilic anti-addition of sulfenyl chlorides to carbon-carbon double bonds by a one pot reaction of triphenylmethanesulfenyl chloride **65** (or its thio **61** and dithio **70** homolog) with various types of olefins is used for the synthesis of a new series of di- and trithio compounds.

We have initiated a study of some of the chemistry of this type of addition hoping to develop a useful pathway to dithietanes like **77** as potentially stable intermediates and/or diatomic sulfur precursors.

The stereochemistry of addition has been determined by x-ray analysis. The x-ray crystal structures of di- and trithio reagents **68, 69, 75** and **76** are reported for the first time. The identity of these reagents was confirmed by ^1H and ^{13}C NMR as well as by elemental analysis.

The preparation of new and unusually stable episulfoxides by the use of triphenylmethanesulfenyl chloride **65** (or its thio **61** and dithio **70** homolog) has been investigated.

Adamantylideneadamantane thiirane **(116)** and bicyclo[3.3.1]nonylidenebicyclo-[3.3.1]nonane thiirane **(117)** (both shelf-stable) are produced in high isolated yields when sulfenyl chlorides **65, 61** or **70** are treated with the corresponding olefins adamantylideneadamantane **(108)** and bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane **(115)**, respectively.

Novel episulfoxides adamantylideneadamantane thiirane 1-oxide **(178)** and bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide **(179)** are produced in 99% isolated yield when episulfides **116** and **117** are subjected to *m*-CPBA oxidation.

The reaction of sulfur monoxide generated by the thermal decomposition of thiirane 1-oxides **178** and **179** has been intensively studied with various 1,3-dienes in a variety of solvents, varying temperature, time and concentration.

The x-ray crystal structures of adamantylideneadamantane thiirane **(116)** and adamantylideneadamantane thiirane 1-oxide **(178)** are reported for the first time. The structure of compounds **116, 117, 178, 179, 200, 201, 203** and **233** was established by ^{1}H and ^{13}C NMR as well as by mass spectrometry.

PRÉCURSSEURS POUR LA FORMATION DE SOUFRE DIATOMIQUE ($^1S_2$) ET DE MONOXIDE DE SOUFRE (SO)

PAR

IMAD ABU-YOUSEF

RÉSUMÉ

L'anti-addition électrophilique des chlorures de sulfényl sur des doubles liaisons carbone-carbone a été utilisée pour la synthèse d'une nouvelle classe de composés soufrés comportant deux ou trois soufres en faisant réagir, en une étape, un chlorure de triphénylméthanesulfényl **65** (ou son homologue soufré **61** et di-soufré **70**) avec différents types d'oléfines.

Nous avons commencé l'étude de ce type d'addition et nous espérons développer une voie vers la synthèse de dithiétanes, comme par example **77**, qui pourraient être des intermédiaires stables et/ou des précursseurs de soufre diatomique.

La stéréochimie de ce type d'addition a été déterminée par analyse cristallographique. La structure cristalline des réactifs di- et tri-soufrés **68**, **69**, **75** et **76** est rapportée pour la première fois. L'identification de ces réactifs a été confirmée par RMN du proton et du carbone ainsi que par analyse élémentaire.

La préparation de nouveaux épisulfoxides qui d'habitude ne sont pas stables, a été réalisée grâce à l'utilisation de chlorure de triphénylméthanesulfényl **65** (ou de son homologue soufré **61** et di-soufré **70**).

L'adamantylidèneadamantane thiirane (**116**) et le bicyclo[3.3.1]nonylidènebicyclo-[3.3.1]nonane thiirane (**117**) (tous les deux stables) ont été synthétisés et isolés avec des rendements élevés en faisant réagir les chlorures de sulfényl **65**, **61** ou **70** avec les oléfines

correspondantes c'est à dire respectivement l'adamantylidèneadamantane (**108**) et le bicyclo[3.3.1]nonylidènebicyclo[3.3.1]nonane (**115**).

De nouveaux épisulfoxides, l'adamantylidèneadamantane thiirane 1-oxide (**178**) et le bicyclo[3.3.1]nonylidènebicyclo[3.3.1]nonane thiirane 1-oxide (**179**) ont été synthétisés et isolés avec un rendement de 99% après oxidation des épisulfures **116** et **117** par du *méta*-chlorure d'acide perbenzoïque.

La réaction du monoxide de soufre qui est généré par la décomposition thermique des thiiranes 1-oxide **178** et **179**, a été largement étudiée avec différents types de 1,3-diènes dans différents solvants et en changeant la température, le temps de réaction et les concentrations.

Les structures cristallines de l'adamantylidèneadamantane thiirane (**116**) et de l'adamantylidèneadamantane thiirane 1-oxide (**178**) ont été rapportées pour la première fois. La structure des composés **116**, **117**, **178**, **179**, **200**, **201**, **203** et **233** a été élucidée par RMN du proton et du carbone, ainsi que par spectrométrie de masse.

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INDEX OF ABBREVIATIONS

Å	Ångstrom
°C	degrees Celsius
°K	degrees Kelvin
Mp.	melting point
ca.	circa
cm	centimeter
L	liter
mL	milliliter
eq.	equivalent
g	gram
mg	milligram
mol	mole
mmol	millimole
lit.	literature
kcal	kilocalories
MS	mass spectrometry
EI	electron impact
eV	electron Volt
min	minute
s	second
h	hour
Ph	phenyl
ether	diethyl ether
THF	tetrahydrofuran
DMSO	dimethylsulfoxide
DMF	dimethylformamide
EESO	ethylene episulfoxide
EtOAc	ethyl acetate
EtOH	ethanol
EPR	electron paramagnetic resonance
NMR	nuclear magnetic resonance
Ad_E2	bimolecular electrophilic addition

MHz	megahertz
Hz	hertz
TMS	tetramethylsilane
s	singlet
d	doublet
dd	doublet of doublets
t	triplet
q	quartet
o	ortho
p	para
m	meta
ppm	parts per million
tert	tertiary
i	iso
d	deuterium
R_f	relative mobility
UV	ultraviolet
IR	infrared
TLC	thin layer chromatography
isc	intersystem crossing

CHAPTER 1

INTRODUCTION

SULFUR EXTRUSION, CONCATENATION OF SULFUR ATOMS AND DIATOMIC SULFUR PRECURSORS

1.1 INTRODUCTION

Sulfur is one of the first elements known to man. It is the thirteenth most abundant element in nature and makes up to 0.052% of the weight of the earth's crust.[1]

In nature it is found as combinations like galena, cinnabar, celestite, sphalerite and iron pyrites.[2] The most important use of sulfur is in the synthesis of sulfuric acid.[3] Sulfur and oxygen are neighbors in the periodic table; sulfur lies directly below oxygen. However, the properties of sulfur and its organic derivatives vary from those of oxygen. For example, while dihydrogen oxide (H_2O)[4] is one of the most essential substances to life, dihydrogen sulfide (H_2S) is an odorous and poisonous gas.[5]

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1 R. C. Weast (Ed.), "Handbook of Chemistry and Physics", C. R. C. Press, Ohio, 1972, p. 176.

2 R. C. Weast (Ed.), "Handbook of Chemistry and Physics", C. R. C. Press, Ohio, 1972, p. 31.

3 E. V. Anderson, *Chem. & Eng. News*, May 5, 1975, p. 30.

4 A. Senning (Ed.), "Sulfur in Organic and Inorganic Chemistry", Marcel Dekker Inc., New York, Vol. 2, 1972, Chap. 15 and 16.

5 P. G. Stecher (Ed.), "The Merck Index", Merck & Co. Ltd. Inc., New Jersey, 1968, p. 545.

Sulfur can have three possible oxidation states (2, 4, 6)[6] because of its 3p and vacant d-orbitals for $p\pi$-$d\pi$ overlap. Several papers in the literature review the bond strengths and angles of sulfur compounds with those of analogs oxygen derivatives.[7] Due to their wide occurrence in organic compounds, especially in those of biological importance,[8] interest in synthesizing and improving the methods of synthesis of organosulfur compounds is an active area of research.

Sulfur compounds are widely used in industry, agriculture and medicine. In addition, some reviews[9] summarize the great utility of organosulfur intermediates in the synthesis of a variety of organic compounds.

---

6 B. E. Douglas and D. H. Mcdaniel, "Concepts and Models of Inorganic Chemistry", Blaisdell Pub. Co., London, 1965, p. 43.

7 a) D. Brewer, R. Rahman, S. Safe and A. Talyor, *J. Chem. Soc., Chem. Commun.*, 1571 (1968); b) N. Nagarajan, L. H. Huckstep, D. H. Lively, D. C. Delong, M. M. Marsh and N. Neuss, *J. Am. Chem. Soc.*, **90**, 2980 (1968); c) M. J. Janssen, "Organosulfur Chemistry", Interscience Pub., New York, 1967, p. 2; d) K. V. Jöst, V. Debabov, H. Nesvabda and J. Rudinger, *Coll. Czech. Chem. Commun.*, **29**, 419 (1964); e) J. Rudinger and K. Jöst, *Experimenta*, **20**, 570 (1964); f) N. Kharasch, "Organic Sulfur Compounds", Pergamon Press, New York, Vol. 1, 1961, p. 453; g) M. Koike and L. J. Reed, *J. Am. Chem. Soc.*, **81**, 505 (1959); h) E. E. Reid, "Organic Chemistry of Bivalent Sulfur", Chemical Pub. Co., New York, Vol. 1, 1958, p. 107; i) M. R. Bell, J. R. Johnson, B. S. Wildi and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 1001 (1958); j) D. F. Bradley and M. Calvin, *Proc. Natl. Acad. Sci.*, **41**, 563 (1655); k) K. G. Stren and A. J. White, *Biol. Chem.*, **117**, 95 (1937).

8 E. S. West, R. W. Todd, H. S. Mason and van J. T. Bruggen, "Textbook of Biochemistry", 4th Ed., Macmillan Co. Ltd., London, 1970.

9 a) B. M. Trost, *Acc. Chem. Res.*, **11**, 453 (1978); b) E. Block, *Aldrichimica Acta*, **11**, 51 (1978); c) E. Block, "Reactions of Organosulfur Compounds", Academic Press Inc., New York, 1978.

1.2 SULFUR EXTRUSION

Chemically, "sulfur extrusion" means the loss of a sulfur atom from any molecule. Raney Nickel desulfurization,[10] and the Ramburg-Backlund rearrangement[11] are very well-known sulfur extrusion reactions. There are innumerable examples in the literature where one of the products in a chemical reaction is elemental sulfur.[12] The sulfur that is lost is often inappropriately represented as S, [S], S^o or S_1.

However, the mechanism through which sulfur is produced from these reactions is not well understood. Extrusion of elemental sulfur is observed under many conditions: thermally, photochemically as well as base and solvent induced. For example, Stark and Duke[13] and Loudon[14] examined extrusions in stable aromatic systems. Whereas, Radl[15] reported extrusions which resulted in the formation of five-membered ring heterocycles. On the other hand, Guziec and Sanfilippo[16] studied some examples of the extrusion of sulfur, selenium and tellurium.

A recent review on thermal decomposition of sulfur compounds including thiiranes, was published by Harpp and Williams.[12]

In several cases, sulfur extrusion is proposed to proceed through a cheletropic loss of a singlet sulfur atom to eventually form elemental sulfur (S_8). However, the energy of formation of a singlet sulfur atom is very high (about 66.3 Kcal/mole),[17] which makes this

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10 J. Bougault, E. Cattelain and P. Chabrier, *Comp. Rend.*, **208**, 657 (1939); b) J. Bougault, E. Cattelain and P. Chabrier, *Bull. Soc. Chim. France*, **7**, 781 (1940).

11 a) S. Yamada, H. Ohsawa, T. Suzuki and H. Takayama, *J. Org. Chem.*, **51**, 4934 (1986); b) W. L. Mock, *J. Am. Chem. Soc.*, **97**, 3666 (1975).

12 C. R. Williams and D. N. Harpp, *Sulfur Reports*, **10**, 103 (1990).

13 B. P. Stark and A. J. Duke, "Extrusion Reactions", Pergamon Press, Oxford, 1967, p. 72.

14 J. D. Loudon, "Organic Sulfur Compounds", N. Kharasch (Ed.), Pergamon Press, Oxford, Vol. 1, 1961, p. 299.

15 S. Radl, *Janssen Chim. Acta.*, **5**, 3 (1987).

16 F. S. Guziec, Jr. and L. J. Sanfilippo, *Tetrahedron*, **44**, 6241 (1988).

17 a) K. J. Miller, K. F. Moschner and K. T. Potts, *J. Am. Chem. Soc.*, **105**, 1705 (1983); b) "JANAF Thermochemical Tables", Dow Chemical Co., Midland Mich., 1966.

pathway of losing sulfur not likely. Instead, a low energy intermediate (S_2), or longer-chain fragments[18] can be proposed.

In many examples of sulfur extrusion, thiiranes, the sulfur analogs of oxiranes, are the proposed intermediates. They can undergo reactions similar to those of oxiranes such as nucleophilic ring opening[19] and olefin formation with phosphorous nucleophiles.[20] However, thiiranes can lose sulfur **(Scheme 1)** whereas oxiranes do not lose oxygen. There are many instances where thiiranes decompose directly to olefins and elemental sulfur.[21]

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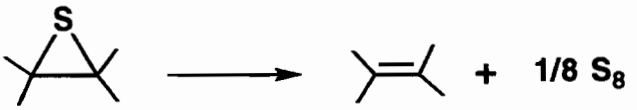
18 D. N. Harpp, "Prespectives in the Organic Chemistry of Sulfur", B. Zwanenburg, A. J. H. Klunder (Ed.), Elsevier, Amsterdam, 1987, p. 1-22.

19 H. R. Snyder, M. Stewart and J. B. Ziegler, *J. Am. Chem. Soc.*, **69**, 2637 (1947).

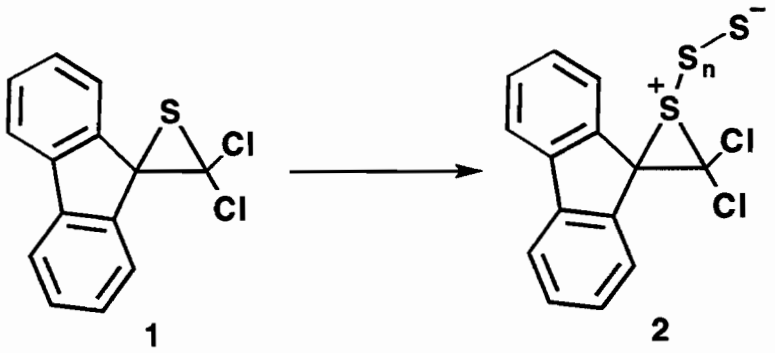
20 D. B. Denny and M. S. Boskin, *J. Am. Chem. Soc.*, **82**, 4736 (1960).

21 a) Y. Gao and B. Sharpless, *J. Org. Chem.*, **53**, 4114 (1988); b) W. Ando, A. Itami, T. Furuhata and N. Tokitoh, *Tetrahedron Lett.*, 1787 (1987); c) G. A. Tolstikov, B. M. Lerman and L. I. Umanskya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1367 (1982); *Chem. Abstr.*, **97** 162438d (1982); d) D. Seyferth, W. Tronich, K. S. Marmor and W. E. Smith, *J. Org. Chem.*, **37**, 1537 (1972); e) T. Sato, Y. Goto, T. Tohyama, S. Hayashi and K. Hata, *Bull. Chem. Soc. Jpn.*, **40**, 2975 (1967); f) E. P. Adams, K. N. Ayad, F. P. Doyle, D. O. Holland, W. H. Hunter, J. H. C. Nayler and A. Queen, *J. Chem. Soc., Chem. Commun.*, 2665 (1960); g) C. G. Moore and M. Proter, *J. Chem. Soc., Chem. Commun.*, 2062 (1958); h) A. Schönberg, K. Fateen and M. A. Sammour, *J. Am. Chem. Soc.*, **79**, 6020 (1957); i) C. O. Guss and D. L. Chamberlain, Jr., *J. Am. Chem. Soc.*, **74**, 1342 (1952); j) G. P. Hagen and R. M. Burgison, *J. Am. Pharm. Assoc.*, **39**, 7 (1950); k) M. Mousseron, M. Bousquet and G. Marett, *Bull. Soc. Chim. France*, 84 (1948); l) A. Schönberg and L. von Vargha, *Chem. Ber.*, **64B**, 1390 (1931); m) A. Schönberg and L. von Vargha, *Justus Liebigs Ann. Chem.*, **483**, 176 (1930); n) M. A. Youtz and P. P. Perkins, *J. Am. Chem. Soc.*, **51**, 3508 (1929); o) A. Schönberg, *Chem. Ber.*, **58**, 1793 (1925); p) H. Staudinger and J. Siegwart, *Helv. Chim. Acta.*, **3**, 840 (1920); q) H. Staudinger and J. Siegwart, *Helv. Chim. Acta.*, **3**, 833 (1920).



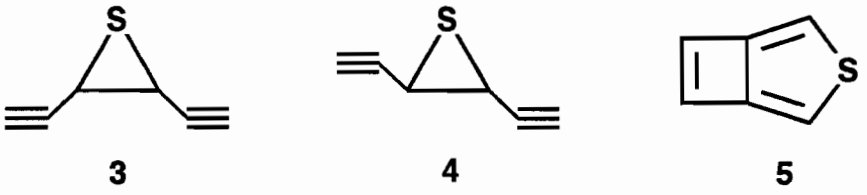
SCHEME 1

The thermal decomposition of thiirane to an olefin and sulfur has been claimed to happen through simple cheletropic loss of one sulfur atom. However, Lutz and Biellmann[22] indicated that the loss of sulfur from the decomposition of **1** took place not by first-order kinetics but through a more complex mechanism, perhaps involving a bridged sulfur species. Such a species **2** **(Scheme 2)** was later proposed in a mechanistic study by Harpp and Chew.[23]



SCHEME 2

An earlier study of sulfur extrusion was the pyrolysis[24] of *cis*- and *trans*-1,2-diethenyl thiiranes **(3)** and **(4)** respectively.



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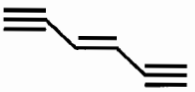
22 E. Lutz and J.-F. Biellmann, *Tetrahedron Lett.*, 2789 (1985).

23 a) W. Chew, R. C. Hynes and D. N. Harpp, *J. Org. Chem.*, **58**, 4398 (1993); b) W. Chew and D. N. Harpp, *J. Org. Chem.*, **58**, 4405 (1993).

24 K. P. C. Vollhardt and R. G. Bergman, *J. Am. Chem. Soc.*, **95**, 7538 (1973).

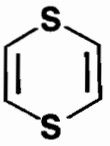
A competition between the sulfur extrusion and the thermal synthesis of thienocyclobutadiene (**5**) occurred. When performed at 100 °C, pyrolysis of the thiiranes yields only the corresponding desulfurized olefins **6** and **7**.

6



7

The mechanism of the reaction is more complicated than a simple cheletropic loss of a sulfur atom. Thermal extrusion was thought to proceed through a loss of sulfur ($^1S_1$) from dithiins **8** and **9** to form thiophenes[25] and from thiepins **10** to form stable aromatic systems.[13,14]



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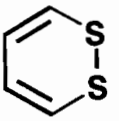

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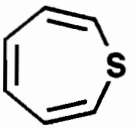
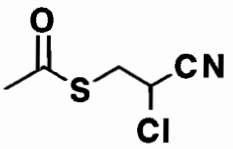


10

Mueller[26] was unsuccessful in trapping sulfur in the reaction of α-chloro-β-(acetylthio)propionitrile (**11**) and diethylamine with an alkene. He proposed a thiirane intermediate which lost sulfur spontaneously. Also, Field and coworkers[27] were unsuccessful in trapping sulfur in the oxidation of phosphothiolate **12** by a peroxy acid.



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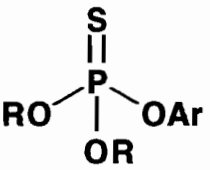

12

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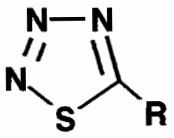
25 a) W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **77**, 68 (1955); b) R. Grigg, R. Hayes and J. L. Jackson, *J. Chem. Soc., Chem. Commun.*, 1167 (1969).

26 W. H. Mueller, *J. Org. Chem.*, **34**, 2955 (1969).

27 L. Field, N. E. Heimer, R. I. McNeil, R. A. Neal, J. Swinson and J. R. Van Wazer, *Sulfur Lett.*, **1**, 135 (1983).

Moreover, photolysis of 5-substituted-1,2,3,4-thiatriazoles **13** in the presence of olefins did not yield the corresponding thiirane. However, under the same conditions, the photolysis of isothiocyanates **14**[28] appears to deliver a sulfur atom as they formed thiiranes.



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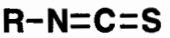
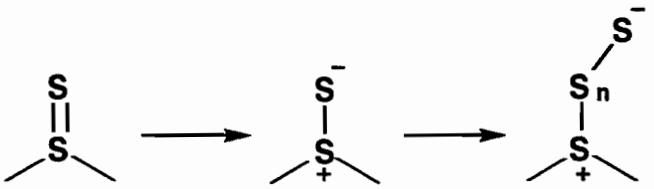


14

The photolysis results were not surprising, since sulfur atoms are usually prepared by the photolysis of carbonyl sulfide (**COS**).[29]

1.3 CONCATENATION OF SULFUR ATOMS

One of the more attractive mechanisms in sulfur extrusion reactions was first conceived by Foss in 1950.[30] The initial step involves the combination of two sulfur species followed by a transfer of a sulfur atom forming a thiosulfoxide-type intermediate **15** which then reacts with another molecule until the sulfur chain **16** is six or eight atom long and could cyclize to S_6 or more likely S_8.



15 **16**

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28 R. Jahn and U. Schmidt, *Monatsh. Chem.*, **109**, 161 (1978).

29 a) K. Gollnick and E. Leppin, *J. Am. Chem. Soc.*, **92**, 2217 (1970); b) E. Leppin and K. Gollnick, *J. Am. Chem. Soc.*, **92**, 2221 (1970).

30 a) O. Foss, *Acta. Chem. Scand.*, 4 (1950); b) O. Foss, "Organic Sulfur Compounds", N. Kharasch (Ed.), Pergamon Press, New York, 1961, p. 75-77.

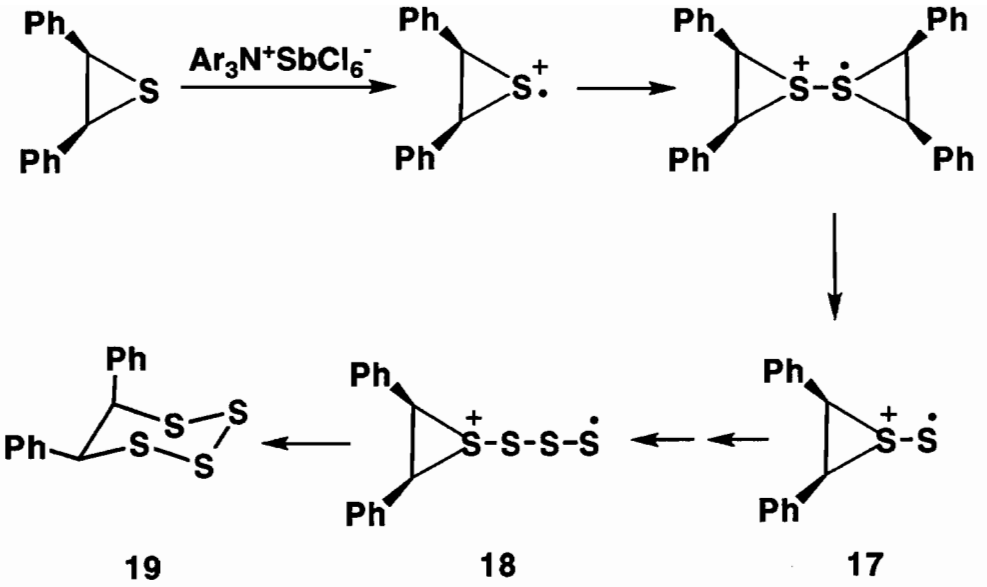
The thiosulfoxide moiety and the sulfur atom concatenation mechanism are well discussed in the literature.[23,31] Davis[32] proposed a similar mechanism to interpret the formation of elemental sulfur in acidified solutions of thiosulfate. Moreover, Kamata and coworkers[33] isolated a tetrathiane in the reaction of *cis*- and *trans*-2,3-diphenylthiirane with a catalytic amount of tris(*p*-bromophenyl)aminium hexachloroantimonate in methylene chloride. The proposed mechanism of formation involved a thiirane cation radical abstracting a sulfur atom from another thiirane cation radical resulting in a two sulfur species cation radical **17** with a concomitant release of stilbene. A further linkage of two sulfur atoms gave intermediate **18** which cyclized affording the tetrathiane **19 (Scheme 3)**.

---

31 a) W. Chew and D. N. Harpp, *Tetrahedron Lett.*, **33**, 45 (1992); b) W. Ando, H. Sonobe and T. Akasaka, *Tetrahedron Lett.*, **31**, 5093 (1990); c) M. Green, E. M. Cown and O. P. Strausz, *J. Am. Chem. Soc.*, **106**, 6938 (1984); d) G. W. Kutney and K. Turnbull, *Chem. Rev.*, **82**, 333 (1982); e) D. N. Harpp, K. Steliou and C. J. Cheer, *J. Chem. Soc., Chem. Commun.*, 825 (1980); f) R. D. Baechler and S. K. Daley, *Tetrahedron Lett.*, 101 (1978); g) R. D. Baechler, S. K. Daley, B. Daly and K. McGlynn, *Tetrahedron Lett.*, 105 (1978); h) G. Höfle and J. E. Baldwin, *J. Am. Chem. Soc.*, **93**, 6307 (1971); i) R. Grigg, R. Hayes and J. L Jackson, *J. Chem. Soc., Chem. Commun.*, 1167 (1969); j) Von F. Seel and H. D. Gölitz, *Z. anorg. allg. Chem.*, 32 (1964).

32 R. E. Davis, *J. Am. Chem. Soc.*, **80**, 3565 (1958).

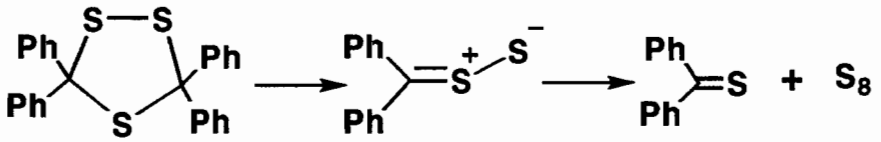
33 M. Kamata, K. Murayama, T. Suzuki and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, 827 (1990).



19 18 17

SCHEME 3

Huisgen and Rapp[34] suggested that in the thermal decomposition of trithiolane **20**, a thiobenzophenone-S-sulfide **(21)** is formed which undergoes abstraction of sulfur atoms leading to the formation of S_8 and thiobenzophenone **(Scheme 4)**.



20 21

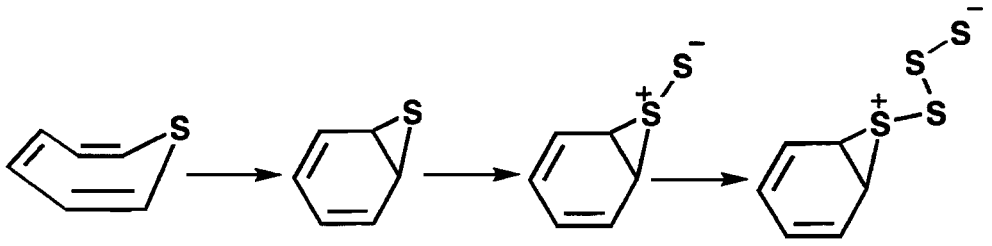
SCHEME 4

Gleiter and coworkers[35] studied the loss of sulfur atoms of thiepins and concluded that the extrusion of sulfur proceeds *via* rearrangement to a thiirane intermediate **22** followed by the linking of sulfur atoms to give intermediate **23** which would eventually lose elemental sulfur. The extrusion of S_2 or S_8 would be an energetically more favorable pathway than expulsion of other species of sulfur **(Scheme 5)**.

---

34 R. Huisgen and J. Rapp, *J. Am. Chem. Soc.*, **109**, 902 (1987).

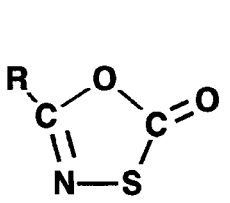
35 R. Gleiter, G. Krennrich, D. Cremer, K. Yamamoto and I. Murata, *J. Am. Chem. Soc.*, **107**, 6874 (1985).



22 23

SCHEME 5

Concatenation was also proposed to account for the formation of elemental sulfur in the decomposition of heterocyclic **24**,[36] when phosphothiolate **12** was oxidized with a peroxy acid[27] and when dipyridol[1,2-a:1',2'-c]imidazolium-11-thiolate **25** was refluxed with hydrobromic acid.[37]



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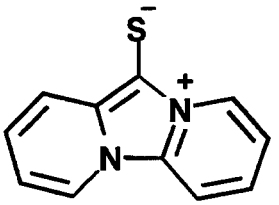

25

Of the possible mechanisms considered for the formation of sulfur in many sulfur extrusion reactions reported above, it appears that both the loss of singlet diatomic sulfur and the concatenation of sulfur atoms to ultimately form elemental sulfur are the most reasonable pathways. The most likely mechanism for sulfur extrusion appears to be the concatenation of sulfur atoms to form a chain which would ultimately cyclize to form elemental sulfur.[23] Thus, singlet diatomic sulfur might not be formed as a distinct species in any of these reactions.

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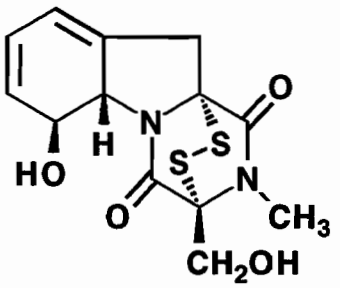
36 a) R. K. Howe and J. E. Franz, *J. Org. Chem.*, **39**, 962 (1974); b) R. K. Howe and B. R. Shelton, *J. Org. Chem.*, **46**, 771 (1981).

37 J. T. Edward and R. H. Sheffler, *J. Org. Chem.*, **50**, 4855 (1985).

1.4 DIATOMIC SULFUR PRECURSORS

Diatomic sulfur, S_2, is isovalent with O_2 and has a similar basic electronic structure. Singlet oxygen chemistry is well developed and has been extensively studied.[38] The rapid development in singlet oxygen chemistry has initiated considerable interest in its analogs sulfur species, $^1S_2$. Singlet oxygen is known to play an important role in many biological processes. So far, singlet diatomic sulfur, $^1S_2$, has been found to be a synthetic tool for organic chemists. Its importance in organic synthetic chemistry and drug synthesis has been reviewed by Steliou.[39] Due to the importance of the S_2 unit in many natural products such as the gliotoxin **26**,[40] methods for the generation of singlet diatomic sulfur have gained prominence.



26

In 1928, Staudinger and Freudenberger[41] proposed a six-membered ring **27** as an intermediate in the photolytic decomposition of thioketones to give the corresponding ketones and elemental sulfur. This ring could undergo a cyclic reversion to form two molecules of ketone and S_2. A similar mechanism involving a six-membered ring intermediate **28** could be involved in a study by Thompson[42] involving the decomposition

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38 H. H. Wasserman and R. W. Murray, "Singlet Oxygen", Academic Press, New York, 1989.

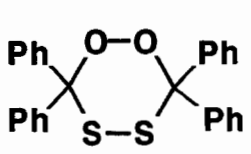
39 K. Steliou, Y. Gareau, G. Milot and P. Salama, Phosphorus, Sulfur and Silicon, C. T. Pedersen and J. Becher (Eds.), Gordon and Breach, Science Publishers Inc., England, 1989, p. 209-241.

40 A. Taylor, "Microbial Toxins VII", S. Kadis, A. Ciegler and J. S. Ajl (Eds.), Academic, New York, 1971, p. 337-376.

41 H. Staudinger and H. Freudenberger, *Chem. Ber.*, **61**, 1576 (1928).

42 Q. E. Thompson, M. M. Crutchfield, M. W. Dietrich and E. Pierron, *J. Org. Chem.*, **30**, 2692 (1965).

of dialkoxy disulfides **29** to the corresponding aldehyde, alcohol and elemental sulfur **(Scheme 6)**.



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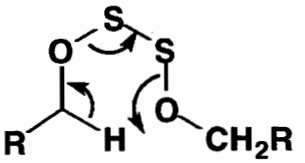

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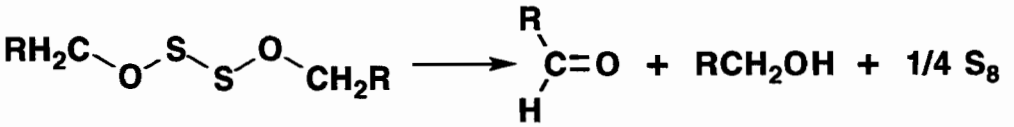
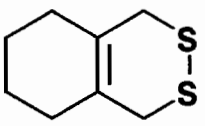


29

SCHEME 6

A variety of methods for the formation of $^1S_2$ were discussed in 1991 by Steliou.[43] Several unsuccessful approaches have been tried when no trapped products were identified.[44] Jahn and Schmidt[45] reported the first successful trapping of S_2 in 1975. Evidence of the production of S_2 has been obtained through trapping experiments with 1,3-dienes in the absence of which, S_2 concatenates to elemental sulfur, S_8. The isolation of the addition adduct **30** of 1,2-dimethylenecyclohexane **(31)** suggested the formation of S_2 as an intermediate in the sulfur loss mechanism, however, the isolated yield of **30** was only 2%. The other isolated products were thiophenes **32** and **33**.



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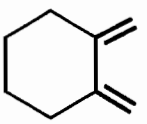

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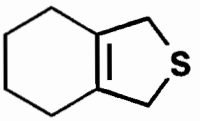

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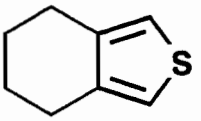

33

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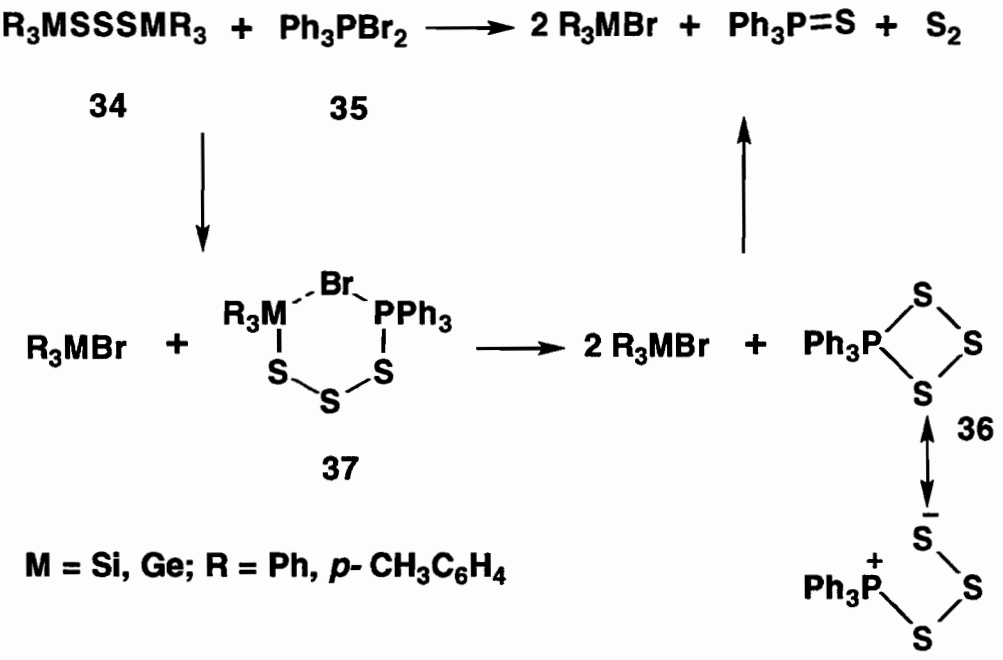
43 K. Steliou, *Acc. Chem. Res.*, 341 (1991).

44 a) A. Orahovatz, M. J. Levinson, P. J. Carroll, M. V. Lakshmikanthan and M. P. Cava, *J. Org. Chem.*, **50**, 1550 (1985); b) W. Ando, Y. Kumamoto, N. Tokitoh, *Tetrahedron Lett.*, **28**, 4833 (1987); c) P. D. Bartlett and T. Ghosh, *J. Org. Chem.*, **52**, 4937 (1987).

45 R. Jahn and U. Schmidt, *Chem. Ber.*, **108**, 630 (1975).

Reactions of activated elemental sulfur with dienes have also been studied.[46] These reactions resulted in the formation of several sulfurated products. The isolation of other sulfuration products in sulfur extrusion reactions indicated that the sulfur may not be lost as S_2 only, but also in other forms of activated sulfur, the structures of which are unknown.

The first synthetically useful S_2 precursors were reported by Steliou[47] in 1984. S_2 was delivered and captured as a Diels-Alder adduct when an organometallic trisulfide **34** reacted with triphenylphosphine dibromide (**35**). Two intermediates were proposed in the reaction. A triphenylphosphine thioozonide intermediate **36** (such a structure would be similar to the oxygen analog found in the reaction of PPh_3 with O_3),[48] as well as the six-membered species depicted in **37** (**Scheme 7**).



SCHEME 7

Two diatomic sulfur precursors were reported almost simultaneously in 1987. Schmidt and Görl[49] reported that a tetrachalcogen **38** undergoes thermal decomposition

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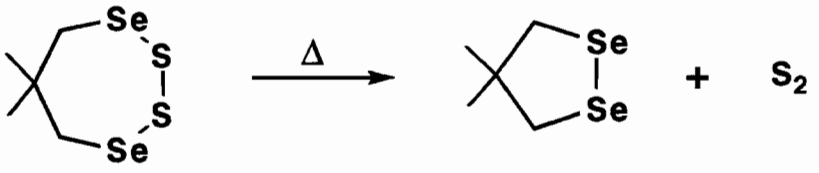
46 a) J. A. Elvidge, S. P. Jones and T. L. Peppard, *J. Chem. Soc., Perkin Trans 1*, 1089 (1982); b) Steudel, *Top. Curr. Chem.*, **102**, 149 (1982).

47 K. Steliou, Y. Gareau and D. N. Harpp, *J. Am. Chem. Soc.*, **106**, 799 (1984).

48 P. D. Partlett and M. Lonzetta, *J. Am. Chem. Soc.*, **105**, 1984 (1983).

49 M. Schmidt and U. Görl, *Angew. Chem., Int. Ed. Engl.*, **26**, 887 (1987).

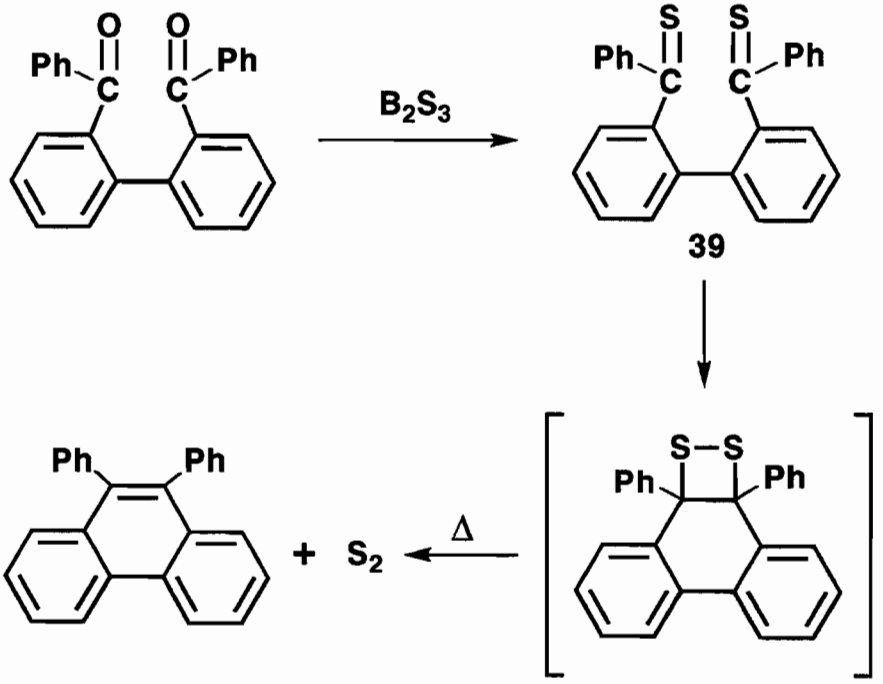
with ring contraction transferring S_2 which was trapped by 2,3-dimethyl-1,3-butadiene **(Scheme 8)**.



38

SCHEME 8

A useful synthetic method to prepare S_2 was reported by Steliou and coworkers.[50] This method was based on a novel head-to-head dimerization of 2,2'-bis(thiobenzoyl)-biphenyl **(39)** generated from 2,2'-bis(benzoyl)biphenyl in the presence of B_2S_3. A dithietane intermediate which was postulated could spontaneously release S_2 and 9,10-diphenylphenanthrene **(Scheme 9)**.

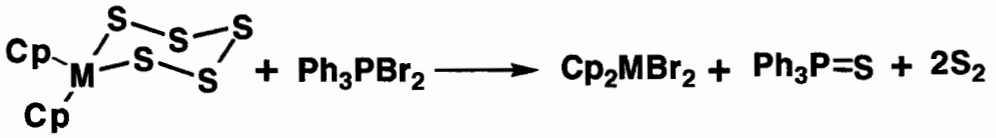


SCHEME 9

50 K. Steliou, P. Salama, D. Brodeur and Y. Gareau, *J. Am. Chem. Soc.*, **109**, 926 (1987).

Diatomic sulfur ($^1S_2$) was trapped when the reaction is carried out in the presence of dienes. The cyclic disulfides were isolated in good yield.

Harpp and McDonald[51] successfully generated S_2 in 1988. Their method is based on the reaction of an organometallic pentasulfides **40** with triphenylphosphine dibromide (**35**) which gives S_2 that is trapped by 1,3-butadienes. The intermediate in the formation of S_2 could again be the thioozonide **36 (Scheme 10)**.

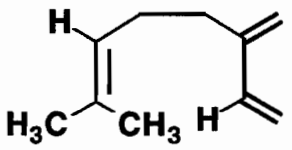


40 **35**

M = Ti, Zr, Hf; Cp = η^5-C_5H_5

SCHEME 10

The generation of S_2 provides a logical one-step synthetic procedure for the preparation of cyclic disulfide *via* Diels-Alder addition to 1,3-dienes. For example, myrcene disulfide (**42**) was successfully synthesized from myrcene (**41**),[46a] by Steliou,[50] as well as by Schmidt and Görl.[49]



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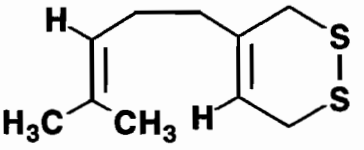

42

Some substituted 3,6-dihydro-1,2-dithiin derivatives **43** prepared by the S_2 methodology,[50] proved to posses anti-HIV activity.[39]

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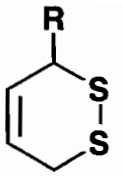
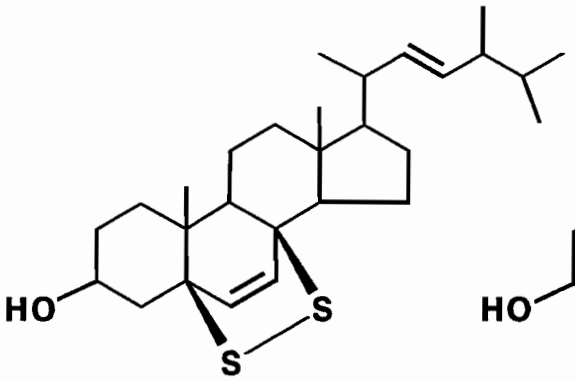
51 D. N. Harpp and J. G. McDonald, *J. Org. Chem.*, **53**, 3812 (1988).



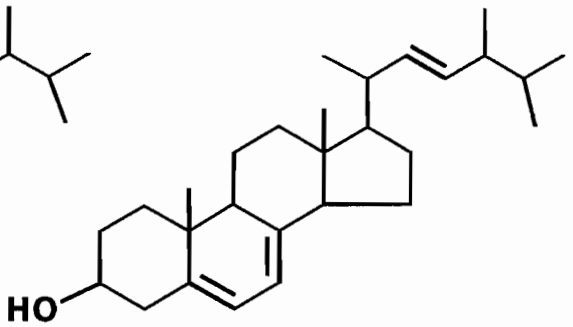
43

R = CH_2CO_2H, CH_2CH_2OH, CH_2CH_2OAc

Diatomic methodology may be used in the synthesis of bridged disulfides where the most difficult step in this synthesis was the formation of the S-S bond like gliotoxin **26**.[52] However, attempts to prepare ergosterol endodisulfide (**44**) from ergosterol (**45**) using the S_2 methodology were unsuccessful.[53]



44



45

Interestingly, in 1985, Cava and coworkers[44a] reported S_2 to be a byproduct of the decomposition of 1,2-dithetane **46**, formed from a Diels-Alder addition of acenaphthene-dithione **47** with its 1,2-dithiete tautomer **48** **(Scheme 11)** but no supporting trapping evidence for its formation was presented.

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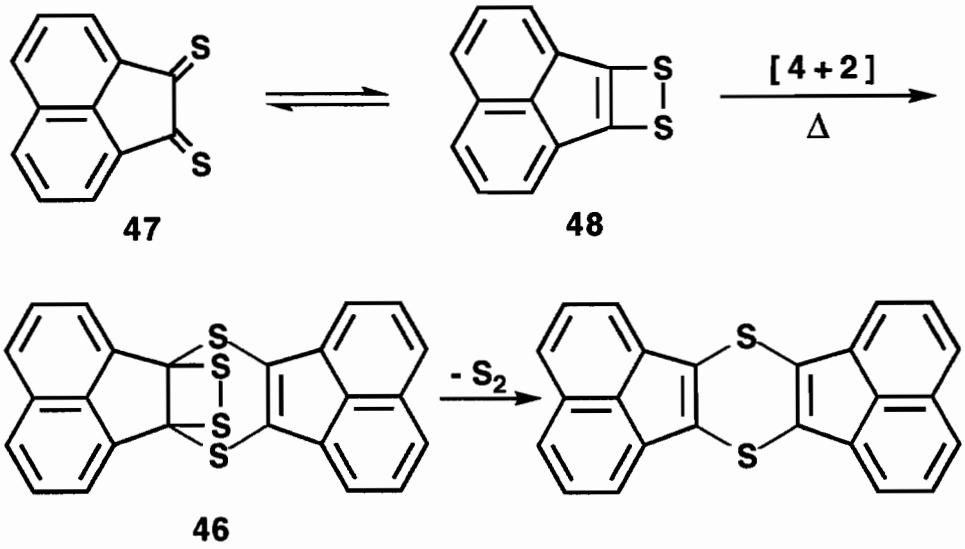
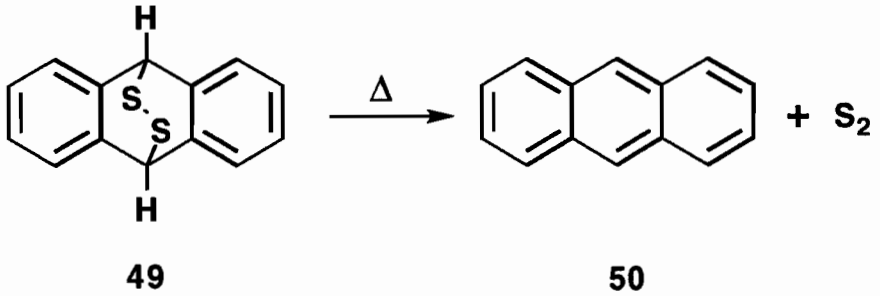
52 a) Y. Kishi, T. Fukayama and S. Nakatsuka, *J. Am. Chem. Soc.*, **95**, 6490 (1973); b) Y. Kishi, T. Fukayama and S. Nakatsuka, *J. Am. Chem., Soc.*, **95**, 6492 (1973).

53 Y. S. Tsantrizos, P. L. Folkins, J. F. Britten, D. N. Harpp and K. K. Ogilvie, *Can. J. Chem.*, **70**, 158 (1992).



SCHEME 11

Another pathway toward the production of S_2 has been reported by Ando and coworkers[54] where the thermal decomposition of anthracene endodisulfide **49** produces diatomic sulfur and anthracene **(50)** **(Scheme 12)**



SCHEME 12

However, it was not clear whether the Diels-Alder adducts were isolated or detected; the yields were based on the amount of recovered product. Bartlett and Ghosh[44c] attempted to trap S_2 in the conversion of pentathiepins **51** to trithiolanes **52** but were unsuccessful.

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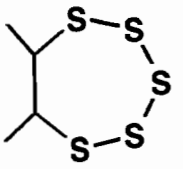
54 W. Ando, H. Sonobe and T. Akasaka, *Tetrahedron Lett.*, **28**, 6653 (1987).



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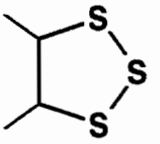
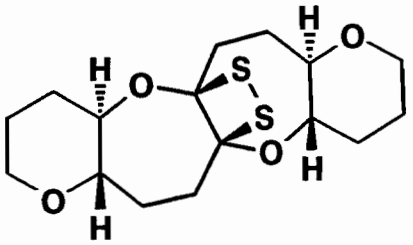


52

Nicolaou and coworkers[55] synthesized and isolated the first stable 1,2-dithietane, dithiatopazine **53**, an intermediate used in the total synthesis of brevotoxin B. When **53** was heated at 100 °C, it smoothly extruded diatomic sulfur which was trapped with 2,3-diphenyl-1,3-butadiene to give the cyclic disulfide in 25% isolated yield and the corresponding olefin **54**.[56] The formation of S_2 may not be the sole mechanistic pathway as the tetrasulfide was also isolated, 28%. These reactions were conducted in a tenfold excess of **53**.



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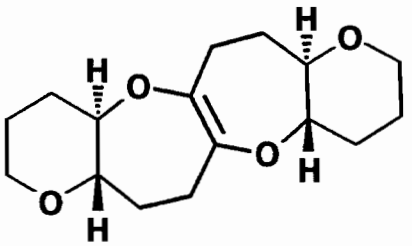

54

In addition, Rapoport and coworkers[57] observed the presence of S_2 in the conversion of the monothiomaleimide **55** to the oxygen analog, maleimide **56**. The proposed six-membered transition state **57** was similar to the one which was proposed by Staudinger and Freudenberger in the air oxidation of thioketones in 1928.[41]

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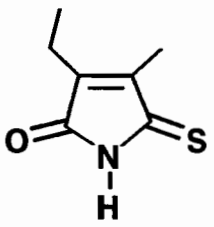
55 K. C. Nicolaou, C.-K. Hwang, M. E. Duggan and P. J. Carroll, *J. Am. Chem. Soc.*, **109**, 3801 (1987).

56 K. C. Nicolaou, C.-K. Hwang, S. DeFrees and N. A. Stylianides, *J. Am. Chem. Soc.*, **110**, 4868 (1988).

57 J. E. Bishop, S. A. Dagam and H. Rapoport, *J. Org. Chem.*, **54**, 1876 (1989).



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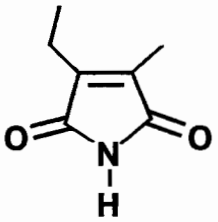

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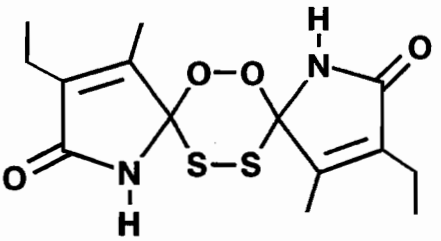
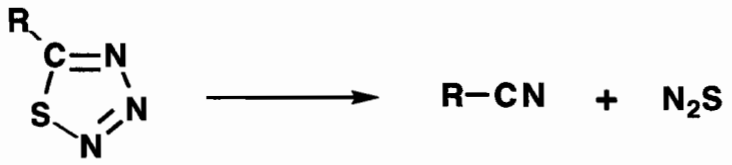


57

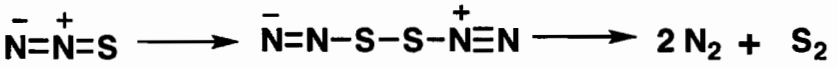
Trapped diatomic sulfur was confirmed by ^1H NMR but the yields were too low to be isolated. Diatomic sulfur, was also identified as one of the decomposition products of the thermal decomposition of 1,2,3,4-thiatriazoles **58** by infrared[58] and photoelectron spectroscopy[59] **(Scheme 13)**.



58

SCHEME 13

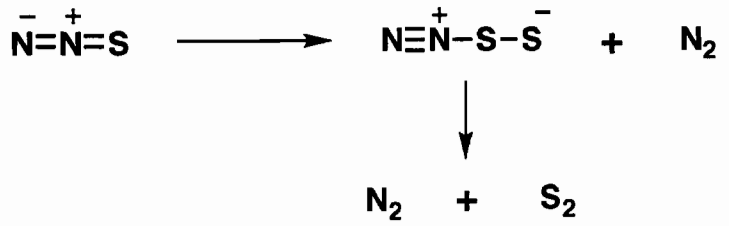
In fact the S_2 was proposed to result from the dimerization of two dinitrogen sulfide **(N_2S)** molecules, which were initially present in the thermal decomposition to give two molecules of nitrogen and one of S_2 **(Scheme 14** and **15)**.



SCHEME 14

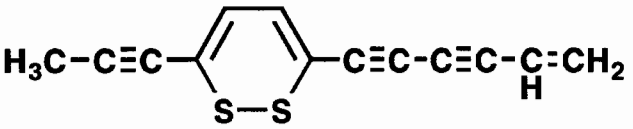
58 C. Wentrup, S. Fischer, A. Maquestiau and R. Flammang, *J. Org. Chem.*, **51**, 1908 (1986).

59 H. Bender, F. Carnovale, J. B. Peel and C. Wentrup, *J. Am. Chem. Soc.*, **110**, 3458 (1988).

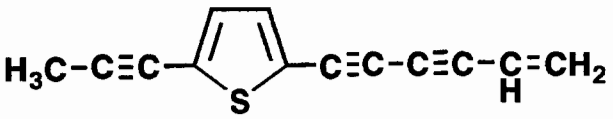


SCHEME 15

Moreover, Constabel and Towers[60] claimed that the singlet sulfur is the toxic product of thiarubin A **(59)**, a 1,2-dithiin, but there was no evidence for this claim. Their results showed that light enhanced conversion of **59** to the thiophene **60** caused toxic effects that were greater than those resulting from **59** or **60** alone. Their claim was based on the analogy that singlet oxygen is the toxic species generated from peroxides.[61]



59



60

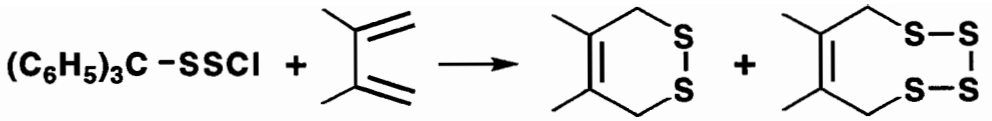
In 1991, Harpp and Williams[62] attempted to generate S_2. Triphenylmethanethiosulfenyl chloride **(61)** reacts with 2,3-dimethyl-1,3-butadiene **(62)** to give a product consistent with the trapping of diatomic sulfur 1,2-dithia-4,5-dimethyl-4-cyclohexene **(63)** as well as the cyclic tetrasulfide 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(64)** **(Scheme 16)**.

---

60 C. R. Constabel and G. H. N. Towers, *Planta Medica*, **55**, 35 (1989).

61 a) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968); b) T. Matsuura, *Tetrahedron*, **33**, 2869 (1977); c) A. Naqui, B. Chance and E. Cadenas, *Ann. Rev. Biochem.*, **55**, 137 (1986).

62 C. R. Williams and D. N. Harpp, *Tetrahedron Lett.*, **32**, 7651 (1991).



61 **62** **63** **64**

SCHEME 16

The identity of compound **64** was confirmed by ^1H NMR and mass spectral data. The isolated yields of **63** and **64** were 30% and 35%, respectively. The mechanistic pathway however was demonstrated to be an addition-elimination reaction and S_2 was not involved. Most recently, work by Tardif, Williams and Harpp has shown effective diatomic trapping by the demonstration of alkoxydisulfide **29**.[63]

From the many examples described above it appears that two sulfur atoms must be adjacent to each other in a molecule in order for it to be considered a viable diatomic sulfur precursor. In many synthetically useful generations, the proposed intermediate for the generation of S_2 was a four-membered ring species. These intermediates could provide direct S_2 formation or the transfer of two sulfur atoms to a 1,3-diene. The presence of two adjacent sulfur atoms make many molecules potential singlet diatomic sulfur precursors, these include disulfides and polysulfides (*vide infra* Results and Discussion Section, Chapter 3).

In a recent paper, we reported[64] the reaction of triphenylmethanesulfenyl (**65**) and thiosulfenyl chloride (**61**) with norbornene (**66**) and bicyclo[2.2.2]octene (**67**).

65 **61** **66** **67**

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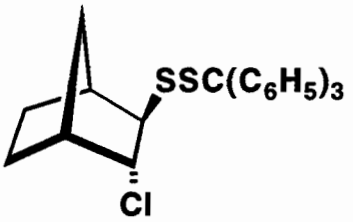
63 S. Tardif, C. R. Williams and D. N. Harpp, *J. Am. Chem. Soc.*, **117**, 9067 (1995).

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

Stable 1,2-addition products **68** and **69** were formed and while diatomic sulfur transfers took place from them to a diene acceptor, the yield of final products was quite low.



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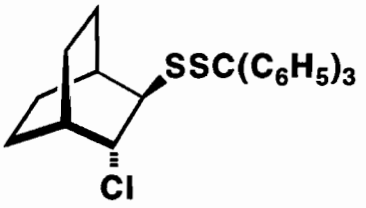
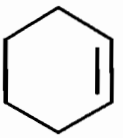


69

Most recently, we[65] reported a new methodology for the generation of diatomic sulfur (S_2) transfer. Triphenylmethanethiosulfenyl chloride **(61)** (and its dithio homolog **70**) give stable addition products (*ca.* 90% yield) with cyclopentene **(71)** and cyclohexene **(72)**.

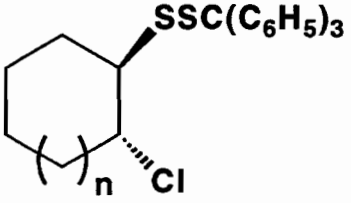
70

71

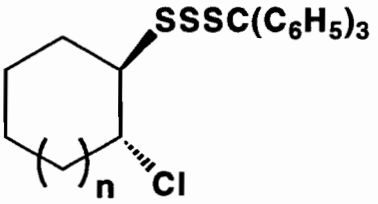


72

We found, in contrast, these addition products (**73**, **74** from **61**; **75**, **76** from **70**) are effective in transferring sulfur to a diene trap.



73; n = 0
74; n = 1



75; n = 0
76; n = 1

When these adducts **73** to **76** were each warmed with 2,3-dimethyl-1,3-butadiene **(62)**, in a variety of solvents, varying temperature, time and concentration, they deliver diatomic sulfur-trapped derivatives. The cyclic tetrasulfide adduct **64** is quantitatively converted to the corresponding disulfide **63** with triphenylphosphine.

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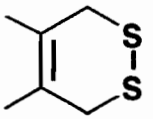
65 I. A. Abu-Yousef and D. N. Harpp, *Tetrahedron Lett.*, **35**, 7167 (1994).



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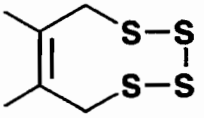
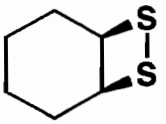
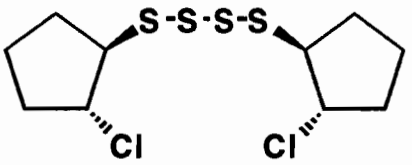


64



77

As a result, this new methodology affords easily cyclic disulfides in > 50% isolated yield from the diene. In addition, evidence has been obtained implicating dithietane intermediate **77**. Moreover, byproducts, acyclic tetrasulfides **78** and **79**, are likely formed by an intermolecular pathway from **73**, **75** and **74**, **76** respectively.



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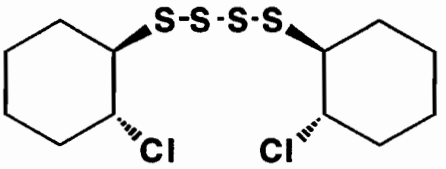

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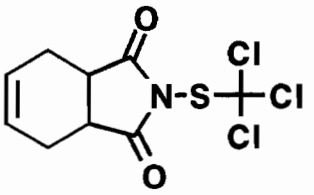
CHAPTER 2

SOME NEW SULFENYL CHLORIDE CHEMISTRY

BACKGROUND, SYNTHESIS, REACTIONS AND MECHANISMS TOWARD CARBON-CARBON DOUBLE BONDS

2.1 BACKGROUND

Sulfenyl chlorides (**RSCl**) were first discovered by Rathke[66] in 1870 through chlorination of carbon disulfide (CS_2). They can be formally considered as the acid chloride derivatives of the unstable sulfenic acid (**RSOH**). Their usefulness in industry was discovered when Kittleson[67] in 1952 derived "Captan" (a potent fungicide) **80**, which utilizes a sulfenyl halide in the preparation.



80

A wide variety of sulfenyl halides (**RSX**) can be obtained by varying the **R** and **X**, each with different physical and chemical properties. They can also undergo a host of reactions like addition, displacements, oxidations and reductions. Because of this fact,

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66 a) B. Rathke, *Chem. Ber.*, **3**, 858 (1870); b) B. Rathke, *Justus Liebigs Ann. Chem.*, **167**, 211 (1874).

67 a) A. R. Kittleson, *Science*, **15**, 84 (1952); b) A. R. Kittleson, *Analyt. Chem.*, **24**, 1173 (1952).

sulfenyl halides have found wide applications in chemistry. Among some of their uses are the following: 2,4-dinitrobenzenesulfenyl chloride is used as an analytical reagent for characterizing many compounds by solid derivative formation,[68] in the synthesis of peptides, nucleosides and nucleotides,[69] sulfenyl halides are used as blocking groups; they are selective chlorinating agents in hydrocarbon chemistry preferentially replacing tertiary hydrocarbon atoms.[70] In addition, the nature of sulfenyl intermediates plays an important role in the chemistry of wool, sulfur containing fibers of all sorts, and in the preparation of various heterocyclic compounds.[70]

Sulfenyl halides have proven their value as alkyl or aryl sulfur transfer reagents as is revealed in a large number of publications and reviews in the literature.[68,71]

Other compounds of interest, triphenylmethanesulfenyl chlorides **(65)**,[72] play a significant role in protective group chemistry, as well as newer varieties such as triphenylmethanethiosulfenyl **(61)**[73] and dithiosulfenyl chloride **(70)**.[74]

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68 a) N. Kharasch, *J. Chem. Ed.*, **33**, 585 (1956); b) R. B. Langford and D. D. Lawson, *ibid.*, 510 (1957).

69 a) L. Zervas, D. Borovas and E. Gazis, *J. Am. Chem. Soc.*, **85**, 3660 (1963); b) P. H. Bentley, H. Gregory, A. H. Laird and J. S. Morley, *J. Chem. Soc., Chem. Commun.*, 6130 (1964).

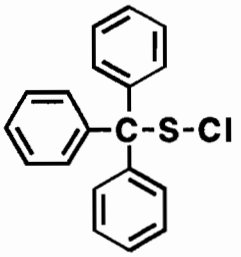
70 N. Kharasch, *Quart. Rep. Sulfur Chem.*, **2**, 289 (1967).

71 a) E. Kühle, *Synthesis*, 561 (1970); b) N. Kharasch, Z. S. Arivan and A. J. Havlik, *Quart. Rep. Sulfur Chem.*, **1**, 93 (1966); c) N. Kharasch, "Organic Sulfur Compounds", Pergamon Press, New York, Vol. 1, 1961, p. 250-260; d) G. Sosnovsky, *Chem. Rev.*, **58**, 509 (1958); e) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946).

72 D. Voländer and E. Mittag, *Chem. Ber.*, **46**, 3450 (1913).

73 D. N. Harpp and D. K. Ash, *Int. J. Sulfur Chem., A*, **1**, 211 (1971).

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



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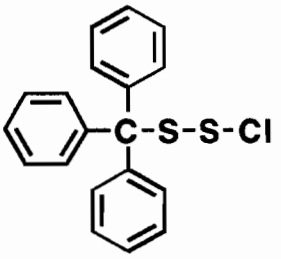
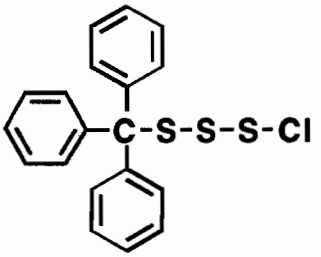


61



70

For example, protected penicillins and cephalosporins have been prepared with compound **65**.[75] In addition, N-sulfenated β-lactams(thiamazins) have been prepared as potential antibiotics with **65** as one of the starting materials.[76] *o*-Sulfenylated carbohydrate derivatives can be prepared with **65**.[77] Compound **65** has been used to decrease the flammability of polypropylene,[78] and uracil derivatives have been N-protected with **65**,[79] in which deprotection is possible with aqueous iodine.[80]

The importance of some of these uses and the synthetic value of the above reactions provide stimulus to further research in this field.

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75 F. Gapp, K. Riedl and F. Knauseder, *Ger. Offen.*, DE 2,344,274 (1974); *Chem. Abstr.*, **80**, 133454 (1974).

76 S. R. Woulfe and M. J. Miller, *J. Org. Chem.*, **51**, 3133 (1986).

77 H. Bazin, J. Heikkilä and J. Chattopadhyaya, *Acta Chem. Scand.*, **B39**, 391 (1985).

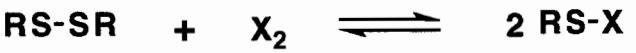
78 E. V. Gnedin and S. N. Novikov, *Plast. Massy*, 79 (1989); *Chem. Abstr.*, **111**, 135330 (1989).

79 H. Alper and C. Blais, *J. Chem. Soc., Chem. Commun.*, 169 (1980).

80 a) M. Sekine, *J. Org. Chem.*, **54**, 2321 (1989); b) H. Takaku, K. Imai and M. Nagai, *Chem. Lett.*, 857 (1988).

2.2 SYNTHESIS

Sulfenyl halides are generally produced by treatment of alkyl or aryl disulfides **81** with halogen **(Scheme 17)**,[81] or with sulfuryl chloride.[82]

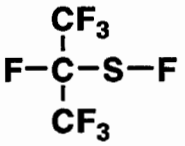


81

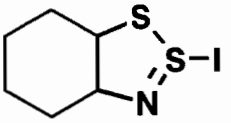
R = alky, aryl; X = Cl, Br

SCHEME 17

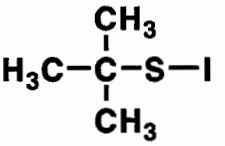
The reversibility of this reaction makes it practical only for chlorine or bromine.[81] Isolation of sulfenyl fluorides like **82**,[83] or sulfenyl iodides like **83**,[84] or **84**,[85] is known for only a limited number of these types of compounds.[85]



82



83



84

One of the disadvantages associated with this approach is that chlorination of the disulfide may lead to carbon-sulfur scission, forming an alkyl chloride and sulfur monochloride instead of the desired sulfenyl chloride.[86] Alternatively, the mercaptan may be treated in a similar fashion to first generate the disulfide which then reacts to form the sulfenyl chloride, however, the yields are much lower with this process **(Scheme 18)**.[87]

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81 K. Fries, *Chem. Ber.*, **45**, 2965 (1912).

82 H. Brintzinger, K. Pfannstiel, H. Koddebusch and K. E. Kling, *Chem. Ber.*, **83**, 87 (1950).

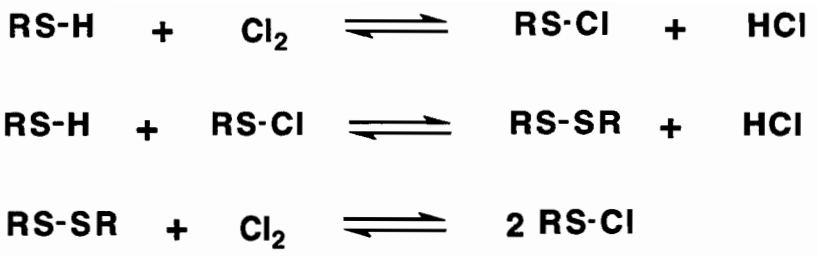
83 R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, **1**, 756 (1962).

84 W. E. Messer, U. S. Patent 2,257,974, (1939); *Chem. Abstr.*, **36**, 930 (1942).

85 L. Field and J. E. White, *Proc. Nat. Acad. Sci.*, **70**, 328 (1973).

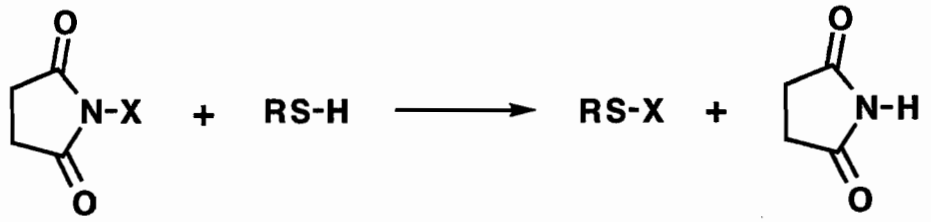
86 a) I. B. Douglass, K. R. Brower and F. T. Martin, *J. Am. Chem. Soc.*, **74**, 5770 (1952); b) W. A. Schultze, G. H. Short and W. W. Crouch, *Ind. Eng. Chem.*, **42**, 916 (1950).

87 H. Lecher and F. Holschneider, *Chem. Ber.*, **57**, 755 (1924).



SCHEME 18

A better approach involves treating the thiol with N-chloro, or N-bromosuccinimide **(Scheme 19)**.[88]



X = Cl, Br

SCHEME 19

Triphenylmethanesulfenyl chloride **(65)**,[72] has been known since 1913 and has been widely employed as a protecting group in amine chemistry.[89] Triphenylmethanethiosulfenyl **(61)**[73] and dithiosulfenyl chloride **(70)** have been recently researched.[74] Compound **65** was obtained by the direct chlorination of triphenylmethanethiol **(85)** following the procedure of Voländer and Mittag **(Scheme 20)**.[72]

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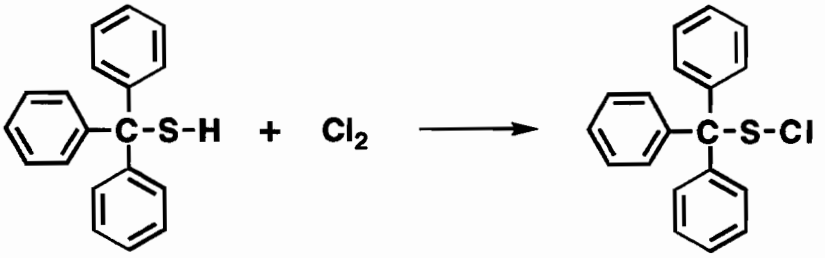
88 H. Emde, *German Patent,* 804,572, (1951); *Chem. Abstr.*, **46**, 529 (1952).

89 B. P. Branchaud, *J. Org. Chem.*, **48**, 3538 (1983).

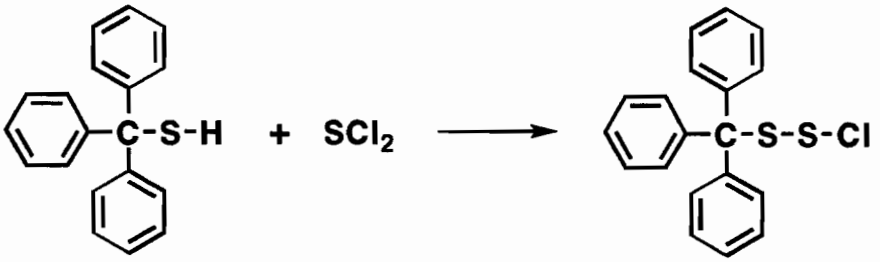


85 **65**

SCHEME 20

In addition, Bowman and Richardson[90] reported that compound **65** could be prepared from the treatment of 2-chloro-2-nitropropane with triphenylmethanethiolate anion.

Thiosulfenyl chlorides (also known as chlorodisulfanes or chlorodisulfides) are less well known due to lower stability. Moltzen and Senning[91] reported the preparation of a number of these compounds but there is little structural information available. Harpp and Ash[73] in 1970 reported the first synthesis for triphenylmethanethiosulfenyl chloride **(61)** from the reaction of thiol **85** with sulfur dichloride **(Scheme 21)**.



85 **61**

SCHEME 21

Compound **61** has received very little attention. It was first used to prepare unsymmetrical trisulfides and later used to prepare di- and trisulfides in the synthesis of fungal metabolites.[92]

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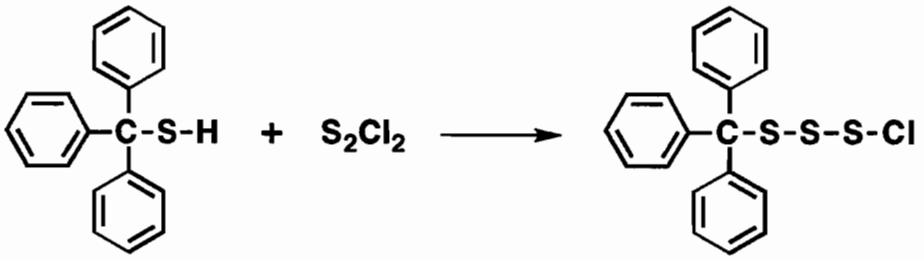
90 W. R. Bowman and G. D. Richardson, *Tetrahedron Lett.*, **22**, 1551 (1981).

91 E. K. Moltzen and A. Senning, *Sulfur Lett.*, **4**, 169 (1986).

92 R. M. Williams and W. H. Rastetter, *J. Org. Chem.*, **45**, 2625 (1980).

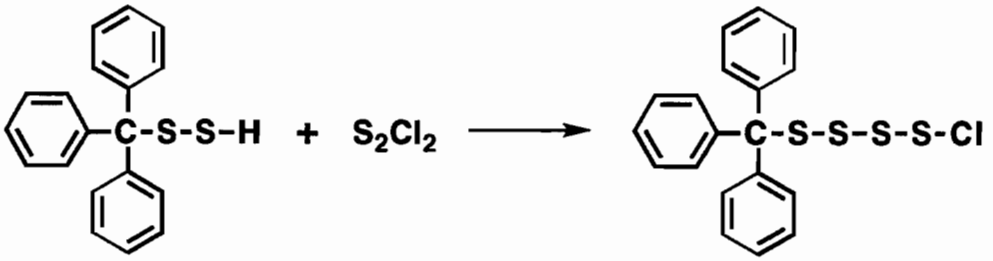
The higher sulfides are prepared *in situ* only and used to synthesize hydrotetrasulfides (**RSSSSH**). No efforts have been made to isolate them.[93]

Most recently, Harpp and coworkers[74] reported the first synthesis of triphenylmethanedithiosulfenyl (**70**) and trithiosulfenyl chloride (**86**) from the condensation of disulfur dichloride with thiol **85** and dithiol **87**,[94] respectively (**Scheme 22 and 23**).



85 **70**

SCHEME 22



87 **86**

SCHEME 23

In addition, the same authors[74] have reported the x-ray structures of compounds **61**, **65** and **70** for the first time.

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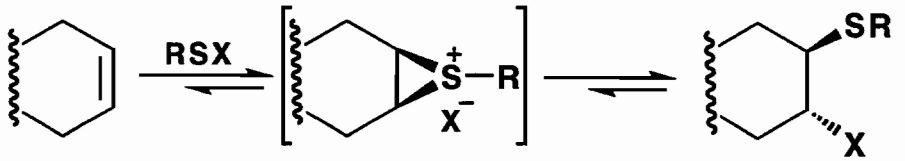
93 H. J. Langer and J. B. Hyne, *Can. J. Chem.*, **51**, 3403 (1973).

94 G. Derbesy, D. N. Harpp, B. Rather and G. Carroll, *Sulfur Lett.*, **14(4)**, 199 (1992).

2.3 ELECTROPHILIC ADDITION TO CARBON-CARBON DOUBLE BONDS

Electrophilic addition to the carbon-carbon double bond is a fundamental reaction in organic chemistry and has been extensively reviewed.[95] Among these reactions is the electrophilic addition of aryl- and alkylsulfenyl halides (**RSX**) to olefins **88** that produces *trans*-β-haloaryl(alkyl)sulfides **89** (or known as β-halo thioethers); it is a very well-established process (**Scheme 24**).[71a,96]



88 **90** **89**

SCHEME 24

The reaction proceeds through an episulfonium salt intermediate **90**[97] which yields products usually resulting from predominant or exclusive attack of the halide ion at the more positively polarized carbon atom as shown in **Scheme 24** above.[96,98]

The carbon residue **R** is usually an alkyl or aryl group and **X** is mostly chlorine, sometimes bromine, but rarely fluorine or iodine. The ability of sulfenyl halides to undergo addition reactions with unsaturated compounds is a well-known and a widely used

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95 a) P. B. D. de La Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems)", Elsevier, Amsterdam, 1966; b) R. S. Fahey, "The Stereochemistry of Electrophilic Additions to Olefins and Acetylenes", Vol. 3, 1968, p. 237.

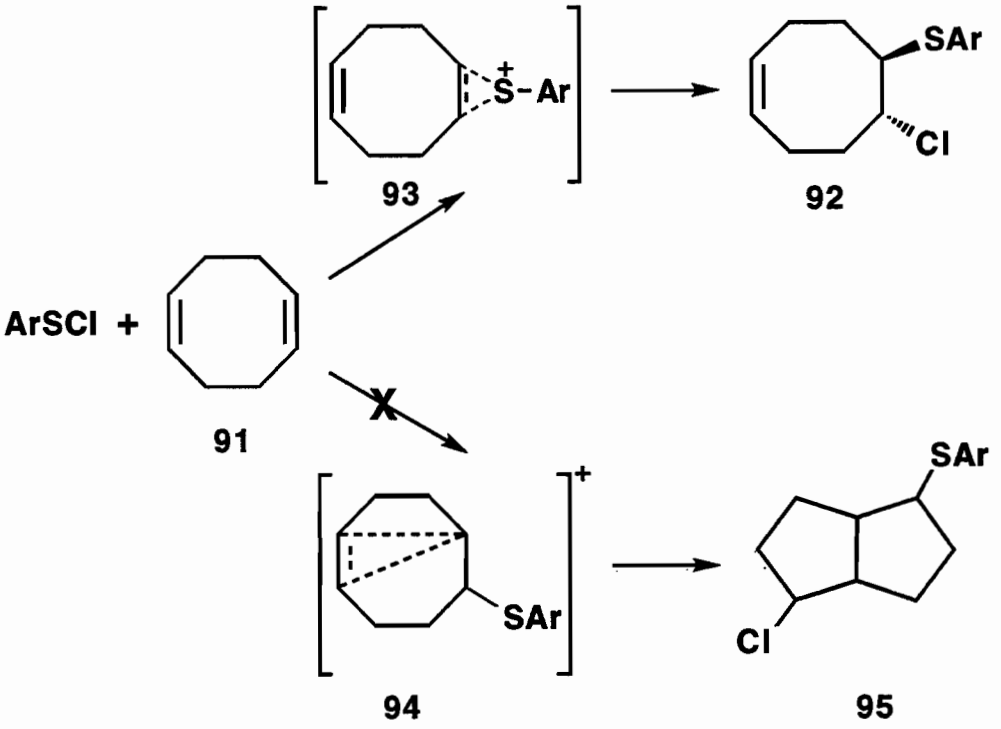
96 a) K. D. Gundermann, *Angew. Chem., Int. Ed., Engl.* **2**, 674 (1963); b) W. H. Mueller, *ibid.*, **8**, 842 (1969); c) E. Kühle, *ibid.*, 563 (1971); d) E. Kühle, *ibid.*, 617 (1971).

97 a) D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **29**, 2702 (1964); b) W. A. Smit, M. Z. Krimer and E. A. Vorobeva, *Tetrahedron Lett.*, 2451 (1975).

98 a) W. A. Thaler, W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **90**, 2069 (1968); b) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **90**, 2075 (1968); c) W. A. Thaler, *J. Org. Chem.*, **34**, 871 (1969); d) W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1968); b) W. H. Mueller and P. E. Butler, *J. Org. Chem.*, **34**, 2642 (1968).

method for the functionalization of alkenes.[99] The most commonly used are arenesulfenyl chlorides and methanesulfenyl chlorides.[99,100] The addition of arenesulfenyl chlorides to alkenes have been extensively studied by a number of workers.[101]

For example, Schmid[102] reported the reaction of 2,4-dinitrobenzenesulfenyl chloride with *cis,cis*-1,5-cyclooctadiene **(91)** in chloroform solution to give the monosulfide adduct **92** in a good yield **(Scheme 25)**.



SCHEME 25

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99 G. H. Schmid and D. G. Garratt, "The Chemistry of the Double Bonded Functional Groups", S. Patai (Ed.), John Wiley and Sons, New York, 1977, Chapter 9.

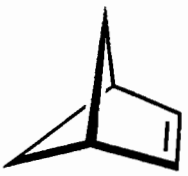
100 a) G. H. Schmid, "Topics in Sulfur Chemistry", A. Senning (Ed.), Georg Thieme Verlag, Stuttgart, Vol. 3, 1977, p. 100; b) E. Kühle, "The Chemistry of Sulfenic Acids", Georg Thieme Verlag, Stuttgart, 1973, p. 2.

101 a) G. M. Beverly and D. R. Hogg, *Chem. Commun.*, 138 (1966); b) W. L. Orr and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 1201 (1956); c) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **80**, 2075 (1968); d) G. H. Schmid V. M. Csizmadia, V. J. Nowlan and D. G. Garratt, *Can. J. Chem.*, **50**, 245 (1972).

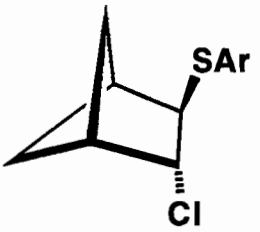
102 G. H. Schmid, *Can. J. Chem.*, **46**, 3757 (1968).

The structural determination of **92** was based on analytical and NMR data. The formation of **92** indicates that the transition state leading to it was similar to an episulfonium ion intermediate **93** rather than a carbonium ion intermediate **94** which would lead to a bicyclic product **95** as shown in **Scheme 25** above.[103]

Bond[104] reported that, the addition of 2,4-dinitrobenzenesulfenyl chloride to bicyclo[2.2.1]hex-2-ene (**96**) gave the monosulfide adduct **97**. The structure of the reaction product was established by ^{1}H NMR.

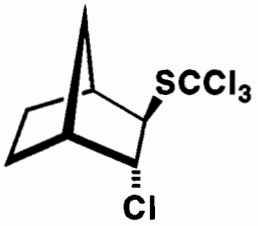


96

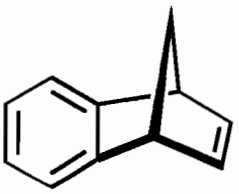


97

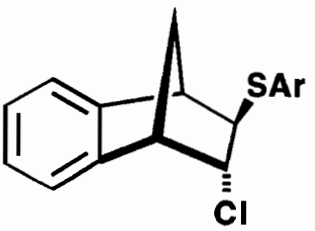
The reaction of trichloromethanesulfenyl chloride with norbornene was studied by Madsen and coworkers[105] to give the *trans*-adduct **98** in good yield. It is considered to be formed by a polar electrophilic addition involving an episulfonium ion intermediate. Martin and Koster[106] studied the reaction of *p*-toluenesulfenyl chloride with benzonorbornadiene (**99**); *endo*-2-chloro-*exo*-1-thiocresylbenzonorbornene (**100**) was formed in low yield and identified by NMR spectroscopy.



98



99



100

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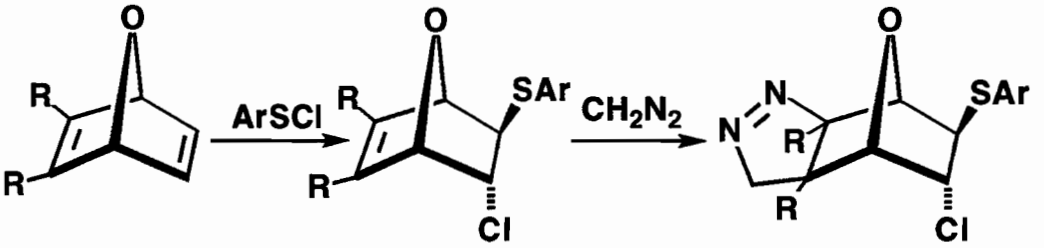
103 T. L. Jacobs, R. Macomber and D. Zunker, *J. Am. Chem. Soc.*, **89**, 7001 (1967).

104 F. T. Bond, *J. Am. Chem. Soc.*, **90**, 5326 (1968).

105 J. O. Madsen and S. O. Lawesson, *Ark. Kemi.*, **28**, 389 (1967).

106 M. M. Martin and R. A. Koster, *J. Org. Chem.*, **33**, 3428 (1968).

2,4-Dinitrobenzenesulfenyl chloride was reported to react with 7-oxabicyclo-[2.2.1]heptadiene derivatives in methylene chloride solution. Only normal addition products were formed **(Scheme 26)**.[107]

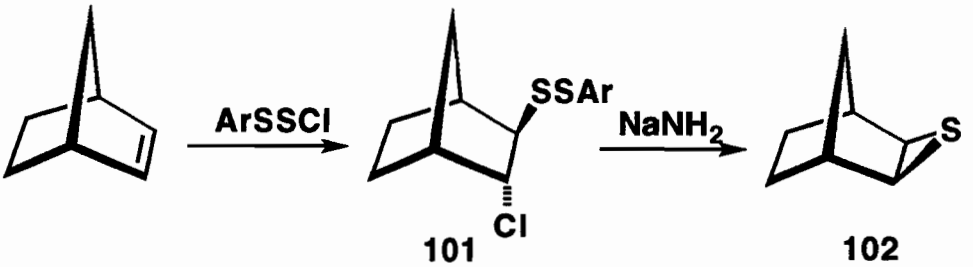


R = CO_2CH_3

SCHEME 26

The absence of rearranged products was shown in **Scheme 26** above, by reaction with diazomethane to give pyrazoline derivatives. Similar results were obtained with 7-oxabicyclo[2.2.1]heptene derivatives.

Fujisawa and Kobori[108] studied the reaction of arenethiosulfenyl chloride with norbornene to give quantitatively a crude disulfide adduct **101**. They found that when the crude adduct **101** was slowly added to sodium amide or sulfide at the temperature of 90-95 °C under reduced pressure, an oily product was collected in good yield in a cold trap and identified as *exo*-2,3-epithionorbornane **(102) (Scheme 27)**.



Ar = *o*-$NO_2C_6H_4$, *p*-$CH_3C_6H_4$

SCHEME 27

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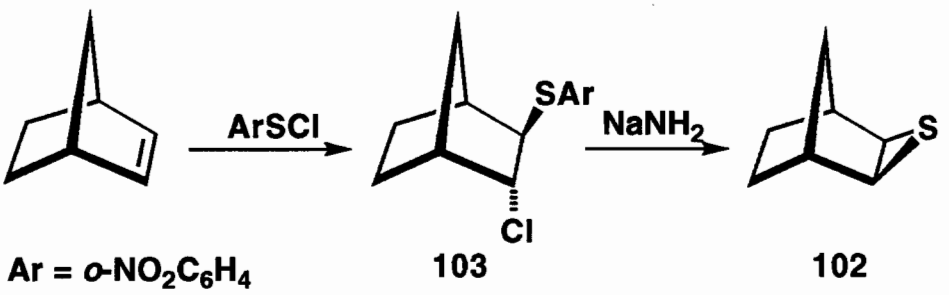
107 N. S. Zefirov, A. F. Daydova, V. F. Bystrov, A. V. Stepanyants and Yu. K. Yur'ev, *Zhur. Obshchei. Khim.*, **36**, 1738 (1966).

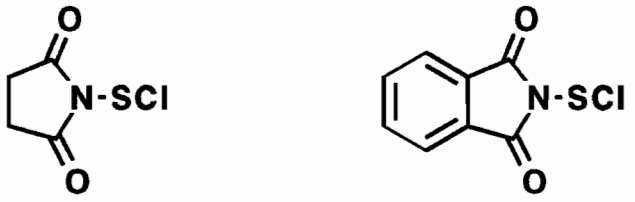
108 T. Fujisawa and T. Kobori, *Chem. Lett.*, 1065 (1972).

It is noteworthy to mention that the same authors also obtained **102** in 20% yield by the treatment of monosulfide adduct **103**, prepared from norbornene and *o*-nitrobenzenesulfenyl chloride, with sodium amide **(Scheme 28)**.



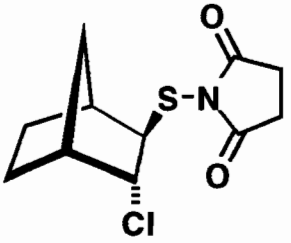
SCHEME 28

In addition, the same authors[109] reported a new series of sulfur transfer reagents to olefins, arenethiosulfenyl chlorides, which lead to the disulfide adducts and could be easily treated with sodium amide or sulfide to get the corresponding episulfide in better yields. The imidosulfenyl chlorides **104** or **105** have been found to react rapidly with norbornene (and other alkenes) to give the corresponding adduct **106** or **107**, respectively.[110]

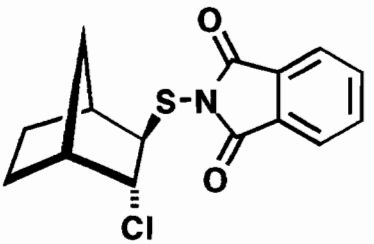


104

105



106

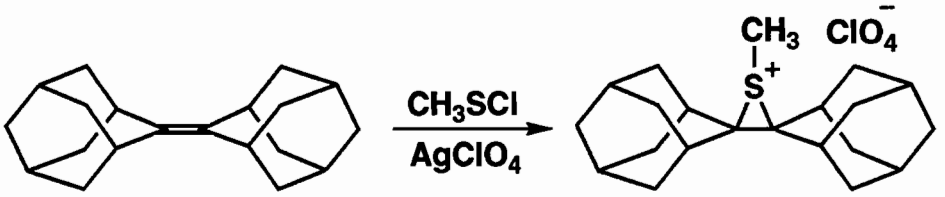


107

109 T. Fujisawa and T. Kobori, *Chem. Lett.*, 935 (1972).

110 M. U. Bombala and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1,* 3013 (1979).

On the other hand, Bolster and Kellogg[111] studied the reaction of adamantylidene-adamantane **(108)** with methanesulfenyl chloride in the presence of silver perchlorate ($AgClO_4$). They found that, thiiranium salt **109** was formed and no evidence for 1,2-addition products of the sulfenyl chlorides to **108** was obtained **(Scheme 29)**.



108 **109**

SCHEME 29

The reaction of triphenylmethanesulfenyl chloride **(65)** with norbornene has been investigated[112] previously. In this reaction a number of products were reported but details were lacking and neither their stereochemistry nor the mechanism of the reaction were demonstrated.

Haufe and coworkers[113] reported that, the reaction of dimethyl(methylthio)-sulfonium tetrafluoroborate (DMTSF) and triethylaminetrishydrofluoride with olefins leads to β-fluoroalkylmethyl thioether in high yields. The main disadvantage of this method is the relatively difficult preparation of DMTSF, which requires the use of trimethyloxonium tetrafluoroborate, which is rather unstable and expensive.

Purrington and Correa[114] proposed another way to obtain β-fluoroalkylphenyl thioethers by the action of phenylsulfenyl chloride on an olefin in the presence of silver fluoride in acetonitrile solution.

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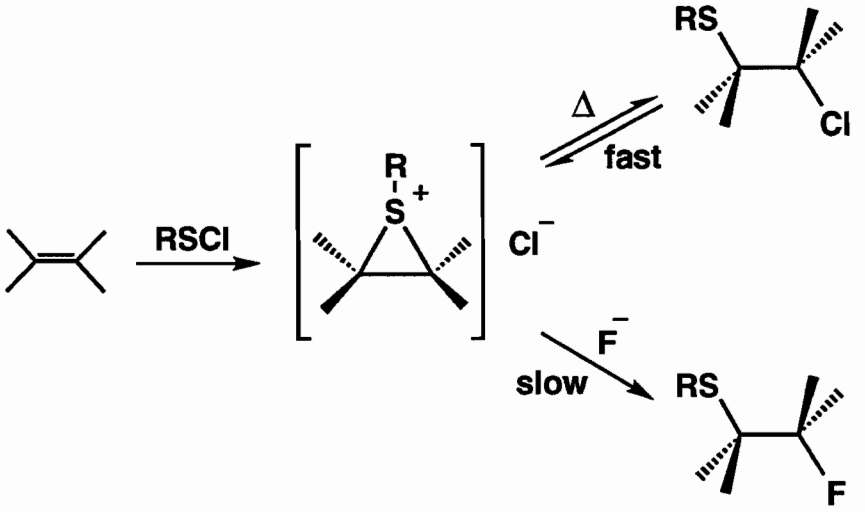
111 J. Bolster and R. M. Kellogg, *J. Chem. Soc., Chem. Commun.*, 630 (1978).

112 J. M. Majewski and J. Zakrzewski, *Tetrahedron Lett.*, **22**, 3659 (1981).

113 G. Haufe, G. Alvernhe, D. Anker, A. Laurent and C. Saluzzo, *Tetrahedron Lett.*, **29**, 2311 (1988).

114 S. T. Purrington and I. D. Correa, *J. Org. Chem.*, **51**, 1080 (1986).

In a recent paper, Haufe and coworkers[115] reported a new method leading to a β-fluoroalkylphenyl (or methyl) thioether, using halogen exchange between a β-chloroalkylphenyl (or methyl) thioether and a fluoride ion **(Scheme 30)**.



SCHEME 30

As a result, the **Ad$_E$2** (**Ad**dition, **E**lectrophilic, **bi**molecular) reaction of sulfenyl halides appears to be one of the most efficient way to transfer alkenes into synthetically useful products and it has been extensively studied and reviewed by a number of workers.[71a,95a,96c,99,116]

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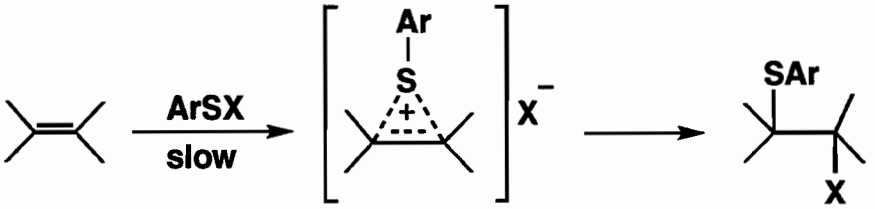
115 C. Saluzzo, G. Alvernhe, D. Anker, A. Laurent and G. Haufe, *J. Fluorine Chem.*, **47**, 467 (1991).

116 a) M. Jaszunski and E. Kochanski, *J. Am. Chem. Soc.*, **98**, 4624 (1977); b) K. Yates, "Application of MO Theory in Organic Chemistry", I. G. Csizmadia (Ed.), Elsevier, Amsterdam, Vol. 2, 1977, p. 261; c) W. A. Smit, *Zh. Vsesousn. Mendeleev Obshch.*, **22**, 300 (1977); d) L. P. Rasteikene, D. I. Greichute, M. G. Lin'kova and I. L. Knunyantz, *Usp. Khim.*, **46**, 1041 (1977); e) P. B. Hopkins and P. L. Fuchs, *J. Org. Chem.*, **43**, 1208 (1976); f) G. H. Schmid, C. L. Dean and D. Garratt, *Can. J. Chem.*, **54**, 1253 (1976); g) F. Freeman, *Chem. Rev.*, **75**, 439 (1975); h) R. D. Bach and H. F. Henneike, *J. Am. Chem. Soc.*, **92**, 5589 (1970); i) W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **81**, 475 (1969); j) N. Kharasch, "Organic Sulfur Compounds", Pergamon Press, New York, Vol. 1,1961, p. 375; k) D. R. Hogg N. Kharasch, *J. Am. Chem. Soc.*, **78**, 2728

2.4 MECHANISM OF ELECTROPHILIC ADDITION TO CARBON-CARBON DOUBLE BONDS

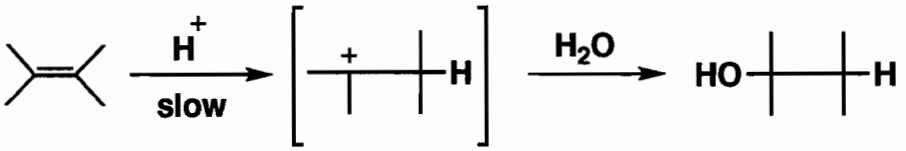
In investigating the mechanism of addition to a carbon-carbon double bond, the intermediate and the transition states leading to them, may be divided into two distinct types. On the one hand, there are those reactions that proceed through bridged transition states and intermediates **110 (Scheme 31)**.



110

SCHEME 31

On the other hand, there are those that involve rate determining attack at carbon to form open carbonium ions **111 (Scheme 32)**.[99,117]



111

SCHEME 32

The best example of the first class of reactions is addition of sulfenyl halide[116f,118] to olefins as shown in **Scheme 31** above. Protonation of alkenes in an acid-catalyzed

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(1956); l) N. Kharasch, A. J. Havlik, *J. Am. Chem. Soc.*, **75**, 3734 (1953); m) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949).

117 T. H. Lowry and K. S. Richardson, "Mechanims and Theory in Organic Chemistry", Harper and Row, New York, 1976, Chapter 7 .

118 a) G. M. Beverly and D. R. Hogg, *J. Chem. Soc., Chem. Commun.*, 175 (1971); b) G. Mehta and P. N. Pandey., *Tetrahedron Lett.*, 3567 (1975); c) W. A. Smit, M. Z. Krimer and E. A. Vorob'eva, *Tetrahedron Lett.*, 2451 (1975); d) G. Capozzi, O. DeLucchi, V. Lucchini and G. Modena, *Tetrahedron Lett.*, 2603 (1975); e) K. Izawa, T. Okuyama and T. Fueno, *Bull. Chem. Soc. Jpn.*, **47**, 1480

hydration is a reaction which clearly fits in the second category[119] as shown in **Scheme 32** above.

The mechanism of sulfenyl halide addition is securely based on rate-structure correlations, product stereochemistry, and direct observation of the bridged intermediates.[118] In terms of the mechanism of the hydration reaction, it is supported by the correlation of rates with structure, solvent isotope effects, acidity dependence, and other kinetic criteria.[119]

An open carbonium ion such as **111**[120] which can give a mixture of *cis*- and *trans*-addition products either by rotating around the carbon-carbon bond or by electronic, steric or conformational effects which in turn cause attack at one or the other side of the carbonium ion giving non-stereospecific addition products.

On the other hand, a bridged species such as **110**[121] can open stereospecifically to *trans*-addition products. In addition, such an ion if formed from an unsymmetrical olefin, would be expected to give isomeric products resulting from attack at both carbon atoms of the intermediate. Thus, while the products are stereospesific they are not regiospecific. Both of these mechanisms are designated $\mathbf{Ad_E2}$ (*vide infra* Results and Discussion Section, Chapter 3).

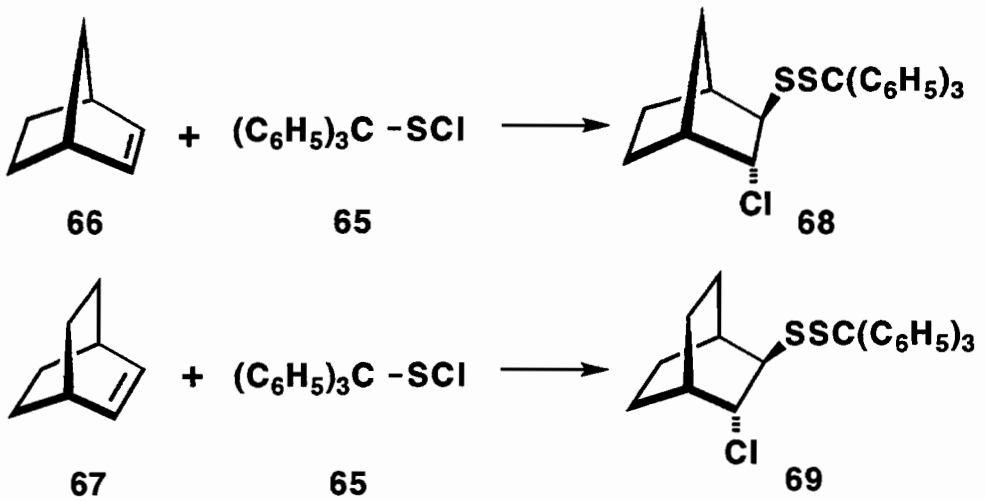
Recently, we reported[64] that the addition of triphenylmethanesulfenyl chloride **(65)** to various bicyclic alkenes (norbornene **(66)** and bicyclo[2.2.2]octene **(67)**) leads, contrary to expectation, to β-chlorodisulfides **68** and **69** respectively, in good isolated yields, rather than to β-chlorosulfides **(Scheme 33)**.

(1974); f) N. S. Zefirov, N. K. Sadovaja, A. M. Maggerramov, I. V. Bodrikov and V. R. Kasrtashov, *Tetrahedron*, **31**, 2948 (1975).

119 a) K. Oyama and T. T. Tidwell, *J. Am. Chem. Soc.*, **98**, 947 (1976); b) W. K. Chwang, P. Knittel, K. M. Koshy and T. T. Tidwell, *J. Am. Chem. Soc.*, **99**, 3395 (1977); c) S. Y. Attia, J. P. Berry, K. M. Koshy, Y.-K. Leung, E. P. Lyznicki, Jr., V. J. Nowlan, K. Oyama and T. T. Tidwell, *J. Am. Chem. Soc.*, **99**, 3401 (1977); d) P. Knittel and T. T. Tidwell, *J. Am. Chem. Soc.*, **99**, 3408 (1977); e) W. K. Chwang, V. J. Nowlan and T. T. Tidwell, *J. Am. Chem. Soc.*, **99**, 7233 (1977).

120 R. A. Ogg, Jr., *J. Am. Chem. Soc.*, **57**, 2727 (1935).

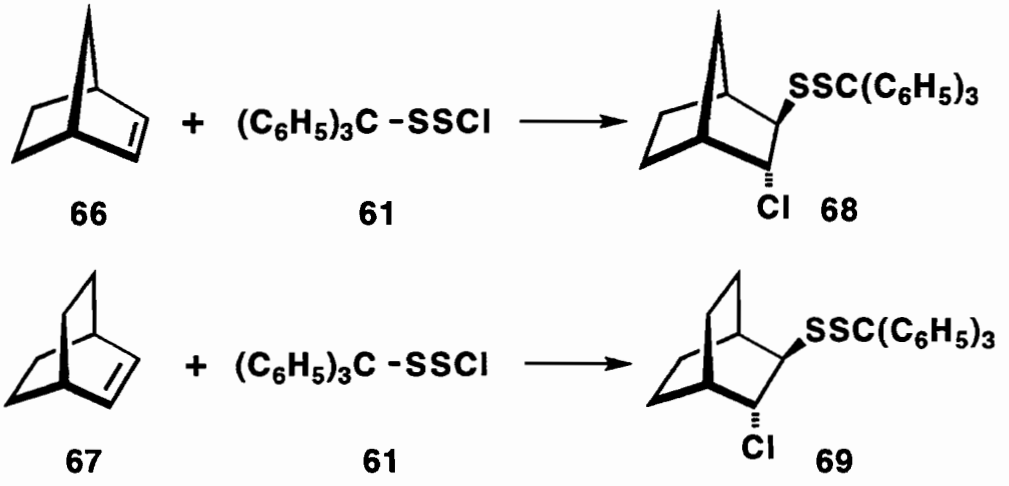
121 I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).



SCHEME 33

It is important to mention that the formation of thiirane was proved as the first step in this reaction and the stereochemistry of addition has been determined by x-ray analysis.

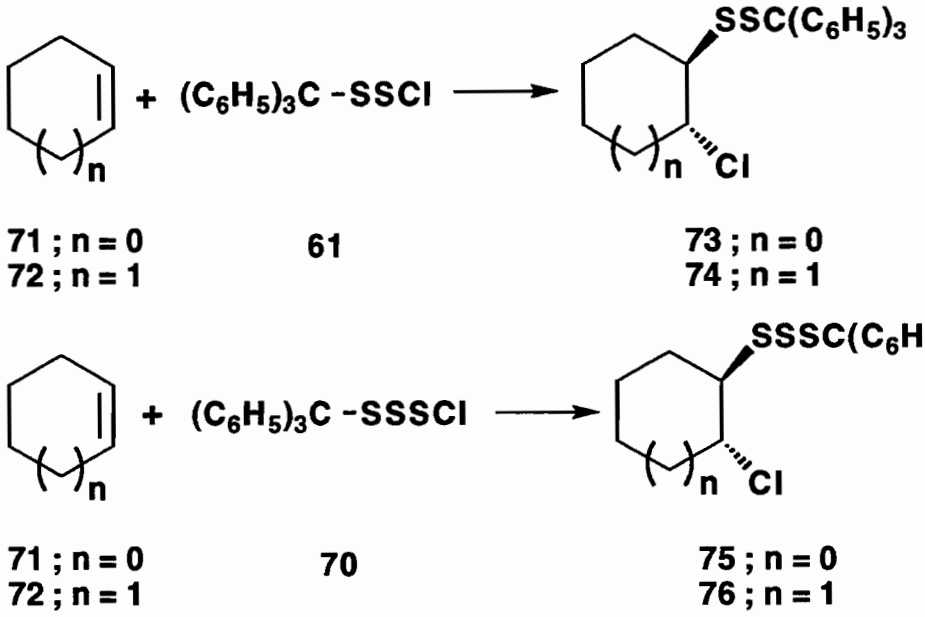
In addition, we[64] also found that the reaction of triphenylmethanethiosulfenyl chloride (**61**) with the same bicyclic alkenes **66** and **67**, furnished the same products (β-chlorodisulfides) **68** and **69**, respectively, in good isolated yields (**Scheme 34**).



SCHEME 34

The structures of **68** and **69** were established by ^1H and ^{13}C NMR as well as by elemental analysis. In addition, the x-ray structures of **68** and **69** were reported for the first time.[64]

In a recent paper, we reported[65] a new reaction of sulfenyl chlorides with various cyclic alkenes. Triphenylmethanethiosulfenyl chloride **(61)** (and its dithio homolog **70**) has been found to react with cyclopentene **(71)** and cyclohexene **(72)** to give stable addition products (**73, 74** from **61**; **75, 76** from **70**), in high isolated yields (*ca.* 90%) **(Scheme 35)**.



SCHEME 35

The structural determination of compounds **73, 74, 75** and **76** was based on ^{1}H and ^{13}C NMR as well as by elemental analysis. In addition, the x-ray structures of **75** and **76** were reported for the first time.[65]

CHAPTER 3

RESULTS AND DISCUSSION

3.1 SYNTHESIS OF DI- AND TRITHIO ADDUCTS

The chemistry of sulfenyl halides has been extensively studied.[71a,96-101] The reaction of sulfenyl halides with olefins has been interpreted mechanistically in terms of the formation of an episulfonium ion intermediate[97] that is intercepted by a halide ion to form a β-halo thioether **(Scheme 24)**. The chemistry of triphenylmethanesulfenyl chloride **(65)** and its thio **61** and dithio **70** homolog are much less examined.[73]

The reaction of triphenylmethanesulfenyl chloride **(65)** with norbornene **(66)** has been investigated previously.[112] 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.[108-110]

In the case of the reaction of sulfenyl chloride **65** with norbornene **(66)**, a number of products were reported[112] but details were lacking and neither their stereochemistry nor the mechanism of the reaction were demonstrated.

Recently, Harpp and Williams[122] investigated an interesting reaction of triphenylmethanesulfenyl chloride **(65)** where its sulfur atom is extruded quantitatively and catalytically by a reaction with thioketones. In another investigation,[62] the reaction of triphenylmethanethiosulfenyl chloride **(61)** 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

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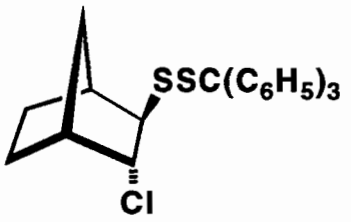
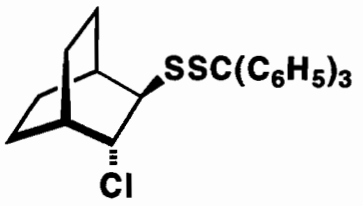
122 C. R. Williams and D. N. Harpp, *Tetrahedron Lett.*, **32**, 7633 (1991).

develop a useful pathway to dithietanes **77** as potentially stable intermediates and/or diatomic sulfur precursors.

3.1.1 FORMATION OF DITHIO ADDUCTS FROM TRIPHENYLMETHANESULFENYL CHLORIDE (65)

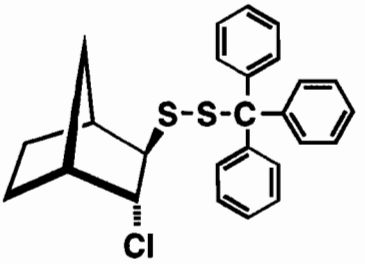
A solution of triphenylmethanesulfenyl chloride **(65)** in methylene chloride (CH_2Cl_2) was added dropwise at room temperature to a stirred solution of olefin bicyclo[2.2.1]heptene **(66)** or bicyclo[2.2.2]octene **(67)** in CH_2Cl_2. The reaction was stirred for a certain time under a nitrogen atmosphere. Chromatography on silica gel afforded an oily product which solidified upon washing with 35-60 °C petroleum ether. Recrystallization from the appropriate solvent gave a pure product of the corresponding dithio adducts in good isolated yields **(Table 1)**.

Table 1: Dithio Adducts From Triphenylmethanesulfenyl Chloride (65): Melting Points, Reaction Times and % Isolated Yields

Entry	Dithio Adduct	Time (h)	%Yield	Mp. (°C)
68		20	63	114-115
69		22	60	118-119

The identity of these adducts **68** and **69** was confirmed by ^{1}H and ^{13}C NMR, elemental analysis as well as by x-ray analysis.

The x-ray crystallographic structure of **68** was reported[64] for the first time. The ORTEP[123] drawing of dithio **68** is shown in **Figure 1**. Selected bond lengths and angles are given in **Table 2.**



68

123 C. K. Johnson, "ORTEP - A Fortran Thermal Ellipsoid Plot Program", Technical Report ORNL-5138, Oak Ridge Tennessee (1976).

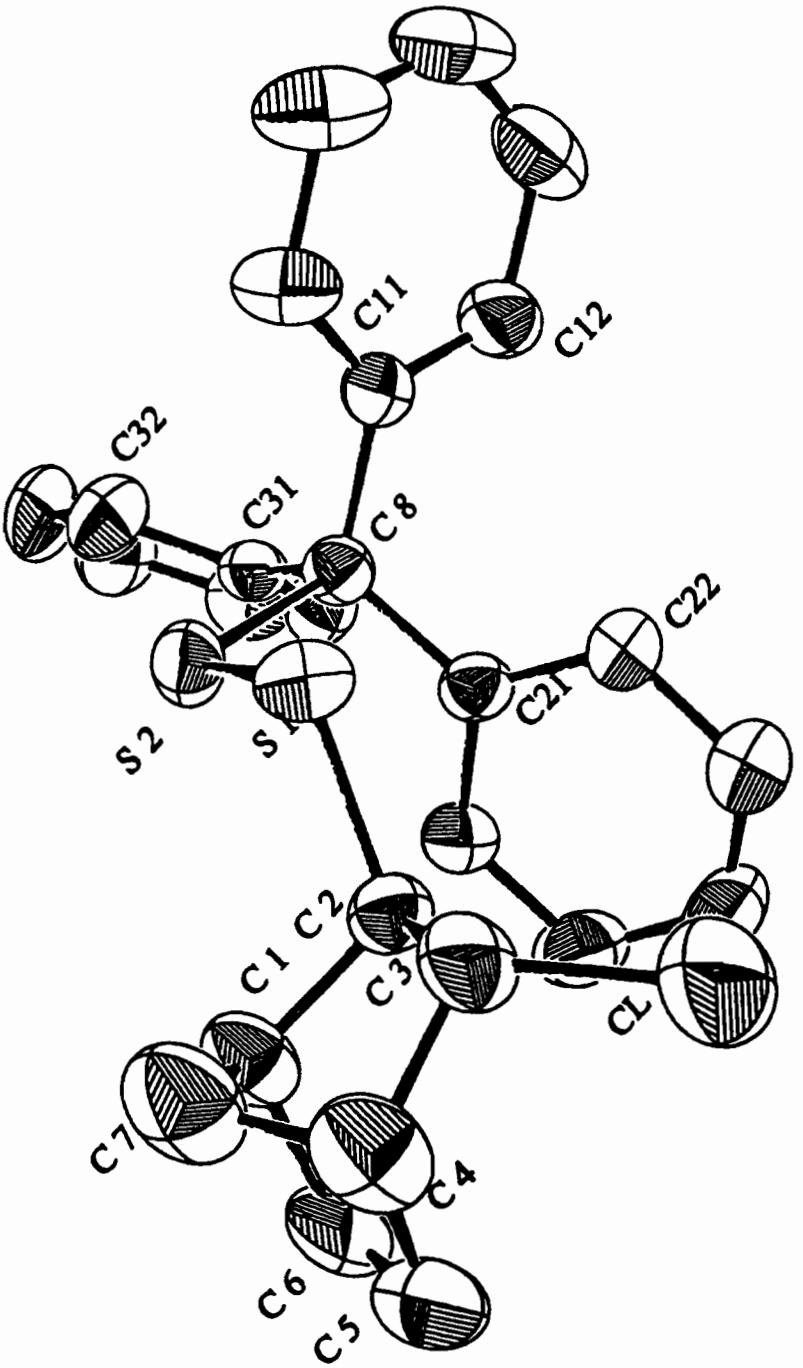
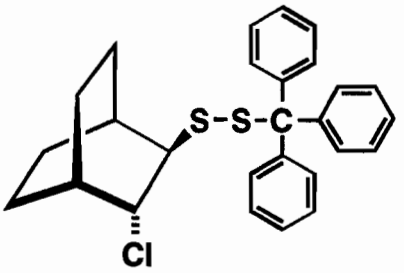


Figure 1: ORTEP Representation of *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane (68)

Table 2: Selected Bond Lengths and Bond Angles for *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane (68)

Bond Lengths (Å)	
S(1)-S(2)	2.026(3)
S(1)-C(2)	1.842(7)
S(2)-C(8)	1.891(7)
Cl-C(3)	1.792(8)
Bond Angles (°)	
S(2)-S(1)-C(2)	105.5(3)
S(1)-S(2)-C(8)	105.84(24)
S(1)-C(2)-C(3)	107.5(5)
Cl-C(3)-C(2)	111.6(6)
Dihedral Angles (°)	
C(2)-S(1)-S(2)-C(8)	-95.6(3)
S(2)-S(1)-C(2)-C(3)	-170.2(5)
S(1)-S(2)-C(8)-C(21)	58.3(3)

In addition, the x-ray crystallographic structure of **69** was also reported[64] for the first time. The ORTEP[123] drawing of dithio **69** is shown in **Figure 2.** Selected bond lengths and angles are given in **Table 3.**



69

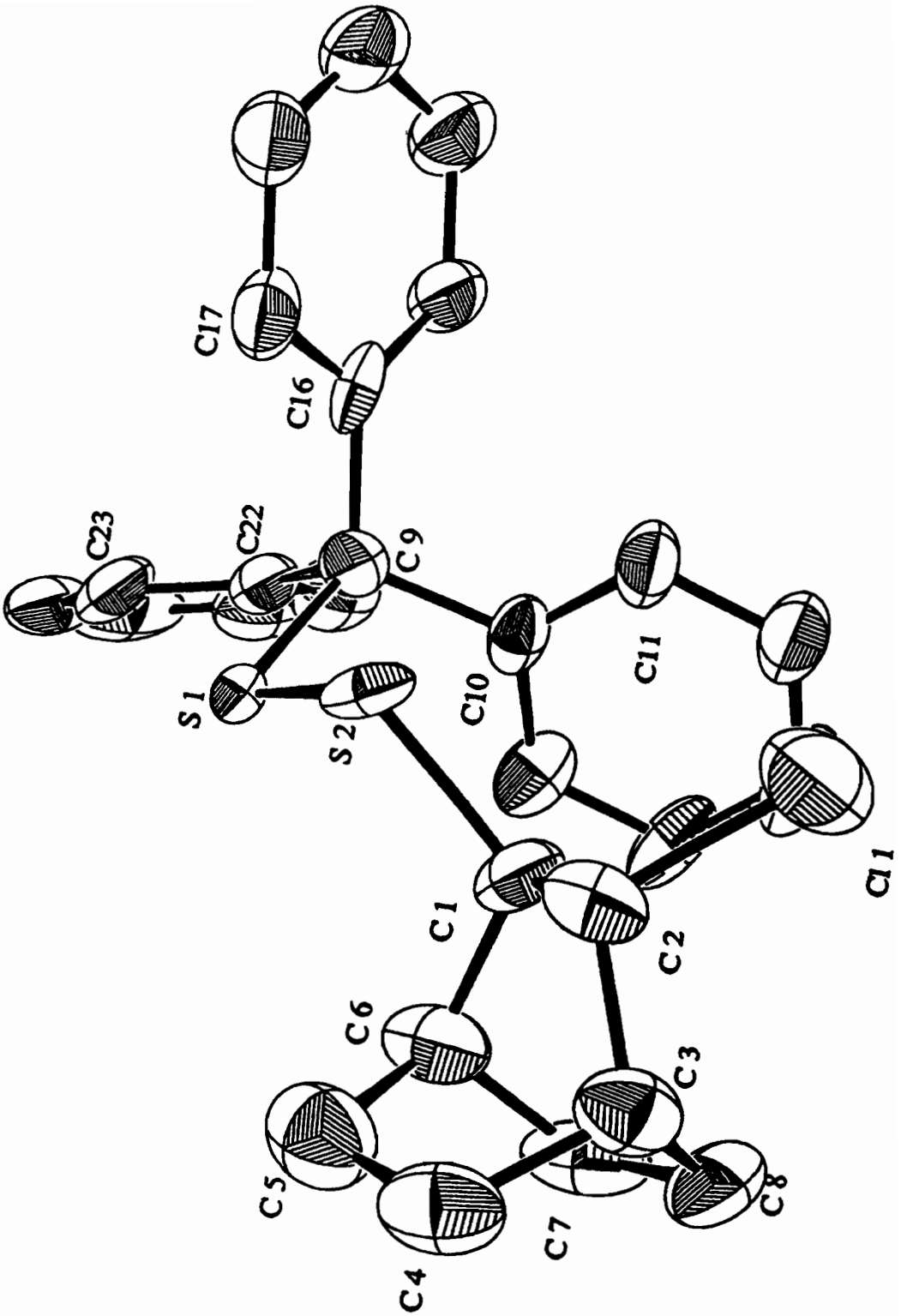
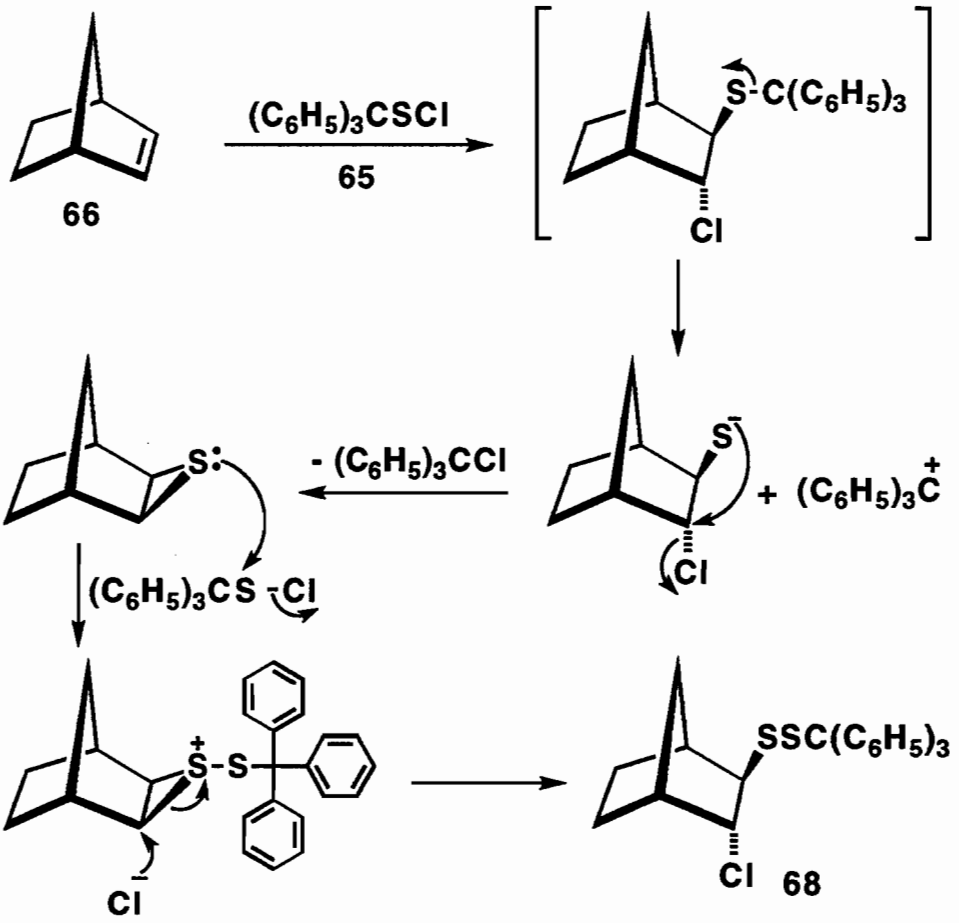


Figure 2: ORTEP Representation of *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane (69)

Table 3: Selected Bond Lengths and Bond Angles for *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane (69)

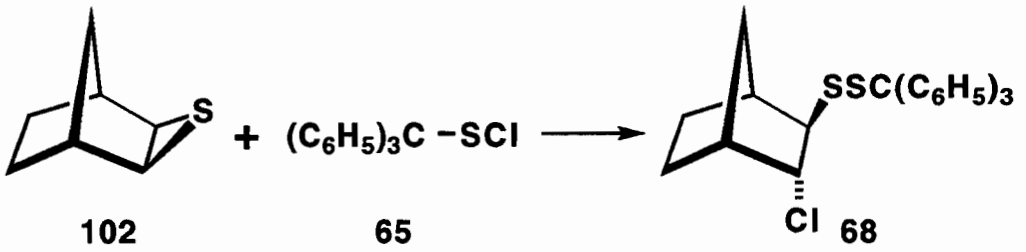
Bond Lengths (Å)	
S(1)-S(2)	2.046(5)
S(1)-C(9)	1.871(9)
S(2)-C(1)	1.854(9)
Cl(1)-C(2)	1.840(10)
Bond Angles (°)	
S(2)-S(1)-C(9)	104.6(3)
S(1)-S(2)-C(1)	105.9(3)
S(2)-C(1)-C(2)	101.5(6)
Cl(1)-C(2)-C(1)	111.8(7)
Dihedral Angles (°)	
C(9)-S(1)-S(2)-C(1)	92.7(5)
S(1)-S(2)-C(1)-C(2)	166.8(8)
S(2)-S(1)-C(9)-C(16)	66.5(5)

The stereochemistry of addition to olefins **66** and **67** has been determined by an x-ray analysis. The analysis revealed the regiochemistry of **68** (**Figure 1**) and the symmetry of **69** permits only one isomer (**Figure 2**). Elemental and x-ray analysis demonstrated that, the addition products **68** and **69** 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 36**.



SCHEME 36

To demonstrate the likelihood of this mechanism we independently prepared *exo*-episulfide **102** and treated it with triphenylmethanesulfenyl chloride (**65**). Dithio **68** was isolated in 90% yield (**Scheme 37**). This explains clearly the likely pathway displayed in **Scheme 36**.



102 65 68

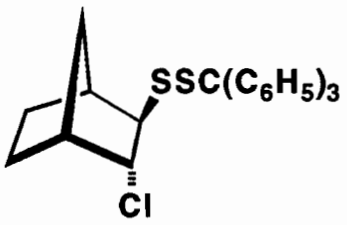
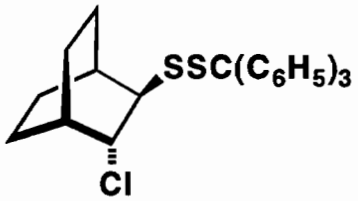
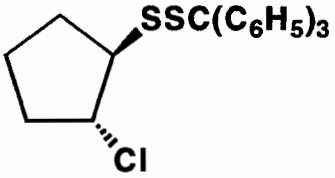
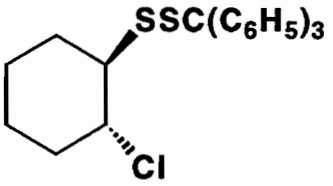
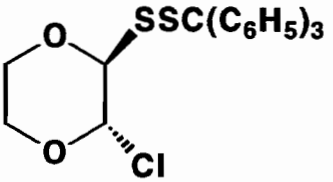
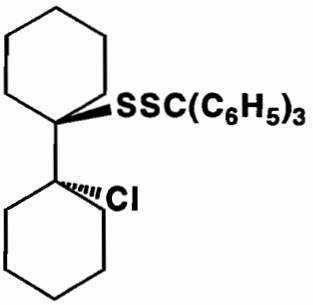
SCHEME 37

3.1.2 FORMATION OF DITHIO ADDUCTS FROM TRIPHENYLMETHANETHIOSULFENYL CHLORIDE (61)

Triphenylmethanethiosulfenyl chloride **(61)** was dissolved in dry methylene chloride (CH_2Cl_2) to form a yellow solution which was added dropwise at room temperature to a stirred solution of an olefin in dry CH_2Cl_2. The mixture was stirred for a certain time under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using about 15 to 20% chloroform in hexane as eluent. Removal of the solvent under reduced pressure and recrystallization from the appropriate solvent gave a pure product of the corresponding dithio adducts in good isolated yields **(Table 4)**.

The structures of these adducts were established by ^1H and ^{13}C NMR as well as by elemental analysis.

Table 4: **Dithio Adducts From Triphenylmethanethiosulfenyl Chloride (61): Melting Points, Reaction Times and % Isolated Yields**

Entry	Dithio Adduct	Time (h)	%Yield	Mp. (°C)
68		6	87	114-115
69		7	82	118-119
73		7	88	99-101
74		5	90	103-104
112		8	61	oil
113		10	68	43-44

The assignments of relevant ^{13}C NMR chemical shifts relative to tetramethylsilane of dithio adducts are reported in **Table 5**. The carbon atoms were identified using the following numbering system.

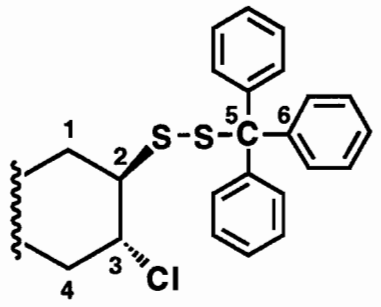


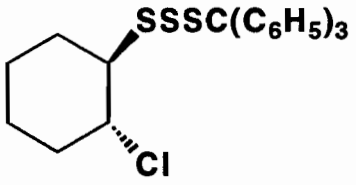
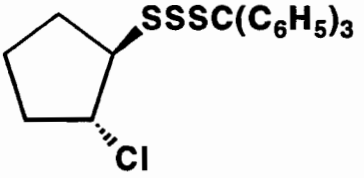
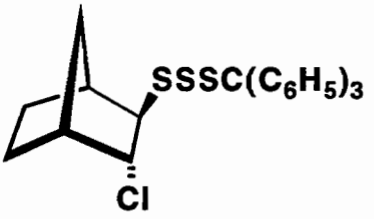
Table 5: Assignments of Relevant ^{13}C Chemical Shifts for Dithio Compounds

Entry	C1	C2	C3	C4	C5	C6
68	42.57	58.76	66.41	44.82	71.26	143.74
69	28.71	55.86	65.00	33.99	71.16	143.76
73	28.89	55.25	65.79	33.66	71.38	143.57
74	28.62	52.78	62.66	32.76	71.44	143.77
112	-	88.16	89.99	-	71.92	143.23
113	-	59.81	60.72	-	72.74	143.78

3.1.3 FORMATION OF TRITHIO ADDUCTS FROM TRIPHENYLMETHANE-DITHIOSULFENYL CHLORIDE (70)

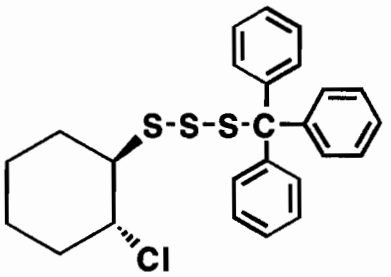
A solution of triphenylmethanedithiosulfenyl chloride (**70**) in methylene chloride (CH_2Cl_2) was added dropwise to a stirred solution of olefin **66** or **71** or **72** in CH_2Cl_2 at room temperature. The reaction was stirred for a certain time under a nitrogen atmosphere. Chromatography on silica gel afforded a solid product. Recrystallization from the appropriate solvent gave a pure product of the corresponding trithio adducts in good isolated yields (**Table 6**).

Table 6: Trithio Adducts From Triphenylmethanedithiosulfenyl Chloride (70): Melting Points, Reaction Times and % Isolated Yields

Entry	Trithio Adduct	Time (h)	%Yield	Mp. (°C)
76		3	92	138-139
75		4	90	73-74
114		10	68	oil

The identity of these adducts was confirmed by ^{1}H and ^{13}C NMR as well as by elemental analysis.

The x-ray crystallographic structure of trithio adduct **76** was reported[65] for the first time. The ORTEP[123] drawing of trithio adduct **76** is shown in **Figure 3**. Selected bond lengths and angles are given in **Table 7**.



76

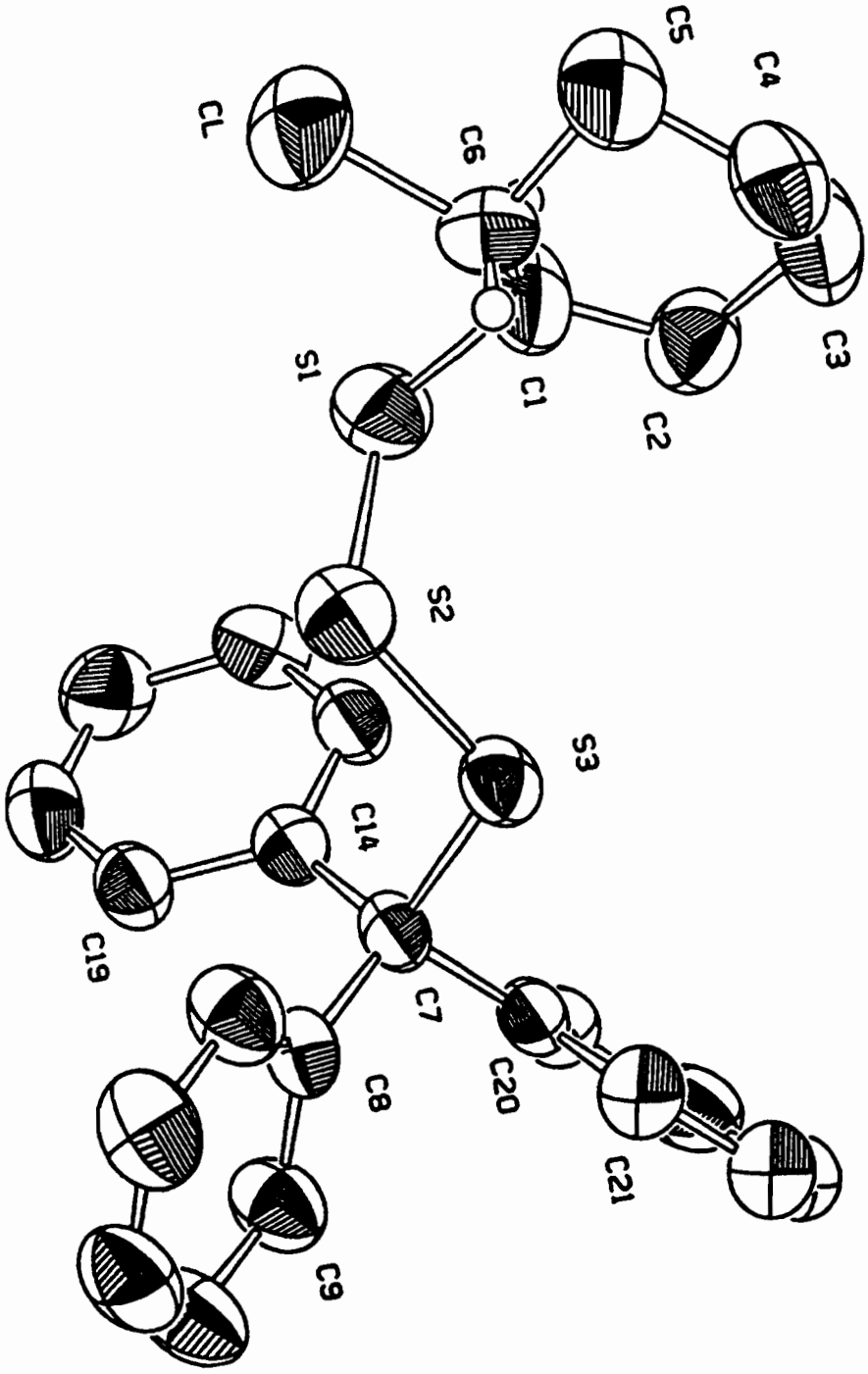
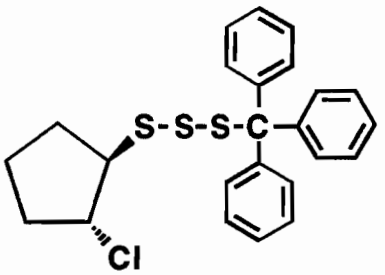


Figure 3: ORTEP Representation of *trans*-2-Chloro-1-(triphenylmethyltrithio)cyclohexane (76)

Table 7: Selected Bond Lengths and Bond Angles for *trans*-2-Chloro-1-(triphenylmethyltrithio)cyclohexane (76)

Bond Lengths (Å)	
S(1)-S(2)	2.032(2)
S(2)-S(3)	2.041(2)
S(3)-C(7)	1.891(4)
S(1)-C(1)	1.824(6)
Cl-C(6)	1.82(1)
Bond Angles (°)	
S(2)-S(1)-C(1)	105.0(4)
S(1)-S(2)-S(3)	108.47(8)
S(2)-S(3)-C(7)	108.2(1)
S(1)-C(1)-C(6)	119.7(7)
Cl-C(6)-C(1)	117.1(9)
Dihedral Angles (°)	
S(3)-S(2)-S(1)-C(1)	-89.2(2)
S(1)-S(2)-S(3)-C(7)	-103.7(2)
S(2)-S(3)-C(7)-C(8)	-80.4(3)
S(2)-S(1)-C(1)-C(6)	-69.0(1)

In addition, the x-ray crystallographic structure of trithio adduct **75** was also reported[65] for the first time. The ORTEP[123] drawing of trithio adduct **75** is shown in **Figure 4**. Selected bond lengths and angles are given in **Table 8**.



75

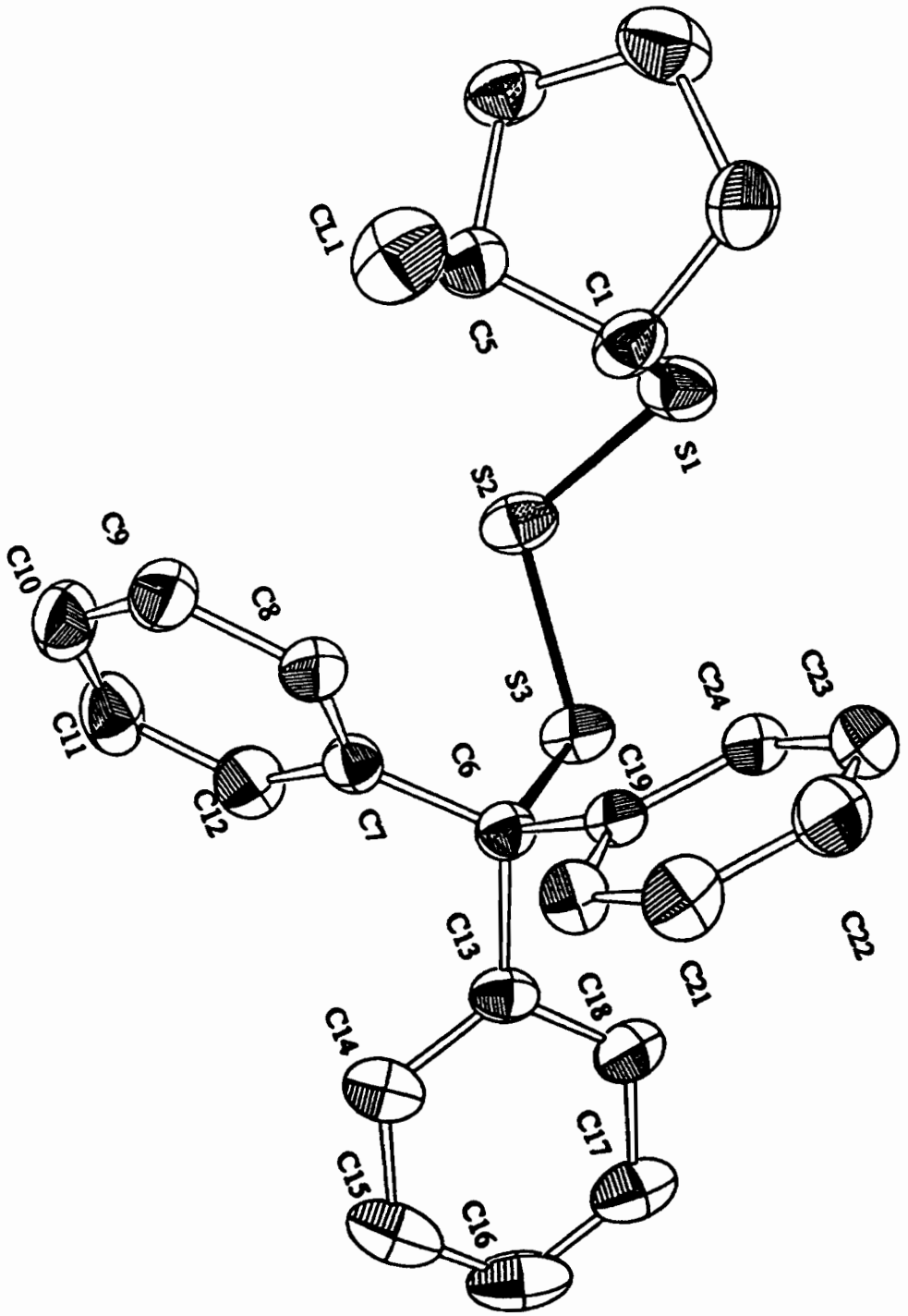


Figure 4: ORTEP Representation of *trans*-2-Chloro-1-(triphenylmethyltrithio)cyclopentane (75)

Table 8: Selected Bond Lengths and Bond Angles for *trans*-2-Chloro-1-(triphenylmethyltrithio)cyclopentane (75)

Bond Lengths (Å)	
S(1)-S(2)	2.0452(18)
S(2)-S(3)	2.0322(14)
S(3)-C(6)	1.887(4)
S(1)-C(1)	1.838(4)
Cl(1)-C(5)	1.826(4)
Bond Angles (°)	
S(2)-S(1)-C(1)	106.85(15)
S(1)-S(2)-S(3)	110.24(7)
S(2)-S(3)-C(6)	107.01(12)
S(1)-C(1)-C(5)	110.7(4)
Cl(1)-C(5)-C(1)	106.6(3)
Dihedral Angles (°)	
S(3)-S(2)-S(1)-C(1)	-97.6(1)
S(1)-S(2)-S(3)-C(6)	91.8(1)
S(2)-S(3)-C(6)-C(13)	158.8(3)
S(2)-S(1)-C(1)-C(5)	-59.0(2)

The assignments of relevant ^{13}C NMR chemical shifts relative to tetramethylsilane of trithio adducts are reported in **Table 9**. The carbon atoms were identified using the following numbering system.

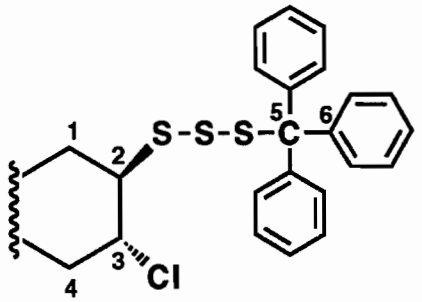
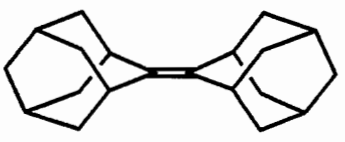


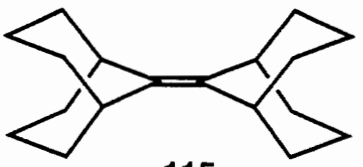
Table 9: Assignments of Relevant ^{13}C Chemical Shifts for Trithio Compounds

Entry	C1	C2	C3	C4	C5	C6
75	30.33	56.49	61.51	34.30	73.42	143.33
76	29.69	59.39	65.08	34.33	73.29	143.23
114	43.15	62.58	66.38	44.52	73.22	143.26

In addition, we investigated the reaction of triphenylmethanesulfenyl chloride **(65)** and its thio **61** and dithio **70** homolog with more hindered olefins such as adamantylideneadamantane **(108)** and bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane **(115)**.

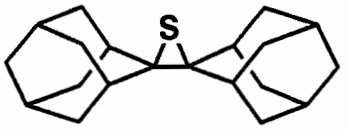


108

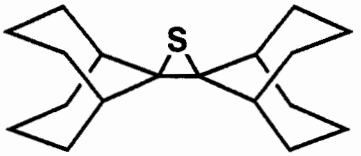


115

1,2-Addition products like **68** and **69** were not isolated, instead cyclization takes place forming the corresponding episulfides adamantylideneadamantane thiirane (**116**) and bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane (**117**) respectively.

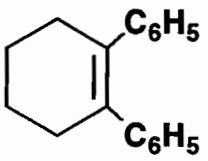


116

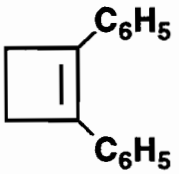


117

In another investigation, we studied the reaction of triphenylmethanesulfenyl chloride (**65**) and its thio **61** and dithio **70** homolog with another series of olefins. Cyclic olefins such as: 1,2-diphenylcyclohexene (**118**); 1,2-diphenylcyclobutene (**119**); 1,4-dimethylcyclohexene (**120**); (1*R*)-(+)-α-pinene (**121**); (1*S*)-(-)-β-pinene (**122**); 3-carene (**123**); 2-carene (**124**); camphene (**125**); 3,4-dihydro-2H-pyran (**126**); 2,5-dihydrofuran (**127**) and 2,5-dimethoxy-2,5-dihydrofuran (**128**) were not reacted with the series of sulfenyl chlorides.



118



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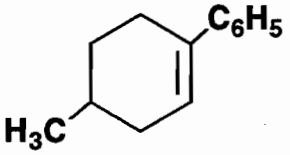

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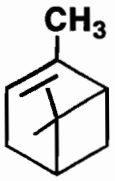

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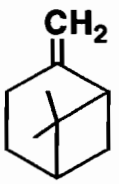

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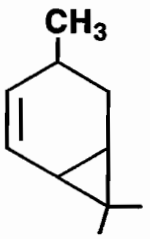

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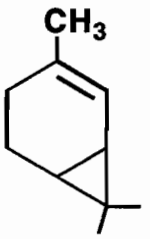

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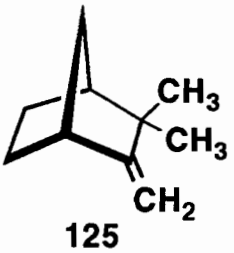
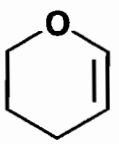
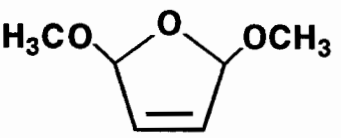


125



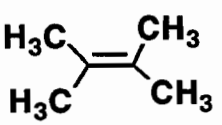
126

127



128

In addition, acyclic olefins such as: 1,1,2,2-tetramethylethylene (**129**); 1,1,2,2-tetraphenylethylene (**130**); 1,1,2,2-tetracyanoethylene (**131**); *trans*-stilbene (**132**); *cis*-stilbene (**133**); 1-bromo-2-methylpropene (**134**); styrene (**135**); bromostyrene (**136**) and vinylcyclohexane (**137**) were also tried.



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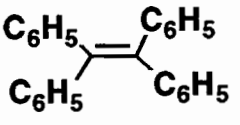

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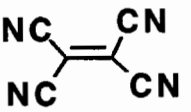

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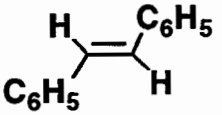

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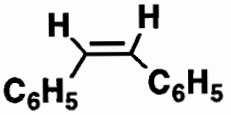

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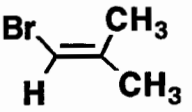

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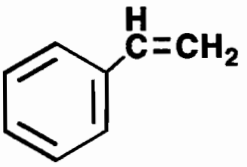
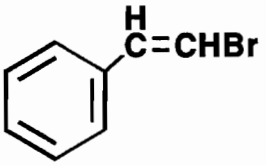
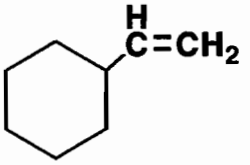


135



136



137

We discovered that these olefins **118-137** 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 **61** or **65** and **70** decomposed upon heating and most of the olefins are stable to addition chemistry, either due to conjugation or because they are vinyl halides.

We found that when each of the 1,2-addition products **68**, **69** or **73-76** were decomposed in the presence of 2,3-dimethyl-1,3-butadiene (**62**) evidence was obtained of the trapping of diatomic sulfur.

3.2 TRAPPING OF DIATOMIC SULFUR FROM DI- AND TRITHIO ADDUCTS

In the literature there are only five reaction systems reported which successfully generated singlet diatomic sulfur in synthetically useful yields.[47,49-51,63] These methods have certain limitations. For example, since triphenylphosphine dibromide **(35)** is light and moisture sensitive as well as reactive towards a wide variety of functionalities, the two procedures[47,49] which require the use of compound **35** are difficult. In addition, the triarylmetal trisulfides **34**[47] are not easy to prepare.

The major limitation in case of the procedure of Steliou[50] is that it must be conducted in the absence of most functionalities. The major sulfurating reagent, hexamethyldisilthiane, which was used in his procedure[124] 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,[49] the major limitation was the preparation of 5,5-dimethyl-1,2-dithia-3,7-diselenacycloheptane **(38)**. Compound **38**, although stable, was difficult to prepare and isolate. In addition, the synthesis required high dilution conditions, and to maximize the production of S_2, a high temperature (140 ^{o}C), at which some substances may be destroyed, was required.

The production of the cyclic tetrasulfide adduct 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(64)** from the reaction of S_2 with dienes has been indicated in three instances.[51,55,63]

Nicolaou[55] isolated cyclic tetrasulfide **64** in the reaction of dithiatopazine **53** with 2,3-diphenyl-1,3-butadiene. In addition, Harpp and McDonald[51] obtained adduct **64** by reacting pentasulfide **40** and dibromide **35** with 2,3-dimethyl-1,3-butadiene **(62)**.

Most recently, Harpp and coworkers[63] isolated cyclic di- and tetrasulfide adducts **63** and **64** from the thermal decomposition of alkoxydisulfide **29** with 2,3-dimethyl- and 2,3-diphenyl-1,3-butadienes, in good yields.

The central theme of our work is to try to trap S_2 in the thermal decomposition of di- and trithio adducts. It is our belief that by carrying out a study of the addition chemistry

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124 K. Steliou and M. Mrani, *J. Am. Chem. Soc.*, **104**, 3104 (1982).

of sulfenyl chlorides **61**, **65** and **70** with various olefins, we might be able to generate species such as **68**, **69** and **74**. These in turn might indeed decompose to species like dithietane intermediate **77** which should then transfer S_2 directly to dienes or lose S_2 which is then captured by dienes.

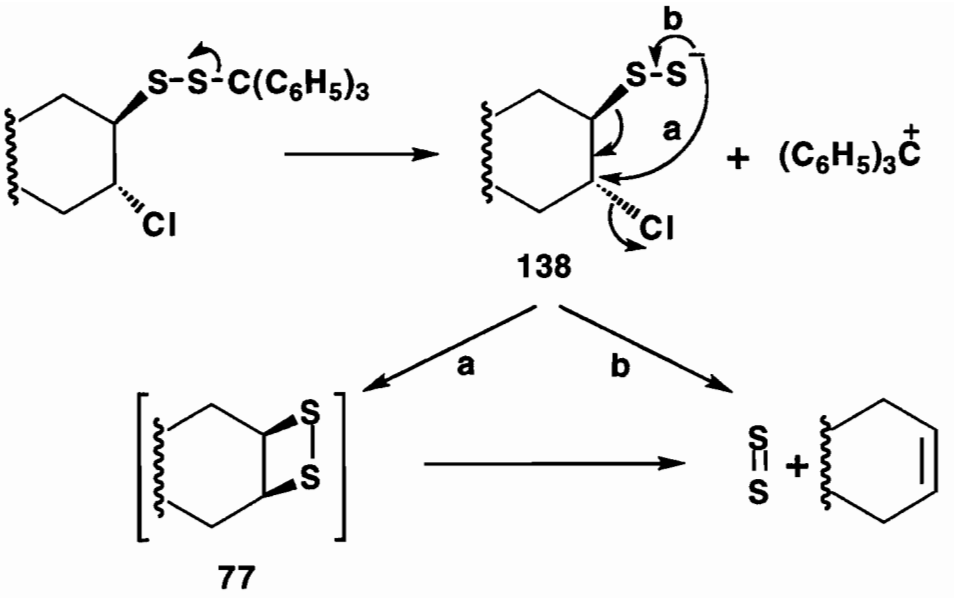
The successful identification of trapped S_2 was realized when signals in the ^1H NMR spectrum corresponding to cyclic disulfide 1,2-dithia-4,5-dimethyl-4-cyclohexene **(63)** or the cyclic tetrasulfide adduct 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(64)** were observed. This took place when the decomposition of the 1,2-addition products **68**, **69** and **74** was conducted in the presence of 2,3-dimethyl-1,3-butadiene **(62)**. Once these adducts were identified, the reaction conditions were modified so that the yield of the trapped adducts **63** and **64** was maximized. This reaction could then be considered as a useful source of S_2 and can be added to the list of those already known.

3.2.1 GENERAL PROCEDURE

A solution of 2,3-dimethyl-1,3-butadiene **(62)** and the di- or trithio adduct were refluxed in an appropriate solvent for a certain time under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 15 to 25% chloroform in hexane as eluent. In each case, cyclic disulfide adduct 1,2-dithia-4,5-dimethyl-4-cyclohexene **(63)** was detected by ^1H NMR in low yield and cyclic tetrasulfide adduct 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(64)** was isolated in good yield.

Byproducts, the acyclic tetrasulfide adduct, chlorotriphenylmethane and starting material along with triphenylmethanethiol and elemental sulfur were isolated in low yields. In addition, the corresponding olefin was also detected by ^1H NMR.

In each case, there are two possible ways olefin could form. **Scheme 38, path a** shows the possible formation of dithietane intermediate **77**. **Scheme 38, path b** displays a concerted fragmentation producing diatomic sulfur and olefin directly from intermediate **138**. At present we have no evidence suggesting which path may be correct.



SCHEME 38

3.2.1.1 FROM DECOMPOSITION OF *endo*-2-CHLORO-*exo*-1-(TRIPHENYLMETHYLDITHIO)BICYCLO[2.2.1]HEPTANE (68)

The reaction of 2,3-dimethyl-1,3-butadiene **(62)** was carried out with 3 equivalents of dithio **68** in refluxing ethyl acetate for 36 h under a nitrogen atmosphere. Chromatography of the crude product gave a 24% yield of cyclic tetrasulfide 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(64)** as an oily product. Cyclic disulfide adduct 1,2-dithia-4,5-dimethyl-4-cyclohexene **(63)** was detected by ^{1}H NMR in low yield. The major product of this reaction is formed by an intermolecular pathway and identified as the acyclic tetrasulfide adduct di[(2-chloro)-1-norbornyl] tetrasulfide **(139)** in 59% yield.

In addition, a number of minor products were formed in low yield. Among these is chlorotriphenylmethane (23%), starting material (10%), along with triphenylmethanethiol (25%) and elemental sulfur (14%). In addition, bicyclo[2.2.1]heptene **(66)** was detected by ^{1}H NMR.

3.2.1.2 FROM DECOMPOSITION OF *endo*-2-CHLORO-*exo*-1-(TRIPHENYLMETHYLDITHIO)BICYCLO[2.2.2]OCTANE (69)

The reaction of 2,3-dimethyl-1,3-butadiene **(62)** was carried out with 3 equivalents of dithio **69** in refluxing ethyl acetate for 40 h under a nitrogen atmosphere. Chromatography of the crude product gave a 19% yield of cyclic tetrasulfide adduct **64**. Cyclic disulfide **63** was detected by ^{1}H NMR in low yield. The major product of this reaction is formed by an intermolecular pathway and identified as the acyclic tetrasulfide adduct di[(2-chloro)-1-bicyclo[2.2.2]octyl] tetrasulfide **(140)** in 51% yield.

A number of minor products such as triphenylmethanethiol (23%) were isolated along with chlorotriphenylmethane (21%), starting material (14%) and elemental sulfur (18%). In addition, bicyclo[2.2.2]octene **(67)** was detected by ^{1}H NMR.

3.2.1.3 FROM DECOMPOSITION OF *endo*-2-CHLORO-*exo*-1-(TRIPHENYLMETHYLTRITHIO)BICYCLO[2.2.1]HEPTANE (114)

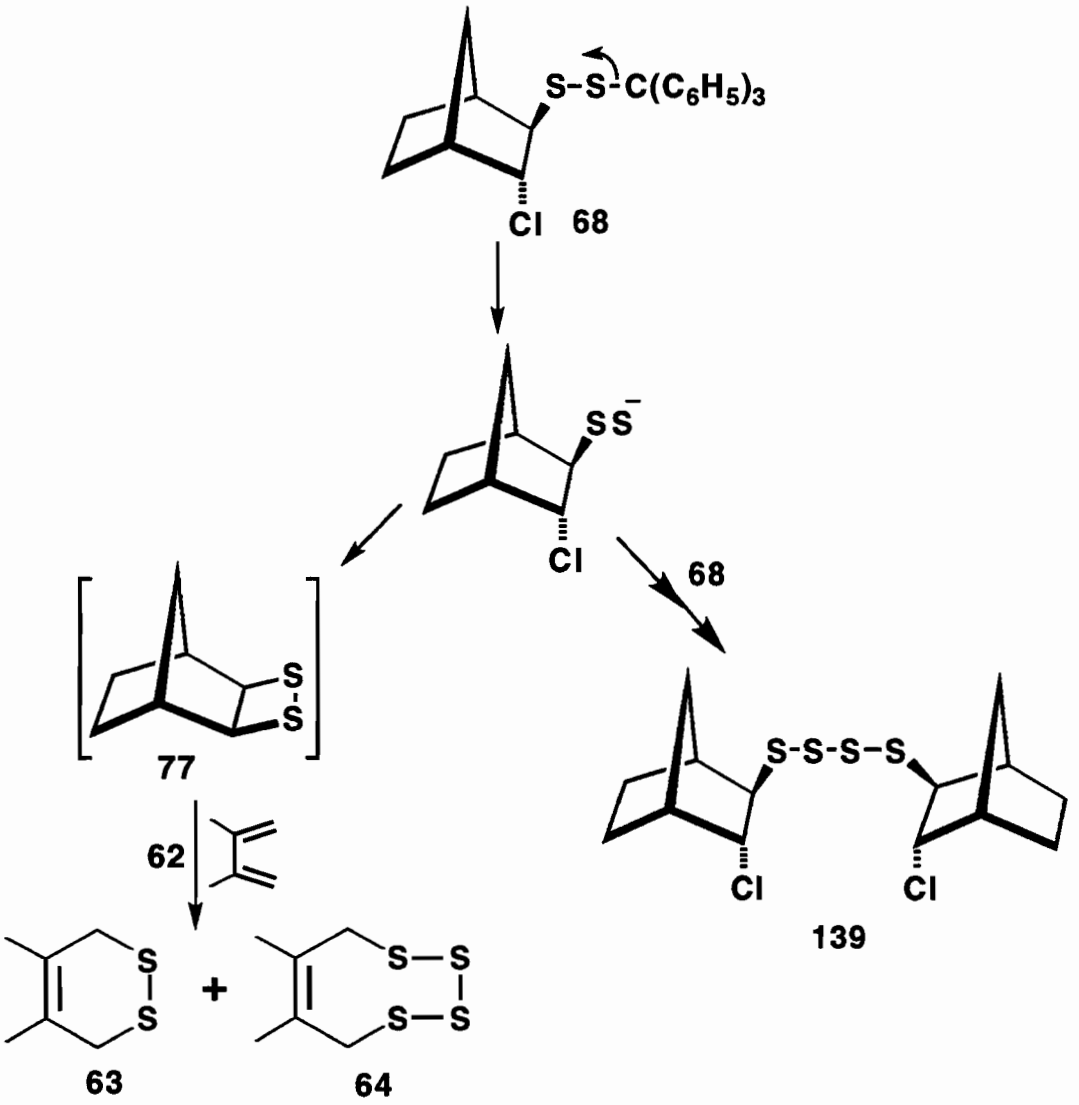
The reaction of 2,3-dimethyl-1,3-butadiene **(62)** was carried out with 3 equivalents of trithio **114** in refluxing ethyl acetate for 36 h under a nitrogen atmosphere. Chromatography of the crude product gave a 15% yield of cyclic tetrasulfide **64**. Cyclic disulfide adduct **63** was detected by ^{1}H NMR in low yield. The major product of this reaction is formed by an intermolecular pathway and identified as the acyclic tetrasulfide adduct di[(2-chloro)-1-norbornyl] tetrasulfide **(139)** in 60% yield.

A number of minor products such as triphenylmethanethiol (27%) were isolated along with chlorotriphenylmethane (19%), starting material (16%) and elemental sulfur (17%). In addition, bicyclo[2.2.1]heptene **(66)** was detected by ^{1}H NMR.

The identity of cyclic tetrasulfide adduct **64** in the above reactions was confirmed by ^{1}H and ^{13}C NMR as well as by mass spectrometry. In addition, the structure of tetrasulfides **139** and **140** was established by ^{1}H and ^{13}C NMR as well as by elemental analysis.

When 3 equivalents of **68** were heated in ethyl acetate with 1 equivalent of a standard diatomic sulfur trap; 2,3-dimethyl-1,3-butadiene **(62)**, both cyclic disulfide adduct 1,2-dithia-4,5-dimethyl-4-cyclohexene **(63)** and cyclic tetrasulfide adduct 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(64)** were detected by ^{1}H NMR.

Eventually, the tetrasulfide adduct **64** was isolated in 24% yield. It is possible that intermediate **77** either transfers its two sulfur atoms to the diene trap to form **63** or gives up S_2 which is then trapped **(Scheme 39)**. However, as stated earlier, we have no direct evidence concerning intermediate **77**. As has been noted by ourselves[63,51,125] and in other labs,[126] a likely second trap of a two sulfur unit takes place forming tetrasulfide **64**.



SCHEME 39

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125 W. Chew and D. N. Harpp, *Sulfur Lett.*, **15**, 247 (1993).

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

The major product of the reaction is formed by an intermolecular pathway when **68** is heated in ethyl acetate eventually giving the corresponding tetrasulfide **139** in 59% yield.

A possible pathway to explain this result is suggested in **Scheme 39**. In addition, starting material was isolated (10%) along with triphenylmethanethiol (25%), chlorotriphenylmethane (23%) and elemental sulfur (14%). Bicyclo[2.2.1]heptene **(66)** was detected by ^{1}H NMR.

We discovered that di- and trithio reagents **68**, **69** and **114** gave a low yield of the trapped adducts **63** and **64** even when the decomposition was carried out under different reaction conditions. We tried to synthesize a new series of 1,2-addition products in order to obtain better yields of **63** and **64**. Other olefins like cyclohexene **(72)** and cyclopentene **(71)** were used for this purpose.

3.2.1.4 FROM DECOMPOSITION OF *trans*-2-CHLORO-1-(TRIPHENYLMETHYLDITHIO)CYCLOHEXANE (74)

The reaction of 2,3-dimethyl-1,3-butadiene **(62)** was carried out with 3 equivalents of dithio **74** in refluxing ethyl acetate for 10 h under a nitrogen atmosphere. Chromatography of the crude product gave a 58% yield of cyclic tetrasulfide 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(64)** as a major product. Cyclic disulfide adduct **63** was detected by ^{1}H NMR (*ca.* 10%). Acyclic tetrasulfide adduct di[(2-chloro)-1-cyclohexyl] tetrasulfide **(79)** was formed by an intermolecular pathway as one of the minor products in a yield of 16%.

Other minor products, such as triphenylmethanethiol (28%), were also isolated along with chlorotriphenylmethane (18%), starting material (10%) and elemental sulfur (17%). In addition, cyclohexene **(72)** was detected by ^{1}H NMR (*ca.* 8%).

The decomposition was further investigated by varying the reaction conditions in an effort to maximize the yield of the trapped adduct. The above reaction was repeated in a variety of solvents, varying temperature, time and concentration **(Table 10)**.

Table 10: Summary of S_2 Trapping Experiments of 2,3-Dimethyl-1,3-butadiene (62) with *trans*-2-Chloro-1-(triphenylmethyldithio)-cyclohexane (74)

R[a]	Solvent	Temp. (°C)	Time (h)	%Yield (A)	%Yield (B)
1 : 3	EtOAc	77	12	27	41
1 : 1	EtOAc	77	12	35	34
3 : 1	EtOAc*	77	10	58	16
3 : 1	EtOAc**	77	10	54	19
5 : 1	EtOAc	77	10	57	15
3 : 1	CH_2Cl_2	36	15	10	62
3 : 1	$CHCl_3$	36	15	15	58
1 : 1	$CHCl_3$	61	15	20	51
3 : 1	$CHCl_3$	61	15	26	42
1 : 1	C_6H_5Cl	132	2	31	36
3 : 1	C_6H_5Cl*	132	2	48	20
3 : 1	C_6H_5Cl* *	132	2	47	18

Table 10: continued

R[a]	Solvent	Temp. (°C)	Time (h)	%Yield (A)	%Yield (B)
3 : 1	C_6H_5Cl	132	10	49	20
5 : 1	C_6H_5Cl	132	2	50	18

R[a] refers to the molar ratio of *trans*-2-chloro-1-(triphenylmethyldithio)-cyclohexane **(74)** to 2,3-dimethyl-1,3-butadiene **(62)**.

A refers to the cyclic tetrasulfide adduct **64**.

B refers to the di[(2-chloro)-1-cyclohexyl] tetrasulfide **(79)**.

* 50 mL of the solvent was used.

** 15 mL of the solvent was used.

3.2.1.5 FROM DECOMPOSITION OF *trans*-2-CHLORO-1-(TRIPHENYLMETHYLTRITHIO)CYCLOHEXANE (76)

The reaction of 2,3-dimethyl-1,3-butadiene **(62)** was carried out with 3 equivalents of trithio **76** in refluxing ethyl acetate for 10 h under a nitrogen atmosphere. Chromatography of the crude product gave a 63% yield of cyclic tetrasulfide 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(64)** as a major product. Cyclic disulfide adduct **63** was detected by ^{1}H NMR (*ca.* 8%). Acyclic tetrasulfide adduct di[(2-chloro)-1-cyclohexyl] tetrasulfide **(79)** was formed by an intermolecular pathway as one of the minor products in a yield of 12%.

Other minor products such as triphenylmethanethiol (29%) were also isolated along with chlorotriphenylmethane (17%), starting material (9%) and elemental sulfur (24%). In addition, cyclohexene **(72)** was detected by ^{1}H NMR (*ca.* 7%).

The decomposition was further investigated by varying the reaction conditions in a variety of ways **(Table 11)**.

Table 11: Summary of S_2 Trapping Experiments of 2,3-Dimethyl-1,3-butadiene (62) with *trans*-2-Chloro-1-(triphenylmethyltrithio)-cyclohexane (76)

R[b]	Solvent	Temp. (°C)	Time. (h)	%Yield (A)	%Yield (B)
1 : 3	EtOAc	77	12	32	37
1 : 1	EtOAc	77	12	42	28
3 : 1	EtOAc*	77	10	63	12
3 : 1	EtOAc**	77	10	60	13
5 : 1	EtOAc	77	10	62	11
3 : 1	CH_2Cl_2	36	15	12	60
3 : 1	$CHCl_3$	36	15	16	55
1 : 1	$CHCl_3$	61	15	25	41
3 : 1	$CHCl_3$	61	15	29	38
1 : 1	C_6H_5Cl	132	2	40	29
3 : 1	C_6H_5Cl*	132	2	56	15
3 : 1	C_6H_5Cl**	132	2	53	14

Table 11: continued

R^b	Solvent	Temp. (°C)	Time. (h)	%Yield (A)	%Yield (B)
3 : 1	C_6H_5Cl	132	10	56	16
5 : 1	C_6H_5Cl	132	2	57	14

R^b refers to the molar ratio of *trans*-2-chloro-1-(triphenylmethyltrithio)-cyclohexane **(76)** to 2,3-dimethyl-1,3-butadiene **(62)**.

A refers to the cyclic tetrasulfide adduct **64**.

B refers to the di[(2-chloro)-1-cyclohexyl] tetrasulfide **(79)**.

* 50 mL of the solvent was used.

** 15 mL of the solvent was used.

3.2.1.6 FROM DECOMPOSITION OF *trans*-2-CHLORO-1-(TRIPHENYLMETHYLDITHIO)CYCLOPENTANE (73)

The reaction of 2,3-dimethyl-1,3-butadiene **(62)** was carried out with 3 equivalents of dithio **73** in refluxing ethyl acetate for 15 h under a nitrogen atmosphere. Chromatography of the crude product gave a 40% yield of cyclic tetrasulfide 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(64)** as a major product. Cyclic disulfide adduct **63** was detected by ^1H NMR (*ca.* 8%). Acyclic tetrasulfide adduct di[(2-chloro)-1-cyclopentyl] tetrasulfide **(78)** was formed by an intermolecular pathway as one of the minor products in a yield of 24%.

Other minor products such as triphenylmethanethiol (26%) were also isolated along with chlorotriphenylmethane (21%), starting material (12%) and elemental sulfur (18%). In addition, cyclopentene **(71)** was detected by ^1H NMR (*ca.* 9%).

The above reaction was repeated in a variety of solvents, varying temperature, time and concentration hoping to maximize the yield of the trapped adduct **(Table 12)**.

Table 12: Summary of S_2 Trapping Experiments of 2,3-Dimethyl-1,3-butadiene (62) with *trans*-2-Chloro-1-(triphenylmethyldithio)-cyclopentane (73)

R[c]	Solvent	Temp. (°C)	Time (h)	%Yield (A)	%Yield (C)
1 : 3	EtOAc	77	15	12	55
1 : 1	EtOAc	77	15	18	54
3 : 1	EtOAc*	77	15	40	24
3 : 1	EtOAc**	77	15	37	27
5 : 1	EtOAc	77	15	39	28
3 : 1	CH_2Cl_2	36	20	7	62
3 : 1	$CHCl_3$	36	20	10	59
1 : 1	$CHCl_3$	61	20	10	57
3 : 1	$CHCl_3$	61	20	11	56
1 : 1	C_6H_5Cl	132	5	16	55
3 : 1	C_6H_5Cl*	132	5	30	40

Table 12: continued

R^c	Solvent	Temp. (°C)	Time (h)	%Yield (A)	%Yield (C)
3 : 1	C_6H_5Cl**	132	5	29	38
5 : 1	C_6H_5Cl	132	5	32	36

R^c refers to the molar ratio of *trans*-2-chloro-1-(triphenylmethyldithio)-cyclopentane **(73)** to 2,3-dimethyl-1,3-butadiene **(62)**.

A refers to the cyclic tetrasulfide adduct **64**.

C refers to the di[(2-chloro)-1-cyclopentyl] tetrasulfide **(78)**.

* 50 mL of the solvent was used.

** 15 mL of the solvent was used.

3.2.1.7 FROM DECOMPOSITION OF *trans*-2-CHLORO-1-(TRIPHENYLMETHYLTRITHIO)CYCLOPENTANE (75)

The reaction of 2,3-dimethyl-1,3-butadiene **(62)** was carried out with 3 equivalents of trithio **75** in refluxing ethyl acetate for 15 h under a nitrogen atmosphere. Chromatography of the crude product gave a 45% yield of cyclic tetrasulfide 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(64)** as a major product. Cyclic disulfide adduct **63** was detected by ^{1}H NMR (*ca.* 9%). Acyclic tetrasulfide adduct di[(2-chloro)-1-cyclopentyl] tetrasulfide **(78)** was formed by an intermolecular pathway as one of the minor products in a yield of 22%.

Other minor products such as triphenylmethanethiol (30%) were also isolated along with chlorotriphenylmethane (20%), starting material (8%) and elemental sulfur (25%). In addition, cyclopentene **(71)** was detected by ^{1}H NMR (*ca.* 6%).

The above reaction was repeated in a variety of solvents, varying temperature, time and concentration hoping to maximize the yield of the trapped adduct **(Table 13)**.

Table 13: Summary of S_2 Trapping Experiments of 2,3-Dimethyl-1,3-butadiene (62) with *trans*-2-Chloro-1-(triphenylmethyltrithio)-cyclopentane (75)

R[d]	Solvent	Temp. (°C)	Time (h)	%Yield (A)	%Yield (C)
1 : 3	EtOAc	77	15	17	55
1 : 1	EtOAc	77	15	21	43
3 : 1	EtOAc*	77	15	45	22
3 : 1	EtOAc**	77	15	42	27
5 : 1	EtOAc	77	15	44	25
3 : 1	CH_2Cl_2	36	20	10	60
3 : 1	$CHCl_3$	36	20	14	59
1 : 1	$CHCl_3$	61	20	11	58
3 : 1	$CHCl_3$	61	20	16	55
1 : 1	C_6H_5Cl	132	4	20	48
3 : 1	C_6H_5Cl*	132	4	39	30
3 : 1	C_6H_5Cl**	132	4	37	29

Table 13: continued

R^d	Solvent	Temp. (°C)	Time (h)	%Yield (A)	%Yield (C)
3 : 1	C_6H_5Cl	132	12	39	29
5 : 1	C_6H_5Cl	132	4	40	27

R^d refers to the molar ratio of *trans*-2-chloro-1-(triphenylmethyltrithio)-cyclopentane **(75)** to 2,3-dimethyl-1,3-butadiene **(62)**.

A refers to the cyclic tetrasulfide adduct **64**.

C refers to the di[(2-chloro)-1-cyclopentyl] tetrasulfide **(78)**.

* 50 mL of the solvent was used.

** 15 mL of the solvent was used.

It is noteworthy to mention that, an independent experiment showed that only about 40% of the theoretical amounts of chlorotriphenylmethane emerges from silica gel chromatography; the trityl group is likely retained by reaction with siloxy functions in the silica gel. By eluting with methanol the chlorotriphenylmethane was obtained (*ca.* 54%) in the form of triphenylmethanecarbinol.

Low yield of triphenylmethanethiol and elemental sulfur was 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 amounts were detected. We had to use a column with this a particular eluent (10-20% chloroform in hexane), since it was the only one which 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 14**. The carbon atoms were identified using the following numbering system.

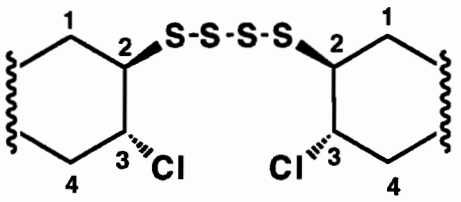


Table 14: Assignments of Relevant ^{13}C Chemical Shifts for the Acyclic Tetrasulfide Adducts

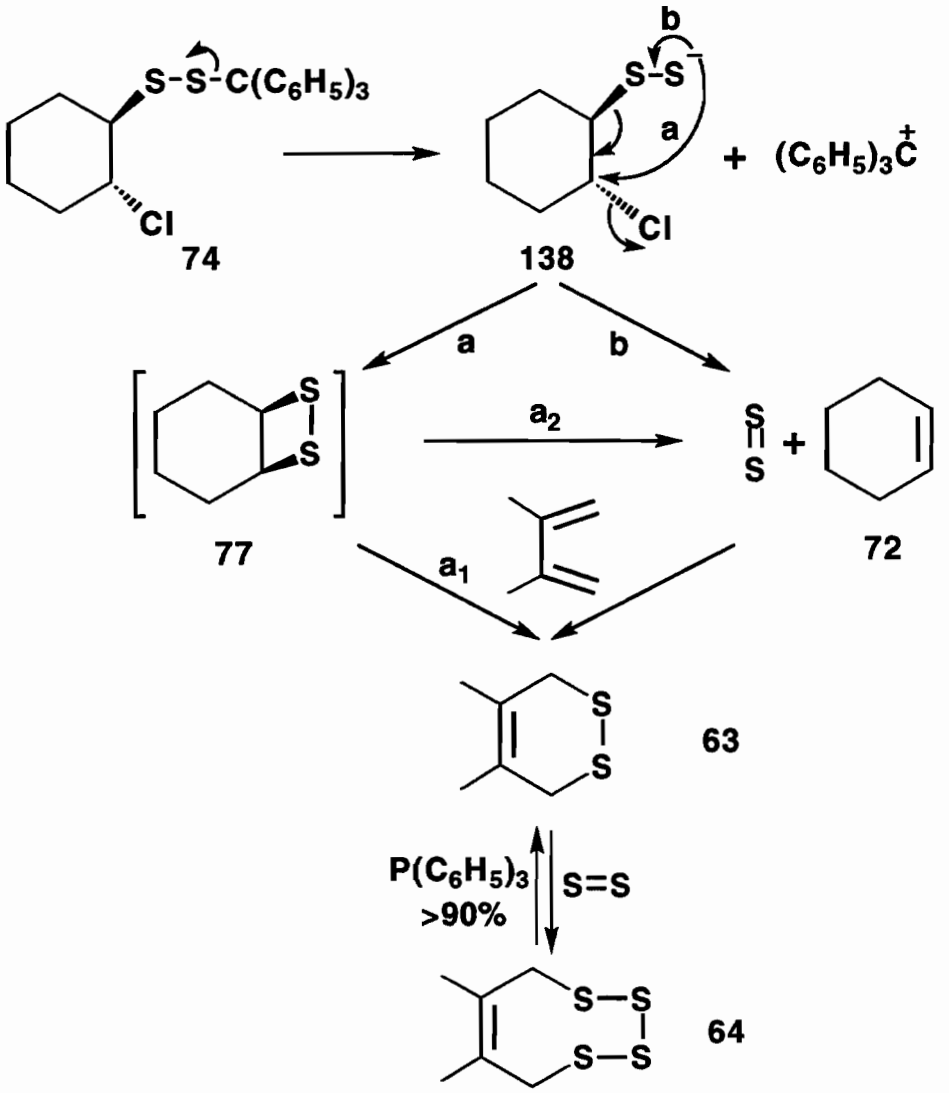
Entry	C1	C2	C3	C4
78	30.22	59.59	65.35	34.79
79	30.60	56.99	61.71	35.07
139	43.61	62.59	66.75	44.75
140	30.61	61.55	64.96	34.48

Recently, we reported[64] that stable 1,2-addition products **68** and **69** were formed when the reaction of triphenylmethanesulfenyl chloride **65** (or its thio **61** and dithio **70** homolog) were treated with bicyclo[2.2.1]heptene (**66**) and bicyclo[2.2.2]octene (**67**). While diatomic sulfur transfers took place from them to a diene acceptor **62**, the yield of final products was quite low.

In contrast, the addition products (**73**, **74** from **61**; **75** and **76** from **70**) are effective in transferring two sulfur units to a diene trap. When di- and trithio adducts **73-76** were each heated in the presence of 2,3-dimethyl-1,3-butadiene (**62**) in a variety of solvents, varying temperature, time and concentration, trapped tetrasulfide adduct 1,2,3,4-

tetrathia-6,7-dimethyl-6-cyclooctene **(64)** was isolated in good overall yield **(Table 10-13)**.

In the case of dithio reagent **74**, two decomposition avenues are possible **(Scheme 40)**.

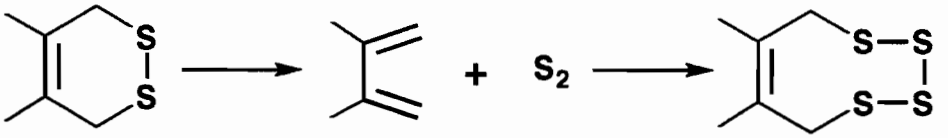


SCHEME 40

Dithietane intermediate **77** **(Scheme 40, path a)** either directly transfers its two sulfur atoms to the diene trap to form **63** **(Scheme 40, path a_1)** or undergoes a cycloreversion to cyclohexene and $^1S_2$ which is then trapped **(Scheme 40, path a_2)**. Conversely, intermediate **138** could fragment directly to deliver $^1S_2$ which is then trapped **(Scheme 40, path b)**.

In addition, we find cyclohexene (**72**) in the crude mixture; it is difficult to rationalize the presence of this molecule except by the decomposition of dithietane intermediate **77** or by a concerted expulsion of $^1S_2$ from intermediate **138** (**Scheme 40**). A second capture of a two sulfur unit apparently takes place which results in cyclic tetrasulfide adduct **64** as the major product.

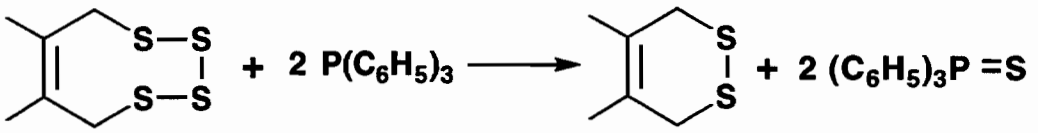
Using an excess amount of precursors **73-76** (which deliver diatomic sulfur) would account for the production of tetrasulfide adduct **64** from disulfide **63**. In addition, preliminary experiments in our lab[63] have shown that disulfide adduct **63** is slowly converted to tetrasulfide **64** by heating in certain solvents. It is also clear that cyclic disulfide **63** can undergo cycloreversion to diatomic sulfur and 2,3-dimethyl-1,3-butadiene (**62**) which, in turn, forms some Diels-Alder addition products like **64** (**Scheme 41**).



63 **62** **64**

SCHEME 41

We found that, cyclic tetrasulfide 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene (**64**) can be converted quantitatively to a disulfide adduct 1,2-dithia-4,5-dimethyl-4-cyclohexene (**63**) by an *in situ* treatment with triphenylphosphine (**141**) (**Scheme 42**).



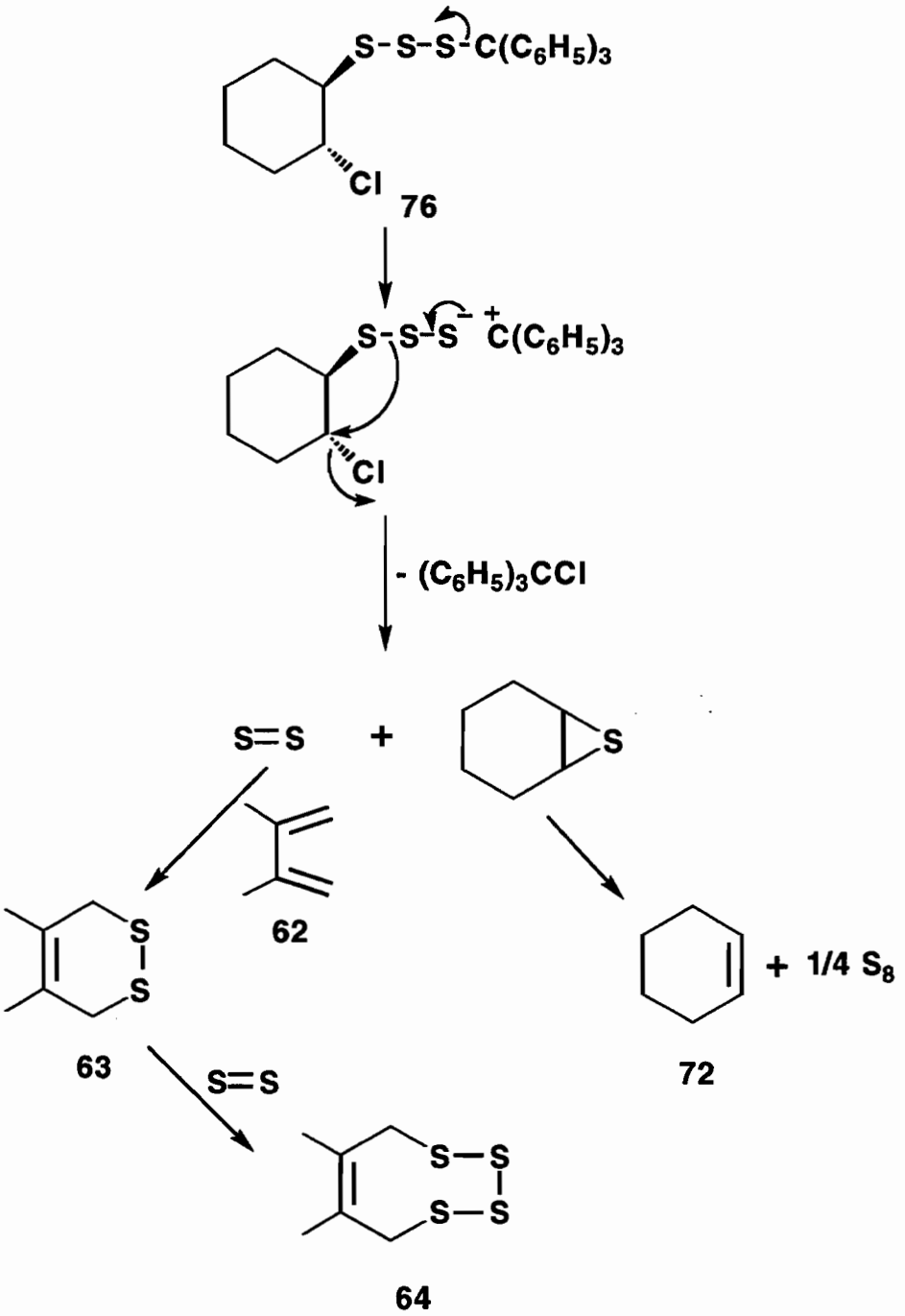
64 **141** **63**

SCHEME 42

As a result, this methodology serves to transfer a two sulfur unit to a diene in over 50% isolated yield.

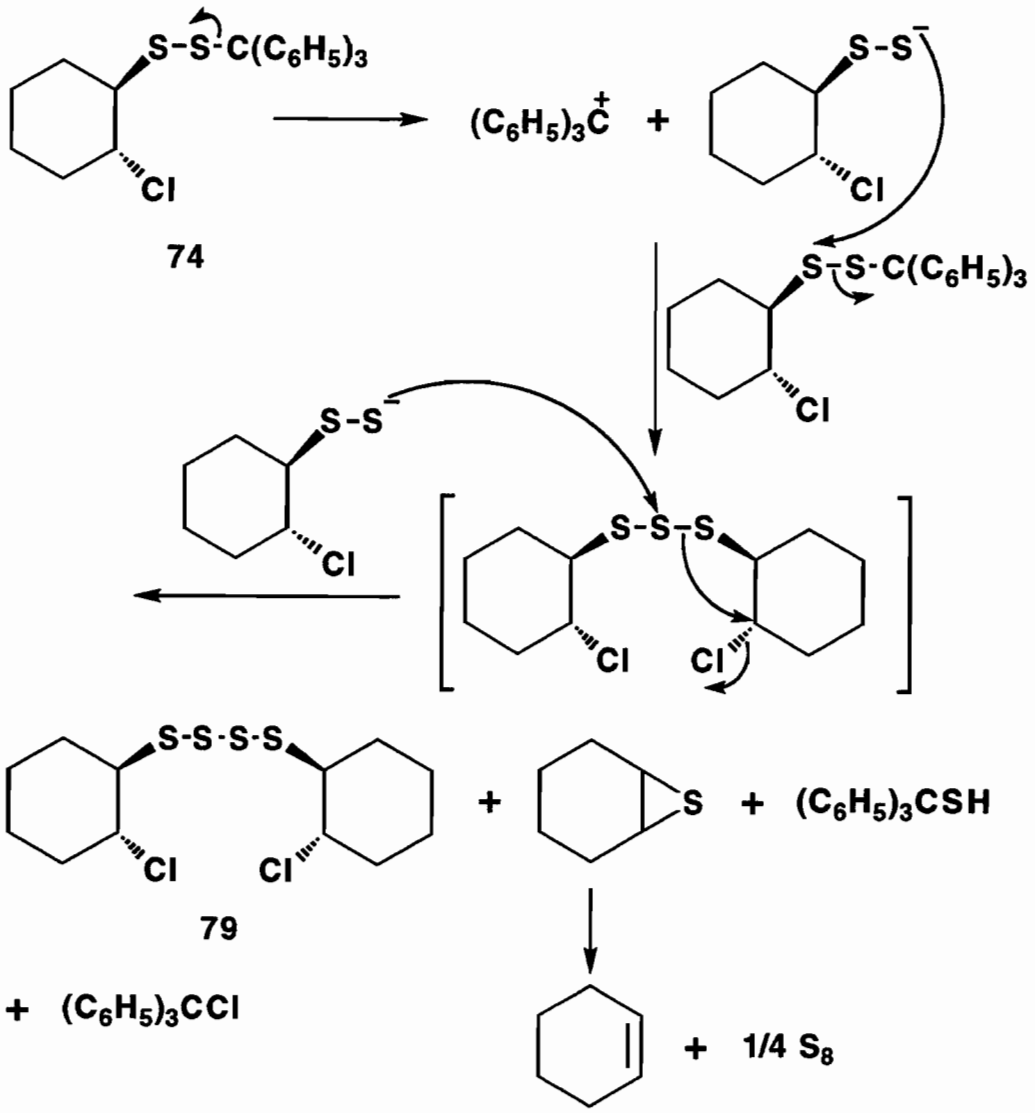
The most probable mechanism for the formation of cyclic tetrasulfide 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene (**64**) from the thermal decomposition of dithio reagent **74** in the presence of 2,3-dimethyl-1,3-butadiene (**62**) is shown in **Scheme 40** above.

The most probable mechanism for the formation of cyclic tetrasulfide 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene **(64)** from the thermal decomposition of trithio reagent **76** in the presence of 2,3-dimethyl-1,3-butadiene **(62)** is shown in **Scheme 43**.



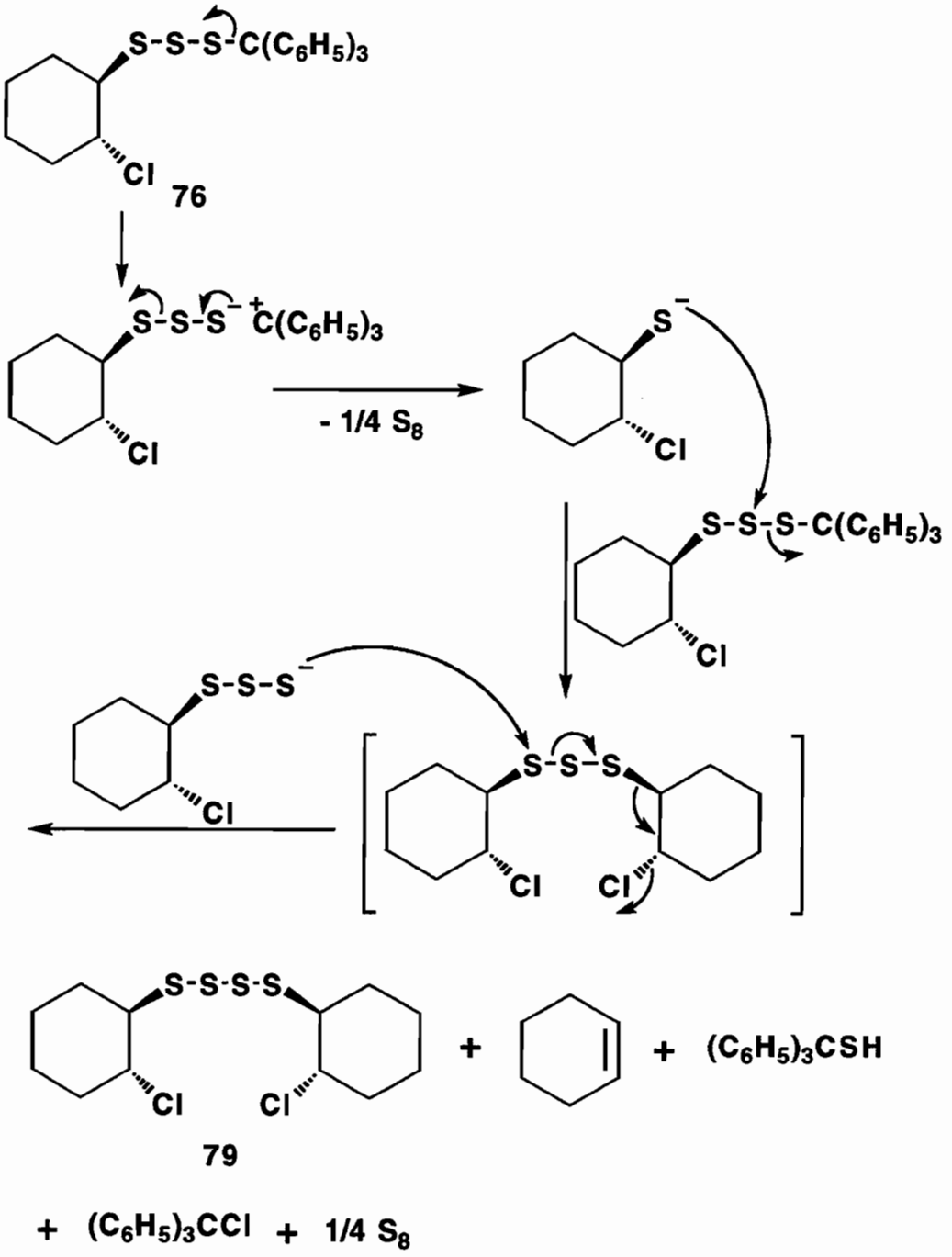
SCHEME 43

The most probable mechanism for the formation of di[(2-chloro)-1-cyclohexyl] tetrasulfide (**79**) from the thermal decomposition of dithio reagent **74** is shown in **Scheme 44.**



SCHEME 44

The most probable pathway explaining the formation of di[(2-chloro)-1-cyclohexyl] tetrasulfide **(79)** from the thermal decomposition of trithio reagent **76** is shown in **Scheme 45.**



SCHEME 45

CHAPTER 4

THIIRANES

INTRODUCTION AND METHODS OF PREPARATION

4.1 INTRODUCTION

Although thiiranes and oxiranes have similar structures and their corresponding hetero atoms, sulfur and oxygen, are in the same family in the periodic table, the chemistry of thiiranes is much less studied. This lacking is attributed to several reasons. First, they are not easily available, are often unstable and the low molecular weight representatives have characteristic unpleasant odors. As compared to the chemistry of oxiranes, thiiranes have a greater tendency to undergo spontaneous polymerization and they are less convenient to store. Also, contrary to the deoxygenation of oxiranes, desulfurization of thiranes is a well-studied reaction. Sometimes they show more effective biological activity than oxiranes and can be used in the synthesis of carbohydrates and other biologically active substances.[127]

4.2 METHODS OF PREPARATION

The classical methods of synthesis of thiiranes[128] form the basis of the known chemistry of this class. Here, we will present some novel methods for the synthesis of thiiranes in which the classical methods are modified in order to improve the range of

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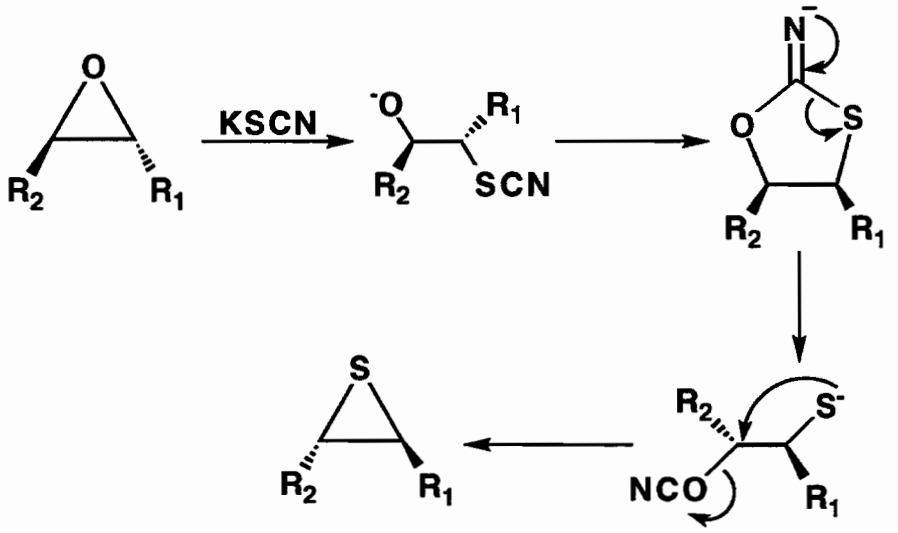
127 D. Miljkovic, M. Popsavin, N. Vukojevic and N. A. Hughes, *J. Carbohydr. Res.*, **9**, 215 (1990).

128 A. V. Fokin and A. F. Kolomiets, Khimiya Tiiranov, "The Chemistry of Thiiranes", Izd. Nauka, Moscow, 1978, P. 343.

reagents used and to improve yields. It has been possible with the discovery of new sulfurating agents to design new non-traditional methods of synthesis.

4.2.1 FROM ALKENE OXIDES (OXIRANES)

A method which is frequently encountered to prepare thiiranes is the reaction of oxiranes with thiourea or alkali metal thiocyanates.[129] The adopted mechanism with thiocyanate involves a nucleophilic attack by the latter resulting in a C-O bond cleavage intermediate, followed by an intramolecular S to O cyano migration and ring closure **(Scheme 46)**.[130]

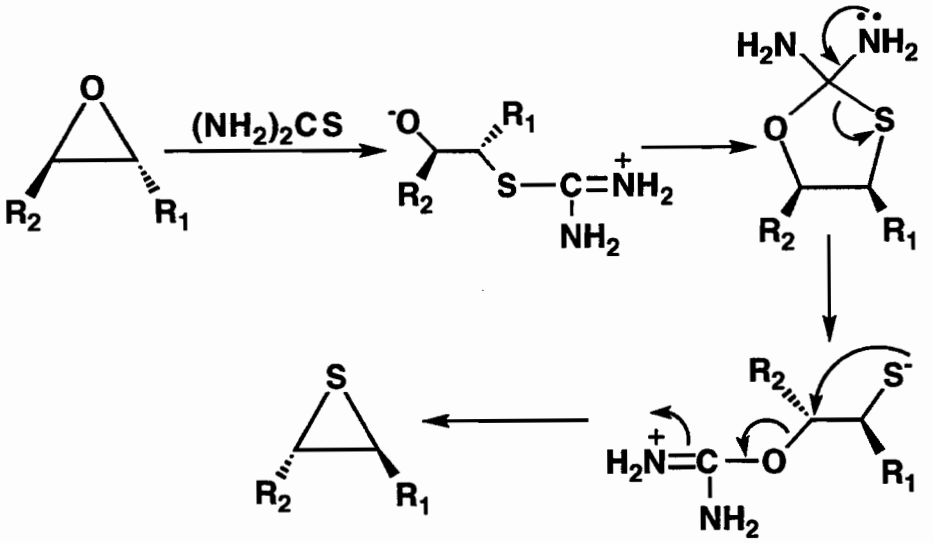


SCHEME 46

129 S. Searles, E. F. Lutz, H. R. Hays and H. E. Mortensen, *Org. Synth.*, **42**, 59 (1962).

130 a) M. G. Ettlinger, *J. Am. Chem. Soc.*, **72**, 4792 (1950); b) E. E. van Tamelen, *J. Am. Chem. Soc.*, **73**, 3444 (1951); c) C. C. Price and P. F. Kirk, *J. Am. Chem. Soc.*, **75**, 2396 (1953).

A similar reaction mechanism has been proposed for the reaction with thiourea **(Scheme 47)**.[130]



SCHEME 47

The stereochemistry is preserved and an optically active (R,R)-oxirane gives an optically active (S,S)-thiirane. Tri- and tetrasubstituted oxiranes generally are not satisfactory substrates and if the substituents are electron-withdrawing, the reaction is slow. Moreover, electron-withdrawing substituents promote the decomposition of thiiranes to alkenes.[131] A number of new thiiranes with a variety of substituents have thus been obtained which were previously unavailable.[132,133] In the presence of trivalent

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131 a) T. C. Owen, C. L. Gladys and L. Field, *J. Chem. Soc., Chem. Commun.*, 501 (1962); b) C. C. Tung and A. J. Speziale, *J. Org. Chem.*, **29**, 1577 (1964).

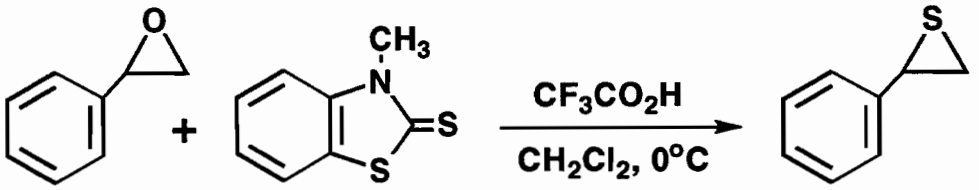
132 S. Boehm, A. Marbold and H. H. Greve, *Eur. Pat.* 455,076; *Chem. Abstr.*, **116**, 257184t (1991).

133 a) H. Plenkiewicz and W. Dmowski, *J. Fluorine Chem.*, **51**, 43 (1991); b) R. Gauthier, M. Bertkowski, H. G. Countant and B. Chabert, *Sulfur Lett.*, **12**, 19 (1990); c) R. L. Pederson, K. K. C. Liu, L. F. Rutan, L. Chen and C. H. Wong, *J. Org. Chem.*, **55**, 4897 (1990); d) H. Bouda, M. E. Borredon, M. Delmas and A. Gaset, *Synth. Commun.*, **17**, 943 (1987); e) B. Rajanikanth and B. Ravindranath, *Ind. J. Chem.*, **23B**, 879 (1984); f) M. P. Schneider and M. Schnaithmann, *J. Am. Chem. Soc.*, **101**, 254 (1979).

phosphorus, extrusion of sulfur is efficient, even for alkyl derivatives. This sequence allows the synthesis of highly substituted alkenes.[134]

The acid catalyzed reaction of oxiranes with triphenylphosphine sulfide[135] gives thiiranes with retention of configuration unlike the reactions with thiourea and thiocyanate.[130]

A silyl thiirane can be prepared by the reaction of the corresponding oxirane with 3-methylbenzothiazole-2-thione.[136] Another way to prepare thiirane is through 3-methyl-benzothiazole-2-thione **(142)** in the presence of an acid which quantitatively converts oxirane **143** to thiirane **144 (Scheme 48)**.[137]



143 **142** **144**

SCHEME 48

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134 a) D. H. R. Barton, F. S. Guziek Jr. and I. Shahak, *J. Chem. Soc., Perkin Trans. 1,* 1794 (1974); b) J. M. Beiner, D. Lecadet, D. Paquer and A. Thuillier, *Bull. Soc. Chim. Fr.*, 1983 (1973); c) J. M. Beiner, D. Lecadet, D. Paquer, A. Thuillier and J. Vialle, *ibid.*, 1979 (1973); d) D. H. R. Barton and B. J. Willis, *J. Chem. Soc., Perkin Trans. 1,* 305 (1972); e) C. E. Diebert, *J. Org. Chem.*, **35**, 1500 (1970).

135 a) T. H. Chan and J. R. Finkenbine, *J. Am. Chem. Soc.*, **94**, 2880 (1972); b) T. H. Chan and J. R. Finkenbine, *Int. J. Sulfur. Chem.*, **8**, 45 (1973); c) W. E. Childers and C. H. Robinson, *J. Chem. Soc., Chem. Commun.*, 320 (1987); d) G. Manuel, A. Faucher and P. Mazerolles, *J. Organomet. Chem.*, **327**, C25 (1991).

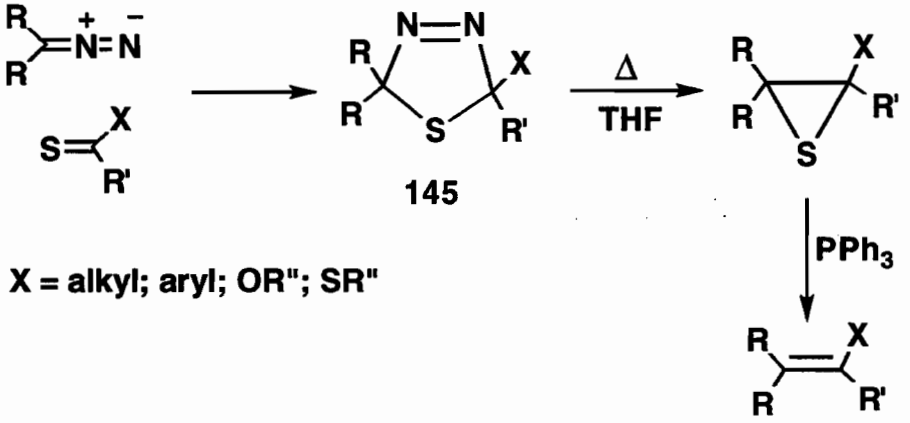
136 G. Barberi, *J. Organomet. Chem.*, **117**, 157 (1976).

137 a) V. Calo, L. Lopez, L. Marchese and G. Pesce, *J. Chem. Soc., Chem. Commun.*, 621 (1975); b) R. C. Cambie, G. D. Mayer, P. S. Rutledge and P. D. Woodgate, *J. Chem. Soc., Perkin Trans. 1*, 52 (1981).

The corresponding perhydrobenzothiazole-2-thione derivative has also been used.[137b] It is worth mentioning that, N,N-dimethylthioformamide[138] is one of the most effective new thiono compounds which can be used for the preparation of thiiranes. Mercaptobenzothiozole[139] and 5-mercapto-1-phenyltetrazole[140] are also effective.

4.2.2 FROM CONDENSATION OF DIAZO COMPOUNDS

This procedure is one of the oldest methods by which it is possible to obtain thiiranes as stable compounds. In the period 1916-1920, Staudinger and coworkers[141] reported the formation of thiiranes in the reaction between diazoalkanes and aromatic thioketones, thiophosgene, and thiobenzoyl chloride. An unstable thiazoline **145** was postulated as an intermediate which is converted to the thiirane after the evolution of nitrogen ceases (**Scheme 49**).[134]



SCHEME 49

The initial formation of a carbene is common in these reactions. In fact, this method has been used with a wide range of both diazo reagents and thioketones to give

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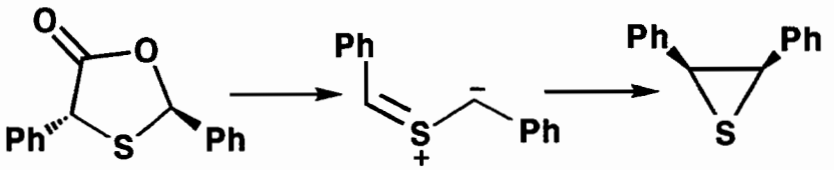
138 a) T. Takido, Y. Kobayashi and K. Itabashi, *Synthesis*, 779 (1986); b) M. S. F. L. K. Jie and Y. F. Zheng, *Synthesis*, 467 (1988).

139 V. Calo, L. Lopez and G. Pesce, *Gazz. Chim. Ital.*, **109**, 703 (1979).

140 E. Lippmann, D. Reifegerste and E. Kleinpeter, *Z. Chem.*, **17**, 60 (1977).

141 a) H. Staudinger and F. Pfenninger, *Chem. Ber.*, **49**, 1941 (1916); b) H. Staudinger and J. Siegwart, *Helv. Chim. Acta.*, **3**, 833; 840 (1920).

many different thiiranes.[142,143] Thiocarbonyl ylides are important as intermediates in the preparation of thiiranes by thermal extrusion methods from heterocyclic precursors.[144] This process is illustrated by the flash vaccum pyrolysis of *trans*-2,4-diphenyl-1,3-oxathiolan-5-one (**146**) to *cis*-stilbene sulfide (**147**); an intermediate ylide **148** undergoes controtatory ring closure (**Scheme 50**).[145]



146 **148** **147**

SCHEME 50

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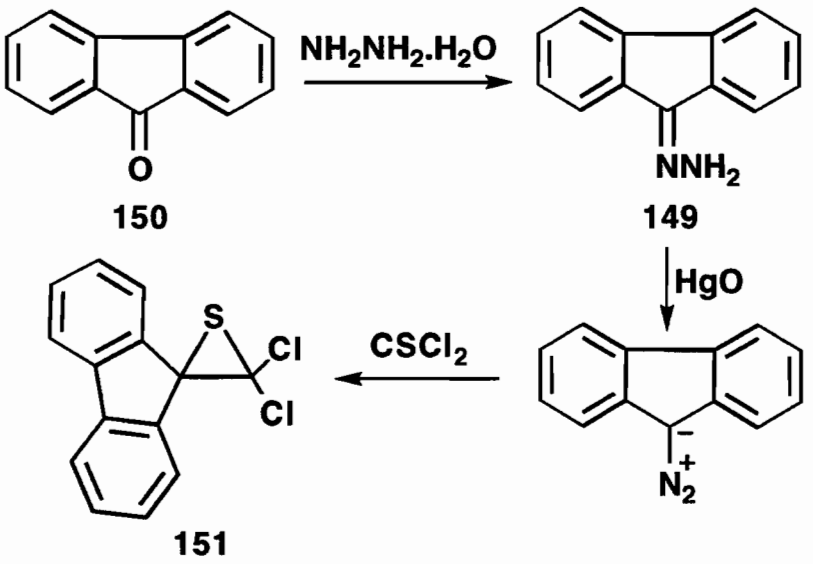
142 a) M. Tashiro, S. Makata and S. Ischi, *Heterocycles*, **12**, 184 (1979); b) M. S. Raasch, *J. Org. Chem.*, **44**, 632 (1979); c) G. L'abbe, J. P. Dekerk, C. Martens and S. Toppet, *J. Org. Chem.*, **45**, 4366 (1980); d) E. Schaumann, H. Behr, G. Adwidjaja, A.Tangerman, B. H. M. Lammerink and B. Zwanenburg, *Tetrahedron*, **37**, 219 (1981); e) G. Barbaro, A. Battaglia, P. Giorgianni, G. Maccagnani, D. Maciantelli, B. F. Bonini, G. Mazzanti and P. Zani, *J. Chem. Soc., Perkin Trans. 1*, 381 (1986); f) T. Furuhata and W. Ando, *Tetrahedron Lett.*, **28**, 1179 (1987); g) N. Tokitoh, H. Hayakawa and W. Ando, *Tetrahedron Lett.*, **29**, 5161 (1988); h) N. Tokitoh, T. Suzuki and W. Ando, *Tetrahedron Lett.*, **30**, 4271 (1989); i) K. Rall and W. Sundermeyer, *J. Fluorine Chem.*, **47**, 121 (1990); j) B. L. Feringa, W. F. Jager and B. de Lange, *Tetrahedron Lett.*, **33**, 2887 (1992).

143 a) R. Huisgen and G. Mloston, *Tetrahedron Lett.*, **26**, 1049 (1985); b) R. Huisgen, and G. Mloston and C. Fulka, *Heterocycles*, **23**, 2207 (1985); c) R. Huisgen and E. Langhals, *Tetrahedron Lett.*, **30**, 5369 (1989); d) R. Huisgen and G. Mloston, *Tetrahedron Lett.*, **30**, 7041 (1989); e) G. Mloston and R. Huisgen, *Tetrahedron Lett.*, **30**, 7045 (1989); f) R. Huisgen and G. Mloston, *Heterocyles*, **30**, 737 (1990); g) R. Huisgen and E. Langhals, *J. Org. Chem.*, **55**, 1412 (1990); h) R. Huisgen, J. Penelle, G. Mloston, A. B. Padias and H. K. Hall Jr., *J. Am. Chem. Soc.*, **114**, 266 (1992).

144 R. M. Kellogg, *Tetrahedron*, **32**, 2165 (1976).

145 T. B. Cameron and H. W. Pinnick, *J. Am. Chem. Soc.*, **102**, 744 (1980).

Grignard reagents and phenyltrihalomethylmercury compounds[146] have been used as a source of carbene to prepare thiiranes. Moreover, phenyliodonium bis(phenylsulphonyl)methylide, which is a carbene precursor, has been used with thioketones to prepare thiiranes.[147] Most recently, Harpp and coworkers[23a] reported that activated diazo compounds **149** generated from fluorenone **150**, react with thiophosgene ($CSCl_2$) to give the corresponding thiirane **151 (Scheme 51)**. In addition, they presented a synthesis of novel derivatives of thiirane **151**.[23a]



SCHEME 51

4.2.3 FROM CARBONYL COMPOUNDS

Thiiranes can be prepared by condensation of carbonyl compounds with certain sulfur-stabilized carbanions.[148] As an example, the lithiated xanthate **152** reacts with heptanal to give thiirane **153** *via* adduct **154 (Scheme 52)**.

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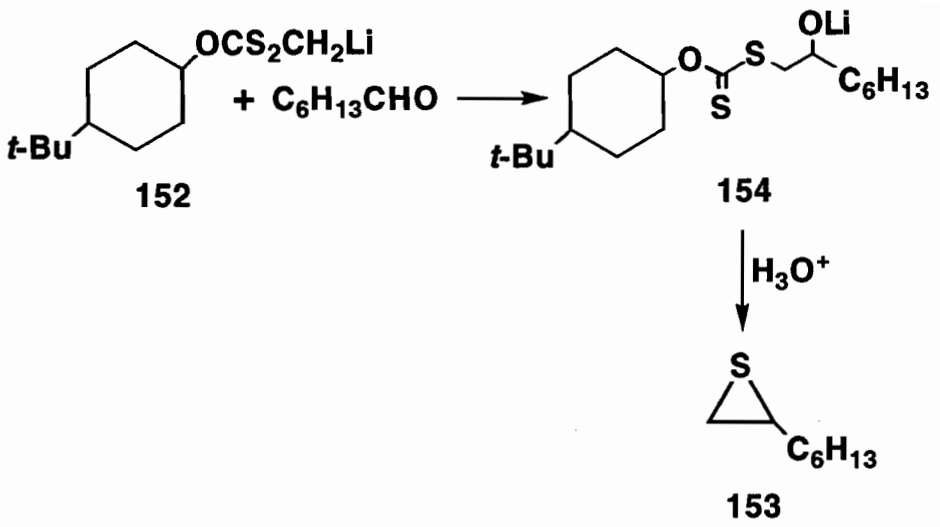
146 D. Seyferth, W. Tronich, R. S. Marmor and W. E. Smith, *J. Org. Chem.*, **37**, 1537 (1972).

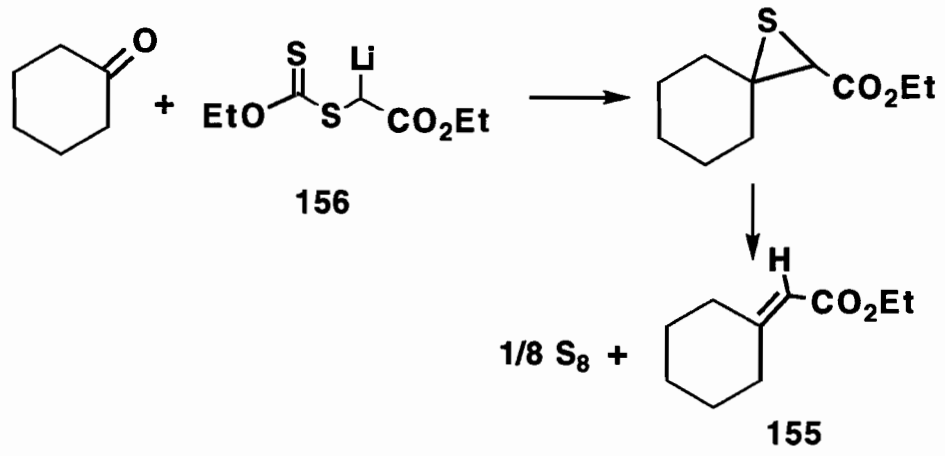
147 L. Hatjiarapoglou and A. Varvoglis, *J. Chem. Soc., Perkin Trans. 1*, 379 (1989).

148 a) C. R. Johnson, A. Nakanishi, N. Nakanishi and K. Tanaka, *Tetrahedron Lett.*, 2865 (1975); b) A. I. Meyers and E. D. Mihelich, *Angew. Chem., Int. Ed. Engl.*, **15**, 270 (1976); c) A. I. Meyers, M. E. Ford, *J. Org. Chem.*, **41**, 1735 (1976); d) D. Hoppe and R. Follmann, *Angew. Chem., Int. Ed. Engl.*, **89**, 478 (1977).



SCHEME 52

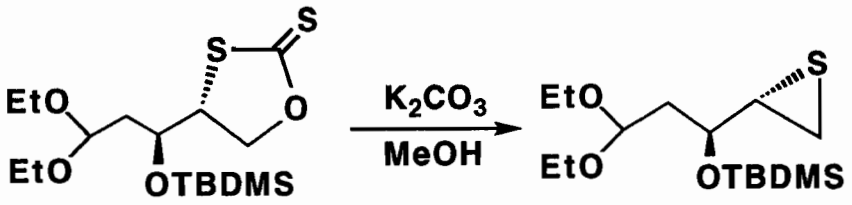
The transformation from **154** to **153** involves migration of a thiono ester fragment from sulfur to oxygen. This method is of limited value for thiirane synthesis because lithiation is difficult unless the starting materials $\mathbf{XSCH_2R}$ has $\mathbf{R = H, C_6H_5}$ or $\mathbf{CH{=}CH_2}$ (**X** = thiono ester, thiazol, etc.). As mentioned earlier, thiiranes having electron-withdrawing substituents are unstable and tend to lose sulfur spontaneously. The result is a synthesis of α,β-unsaturated compounds **155** starting from lithiated xanthates **156 (Scheme 53)**.[149]



SCHEME 53

149 K. Tanaka, N. Yamagishi, R. Tanikaga and A. Kaji, *Bull. Chem. Soc. Jpn.*, **52**, 3619 (1979).

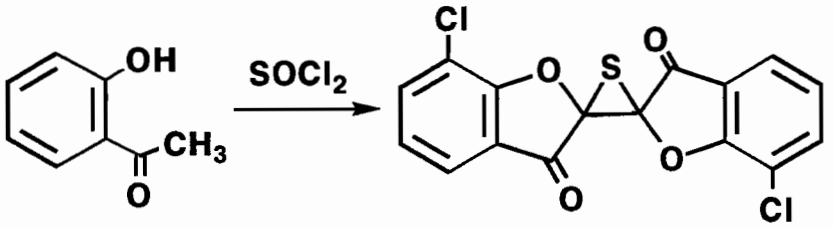
When a cyclic xanthate **157** is treated with potassium carbonate in methanol, it gives thiirane **158** which is then used to prepare 4'-thionucleosides **(Scheme 54)**.[150]



157 **158**

SCHEME 54

In a similar way, sodium carbonate was used to prepare L-methionine analogs bearing an episulfide function which could inhibit the S-adenosyl transferase reaction.[151] An unusual reaction for the preparation of thiirane was reported by Ali and coworkers.[152] They treated 2-hydroxyacetophenone **(159)** with thionyl chloride in pyridine to prepare thiirane **160 (Scheme 55)** .



159 **160**

SCHEME 55

Most recently, Calo and coworkers[153] reported that the carbonyl reduction of diallylated keto sulfide **161** with sodium borohydride in isopropanol afforded directly the corresponding thiirane **162** in a high yield **(Scheme 56)**.

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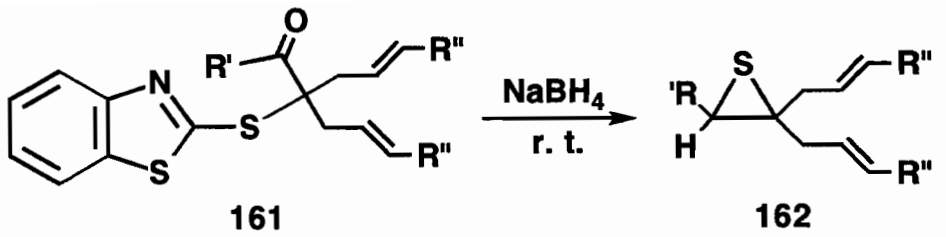
150 J. Uenishi, M. Motoyama, Y. Nishiyama and S. Wakabayashi, *J. Chem. Soc., Chem. Commun.*, 1421 (1991).

151 D. Guillerm and G. Guillerm, *Tetrahedron Lett.*, **33**, 5047 (1992).

152 S. M. Ali, M. Ilyas and S. Tanimoto, *Bull. Chem. Soc. Jpn.*, **61**, 3289 (1988).

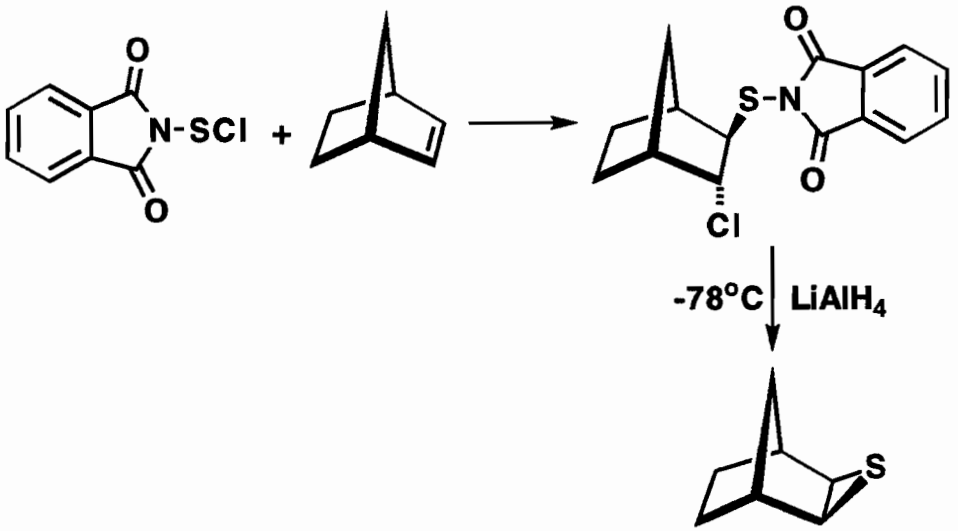
153 V. Calo, V. Fiandanese, A. Nacci and A. Scilimati, *Tetrahedron Lett.*, **36**, 171 (1995).



SCHEME 56

4.2.4 FROM OLEFINS

The use of olefin precursors represents a convenient way to prepare thiiranes by the addition of sulfenyl chlorides to alkenes followed by ring closure (**Scheme 57**).[108-110,154]



SCHEME 57

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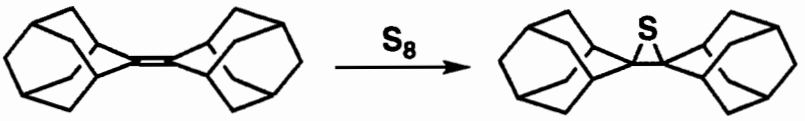
154 a) F. K. Lautenschlaeger and N. V. Schwartz, *J. Org. Chem.*, **34**, 3991 (1969); b) F. K. Lautenschlaeger, *J. Org. Chem.*, **34**, 3998 (1969); c) W. A. Smit, N. S. Zefirov and I. V. Bodrikov, "Organic Sulfur Chemistry", R. K. Freidlina and A. E. Skorova (Eds.), Pergamon Press, 1981, p. 159.

A perfluorinated thiirane was synthesized by chlorination.[155] The use of sodium sulfide with alkenes also yields thiiranes.[156] Another new method was discovered by Zipplies[157] in which N,N-dimethylaniline N-oxide reacted with CS_2 in the presence of alkenes producing thiiranes. The reaction of a hindered thioaldehyde with a Wittig reagent also gives thiirane,[158] and the interaction between SCl_2 and adamantylideneadamantane produces epithio compounds.[159] Recently, Nakayama and coworkers[160] reported that adamantylideneadamantane **(108)** reacts with elemental sulfur to give the corresponding thiirane **116**, however, the yield was low **(Scheme 58)**.



108 **116**

SCHEME 58

In addition to the methods mentioned above, thiiranes have also been synthesized by adding lithium aluminum hydride to 2-chloro disulfides.[161] By the treatment of methyl cysteinate with sodium nitrite in aqueous HCl, thiirane carboxylic acids can be prepared as well.[162] Another method for the preparation of thiiranes is the reaction of dihaloalkanes in the presence of sodium sulfide.[163] Treatment of β-hydroxyethanesulfenyl chlorides with phosphines leads to the formation of thiirane.[164] In addition, vinylthio substituted thiiranes

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155 V. Y. Popkova, L. S. German, S. Szonyi and A. Cambon, *J. Fluorine Chem.*, **46**, 159 (1990).

156 H. Bader, H. Hopf and K. Sieper, *Chem. Ber.*, **122**, 383 (1989).

157 M. F. Zipplies, M. -J. de Vos and T. C. Bruice, *J. Org. Chem.*, **50**, 3228 (1985).

158 E. Vedejs, D. A. Perry and R. Wilde, *J. Am. Chem. Soc.*, **108**, 2985 (1986).

159 G. A. Tolstikov, B. M. Lerman and L. I. Umanskaya, *Tetrahedron Lett.*, **21**, 4189 (1980).

160 J. Nakayama, Y. Ilto and A. Mizumura, *Sulfur Lett.*, **14(6)**, 247 (1992).

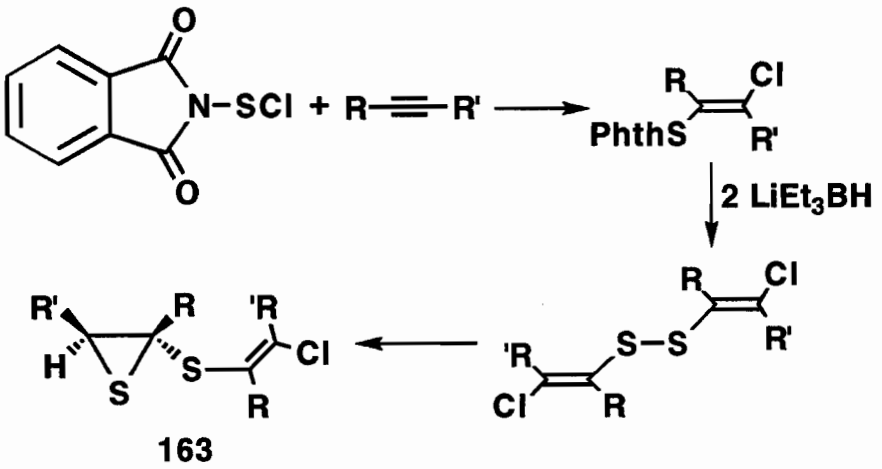
161 M. Hürzeler, B. Bernet and A. Vasella, *Helv. Chim. Acta.*, **75**, 557 (1992).

162 C. D. Maycock and R. J. Stoodley, *J. Chem. Soc., Chem. Commun.*, 234 (1976).

163 S. B. Solway, *U. S. Patent,* 2,694,073 (1954); *Chem. Abstr.*, **49**, 3465 (1955).

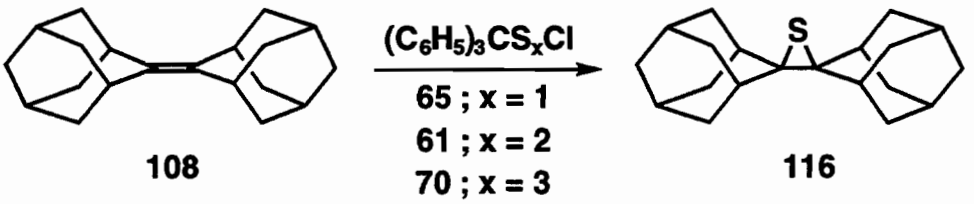
164 J. E. Baldwin and D. P. Hesson, *J. Chem. Soc., Chem. Commun.*, 667 (1976).

163 have been synthesized from sulfenyl chlorides in the presence of alkynes and boron superhydride **(Scheme 59)**[165] (*vide infra* Results and Discussion Section, Chapter 7).



SCHEME 59

Most recently, we reported a new methodology for the synthesis of thiiranes.[166] An equimolar amount of triphenylmethanesulfenyl chloride **(65)** (or analogs thio **61** and dithio **70**) reacts with sterically hindered olefins such as adamantylideneadamantane **(108)**, in methylene chloride solution to give the corresponding thiirane **116** in 92% isolated yield **(Scheme 60)**.



SCHEME 60

Moreover, bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane **(117)** was also produced in a high isolated yield upon the treatment of a sterically hindered olefin

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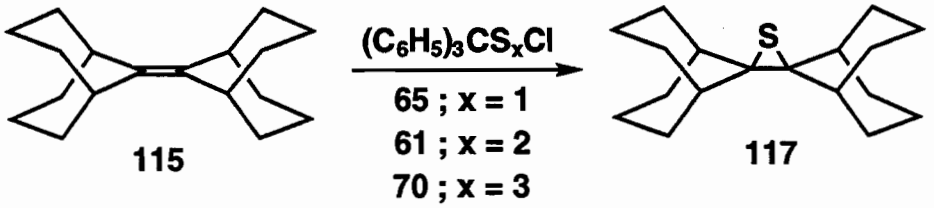
165 G. Capozzi, L. Gori and S. Menichetti, *Tetrahedron*, **47**, 7185 (1991).

166 I. A. Abu-Yousef and D. N. Harpp, *Tetrahedron Lett.*, **36**, 201 (1995).

bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane **(115)** with sulfenyl chlorides **61** or **65**, and **70 (Scheme 61)**.[167]



115 **117**

SCHEME 61

We felt that episulfide adducts **116** and **117** (easily prepared and stable) could serve as precursors to a possible sulfur monoxide **(SO)** transfer reagent.

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167 I. A. Abu-Yousef and D. N. Harpp, "New Sulfenyl Chloride Chemistry. Stable Precursors For Sulfur Monoxide Transfer", *78th Canadian Chemical Conference*, Guelph, Ontario, Canada, June (1995).

CHAPTER 5

SULFUR MONOXIDE

BACKGROUND AND GENERATION

5.1 BACKGROUND

Sulfur monoxide was first detected by Henri and Wolff[168] in 1929. It is isoelectronic with the oxygen molecule and spectral data have shown that sulfur monoxide (SO), like the oxygen molecule, exists in three electronic states: a triplet ground state $^3\Sigma^-$ and two singlet excited states $^1\Delta$ and $^1\Sigma^+$. Because of the great reactivity of sulfur monoxide, very little is known about its chemical reaction, except for some knowledge of its mode of decomposition and its reaction with oxygen atoms, ozone (O_3) and nitrogen monoxide (NO).

The physical properties of sulfur monoxide have been intensively investigated. Like that of O_2 and S_2, the electronic ground state of sulfur monoxide has been found to be a $^3\Sigma^-$ state by ultraviolet (UV)[169] and microwave[170] spectroscopy. Unlike O_2, however, sulfur monoxide is thermodynamically unstable with regard to both its theoretical dissociation into its elements and its actual dissociation into elemental sulfur and sulfur dioxide (SO_2).

Schenk and coworkers[171] prepared sulfur monoxide by different methods; for example by using an electric discharge through a mixture of sulfur vapor,[171a-d] or through

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168 V. Henri and F. Wolff, *J. Chem. Phys. Rad.*, **10**, 81 (1929).

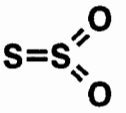
169 A. L. Myerson, F. R. Taylor and P. L. Hanst, *J. Chem. Phys.*, **26**, 1309 (1957).

170 S. Saito, *Tetrahedron Lett.*, **48**, 4961 (1968).

171 a) P. W. Schenk, *Z. anorg. allg. Chem.*, **211**, 150 (1933); b) H. Cordes and P. W. Schenk, *Z. Elcktrochem.*, **39**, 594 (1933); c) H. Cordes and P. W. Schenk,

a mixture of sulfur vapor and sulfur dioxide.[171p,172] It can be, also, prepared by the thermal dissociation of sulfur dioxide,[171e,f] or by incomplete combustion of sulfur at low pressure.[171d] The thermal pyrolysis of thionyl chloride ($SOCl_2$) or thionyl bromide ($SOBr_2$),[171f] or polysulfur oxides[171h] is also a way to generate sulfur monoxide.

However, when Kondrat'ev[173] examined the absorption spectrum of "Schenk's sulfur monoxide" he realized that it was not a spectrum of a diatomic molecule, therefore, Schenk's material was really a dimer that could have a structure shown below.



This was later proposed by Jones.[174]

In 1956, it was asserted by Meschi and Meyers[175] using microwave analysis, that Schenk's material was a mixture of disulfur monoxide (S_2O) and sulfur monoxide. Disulfur monoxide could be isolated from the reaction of thionyl chloride with silver sulfide (Ag_2S) at 160 °C.[176]

Trans. Farady Soc., **30**, 31 (1934); d) H. Platz and P. W. Schenk, *Z. anorg. allg. Chem.*, **215**, 113 (1933); e) H. Platz and P. W. Schenk, *ibid.*, **222**, 177 (1935); f) H. Triebel and P. W. Schenk, *ibid.*, **229**, 305 (1936); g) P. W. Schenk, *ibid.*, **233**, 385 (1937); h) P. W. Schenk, *ibid.*, **248**, 297 (1941); i) P. W. Schenk, *Z. Elecktrochem.*, **47**, 855 (1941); j) P. W. Schenk, *Z. Physik. Chem.*, **51B**, 113 (1942); k) P. W. Schenk, *ibid.*, **52B**, 295 (1942); l) F. Thoma, E. Bohn and P. W. Schenk, *Monatsh. Chem.*, **81**, 907 (1950); m) P. W. Schenk, *Z. anorg. allg. Chem.*, **270**, 301 (1952); n) P. W. Schenk and H. Bloching, *Chem. Ber.*, **92**, 2333 (1959); o) W. Kretschmer and P. W. Schenk, *Angew. Chem., Int. Ed. Engl.*, **1**, 550 (1962); p) H. Halst P. W. Schenk, *Z. anorg. allg. Chem.*, **319**, 337 (1963); q) R. Steudel and P. W. Schenk, *Angew. Chem., Int. Ed. Engl.*, **76**, 93 (1964); r) R. Steudel and P. W. Schenk, *Angew. Chem., Int. Ed. Engl.*, **4**, 402 (1965).

172 D. J. Meschi and R. J. Meyers, *J. Am. Chem. Soc.*, **78**, 6220 (1956).

173 A. Yakovleva and V. Kondrat'ev, *Acta. Physiochim.*, **13**, 241 (1940).

174 A. V. Jones, *J. Chem. Phys.*, **18**, 1263 (1950).

175 D. J. Meschi and R. J. Meyers, *J. Mol. Spectrosc.*, **3**, 405 (1956).

176 L. F. Phillips, J. J. Smith and B. Meyer, *J. Mol. Spectrosc.*, **29**, 230 (1969).

Other workers[169] concluded that the ground state of sulfur monoxide is the $^3\Sigma^-$ state by studying the UV spectrum of sulfur monoxide which resulted from the explosion of carbon disulfide (CS_2) in oxygen at low pressure. After that, Norrish and coworkers[177] studied the absorption spectrum of sulfur monoxide by the flash photolysis of sulfur dioxide. McGrath and McGarvey[178] did so by flash photolysis of a mixture of oxygen and carbon disulfide (CS_2) or dihydrogen sulfide (H_2S) at low pressure. Those authors concluded that there existed 27 bands from 1900 to 2400 Å which constituted the complete spectral analysis of sulfur monoxide. The microwave spectrum was observed from sulfur monoxide generated by the reaction of an oxygen atom with H_2S[179] or sulfur vapor[180] or carbonyl sulfide (COS)[181] at low pressure. The spectrum agrees with the computed spectrum by treating sulfur monoxide as a rigid rotor. A Zeeman splitting[180] in the spectrum confirms the $^3\Sigma^-$ state of sulfur monoxide. Saito[170] has detected the $^3\Sigma^-$ state of sulfur monoxide from the pyrolysis of thiirane 1-oxide **184** by microwave spectroscopy. However, the amount of sulfur monoxide detected was small (31%) and large amounts of disulfur monoxide (24%) and sulfur dioxide (20%) were also detected. The electron paramagnetic resonance (EPR) spectrum of the $^3\Sigma^-$ state has been observed experimentally at low pressure. The sulfur monoxide in the previous experiment was generated by different means: reacting dissociated water with H_2S;[182] subjecting sulfur dioxide to a microwave discharge[183] or oxygen atoms with sulfur[184] and carbonyl sulfide.[185] The EPR

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177 R. C. Norrish and G. A. Oldershaw, *Proc. Roy. Soc. (London)*, **A249**, 498 (1958).

178 a) W. D. McGrath and J. J. McGarvey, *J. Chem. Phys.*, **37**, 1574 (1962); b) W. D. McGrath and J. J. McGarvey, *Proc. Roy. Soc. (London)*, **A278**, 490 (1963).

179 F. X. Powell and D. R. Lide Jr., *J. Chem. Phys.*, **42**, 1413 (1964).

180 M. Winnewisser, K. V. L. N. Sastry, R. L. Cook and W. Gordy, *J. Chem. Phys.*, **41**, 1687 (1964).

181 T. Amano, E. Hirota and Y. Morino, *J. Phys. Soc. Jpn.*, **22**, 399 (1967).

182 a) C. C. McDonald, *J. Chem. Phys.*, **39**, 2587 (1963); b) C. C. McDonald and R. J. Gold, *ibid.*, **69**, 293 (1965).

183 a) J. M. Daniels and P. B. Dorian, *J. Chem. Phys.*, **40**, 1160 (1964); b) J. M. Daniels and P. B. Dorian, *ibid.*, **45**, 26 (1966).

184 H. E. Radford, *J. Chem. Phys.*, **40**, 2732 (1964).

185 a) A. Carrington, D. H. Levy and T. A. Miller, *Trans. Farady Soc.*, **62**, 2994 (1966); b) A. Carrington, D. H. Levy and T. A. Miller, *Proc. Roy. Soc. (London)*,

spectrum of the $^1\Delta$ state of sulfur monoxide was observed by Carrington and coworkers[185] and it arises exclusively from the reaction:[185a]

$$SO\ (^3\Sigma^-) + O_2\ (^1\Delta) \longrightarrow SO\ (^1\Delta) + O_2\ (^3\Sigma^-)$$

Since the $^1\Delta$ state of O_2 lies 23 Kcal/mole above the $^3\Sigma^-$ state of O_2, the $^1\Delta$ state of SO has to be less than 23 Kcal/mole above the $^3\Sigma^-$ state of SO. The following results were also obtained.[185e,f]

	Electric Dipole Moment	SO Bond Distance
$^1\Delta$ SO	1.47 D	1.493 Å
$^3\Sigma^-$ SO	1.55 D	1.484 Å

Mass spectrometry was also used to study sulfur monoxide. Sulfur monoxide was generated by different methods like the decomposition of sulfur dioxide on a hot tungsten filament at low pressure,[186] and the reaction of oxygen atoms with sulfur or carbonyl sulfide.[187] In addition to the sulfur monoxide peak at m/z 48, they reported a peak at m/z 96 which was assigned to $(SO)_2$ and a peak at m/z 98 which was consistent in intensity with a $(SO)_2$ peak at m/z 96 and the naturally occurring $^{32}S/^{34}S$ ratio.[171r] Rapid sampling mass spectrometry[188] was used and the peak at m/z 48 was conclusively shown to be due to SO by isotopic studies using ^{18}O enriched oxygen in the explosion; however, peaks for $(SO)_2$ were not identified in this experiment. Some data were obtained using fast flow techniques with mass spectrometry[189] to study the reaction of oxygen atoms with carbonyl sulfide at low pressure as shown below.

A293, 103 (1966); c) A. Carrington, D. H. Levy and T. A. Miller, *ibid.*, **35**, 340 (1967); d) A. Carrington, D. H. Levy and T. A. Miller, *Mol. Phys.*, **13**, 401 (1967); e) A. Carrington, D. H. Levy and T. A. Miller, *J. Chem. Phys.*, **47**, 3801 (1967); f) A. Carrington, D. H. Levy and T. A. Miller, *ibid.*, **71**, 2 (1967).

186 L. P. Blauchard and P. LeGoff, *Can. J. Chem.*, **35**, 89 (1957).

187 G. liusti, S. Dondes and Harteck, Abstract **401**, Division of Physical Chemistry, American Chemical Society, New York, Sept., 1963.

188 D. G. H. Marsden, *Can. J. Chem.*, **41**, 2607 (1963).

189 J. O. Sullivan and P. Warneck, *Ber. Bunsenges. Phys. Chem.*, **69**, 7 (1965).

	Rate Constant at 0.1 mm Hg & 298 °K
$O + COS \longrightarrow CO + SO$	5.5×10^9 cm^{3}mole^{-1}sec^{-1}
$SO + SO \longrightarrow SO_2 + S$	2.5×10^{12} cm^{3}mole^{-1}sec^{-1}

The reaction of oxygen with carbonyl sulfide was also studied using EPR and mass spectrometry[190] and the following data were obtained:

	Rate Constant at 0.1 mm Hg & 298 °K
$O + COS \longrightarrow CO + SO$	6.8×10^9 cm^{3}mole^{-1}sec^{-1}
$SO + SO \longrightarrow SO_2 + S$	$< 10^{10}$ cm^{3}mole^{-1}sec^{-1}

A peak for $(SO)_2$ could not be seen in this experiment. The same reaction was studied by chemiluminescent techniques[191] and the following data were reported:

	Rate Constant at 5×10^{-3} mm Hg & 298 °K
$O + COS \longrightarrow CO + SO$	4.2×10^8 cm^{3}mole^{-1}sec^{-1}
$S + 2O \longrightarrow SO_2 + h\upsilon$	6.0×10^{10} cm^{3}mole^{-1}sec^{-1}

Here, it was concluded that the reaction of sulfur monoxide with oxygen atoms proceeds by a two body radiative association because the intensity of the emitted light was independent of pressure between 0.001 and 0.020 mm Hg. Also, no emission was observed when the concentration of oxygen atoms was equal to or less than the carbonyl sulfide concentrations. Thrush and coworkers[192] studied the after-glow of sulfur dioxide

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190 K. Heyermann, H. G. Wagner and J. Wolfrum, *Ber. Bunsenges. Phys. Chem.*, **71**, 603 (1967).

191 T. R. Rolfers, R. R. Reeves Jr. and P. Harteck, *J. Phys. Chem.*, **69**, 849 (1965).

192 a) M. A. A. Glyne, C. J. Halstead and B. A. Thrush, *Proc. Roy. Soc. (London)*, **A295**, 355 (1966); b) C. J. Halstead and B. A. Thrush, *ibid.*, **A295**, 363 (1966);

with radio frequency or a mild electric discharge. They varied pressures from 0.50 to 2.0 mm Hg using reactive species like NO, NO_2 and O_3 and reported the following:

	Rate Constant at 0.2 mm Hg & 298 °K
$SO + NO_2 \longrightarrow SO_2 + NO$	1.5×10^{12} cm^{3}mole^{-1}sec^{-1}
$SO + O_3 \longrightarrow SO_2 + O_2$	1.1×10^{9} cm^{3}mole^{-1}sec^{-1}
$SO + O \xrightarrow{Ar} SO_2 + h\upsilon$	3.2×10^{17} cm^{3}mole^{-1}sec^{-1}

They obtained an expression for the intensity of the sulfur dioxide after-glow: $I = 1.5 \times 10^8$ [O][SO] cm^{3}mol^{-1}sec^{-1} at a pressure between 0.25 and 3.00 mm Hg.[192b]

The determination[189,190] of the reactivity of sulfur monoxide shows that it is a very short-lived species even when no other reactive molecules are present. This was supported by Evans and coworkers.[193] In addition, Colin[194] studied the after-glow emission obtained by rapid pumping mixtures of oxygen and carbonyl sulfide through a microwave discharge and concluded the following about the electronic states of sulfur monoxide:

State of SO	HOMO	Relative Energy (Kcal. mole^{-1})
$^1\Sigma^+$		29.2
$^1\Delta$		18.6
$^3\Sigma^-$		0

c) C. J. Halstead and B. A. Thrush, *ibid.*, **A295**, 380 (1966); d) A. Mckenzie and B. A. Thrush, *ibid.*, **A308**, 133 (1968).

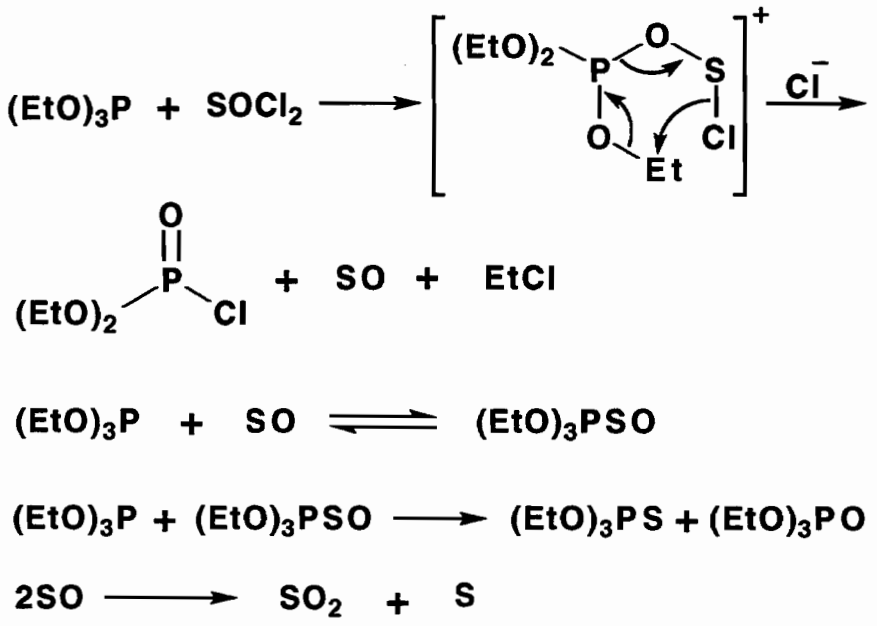
193 E. A. Evans, A. B. Scott and J. L. Huston, *J. Am. Chem. Soc.*, **74**, 5525 (1952).

194 R. Colin, *Can. J. Phys.*, **46**, 1539 (1968).

Theoretically, Moffitt[195] has concluded the same thing on the basis of molecular orbital calculations.

5.2 GENERATION

Sulfur monoxide was postulated as a reaction intermediate in several cases. The reaction of thionyl chloride with dimethyl sulfide,[196] 1,1-diarylethylene,[197] or phenylacetylene[197] yield monochlorodimethyl sulfide, 1,1-diaryl-2-chloroethylene, and 1-phenyl-1,2-dichloro- ethylene, respectively and sulfur monoxide was suggested as a product; however, there was no evidence presented. Sulfur monoxide was speculated to be a primary reaction intermediate in the reaction of trialkylphosphates with thionyl chloride **(Scheme 62)**.[198]



SCHEME 62

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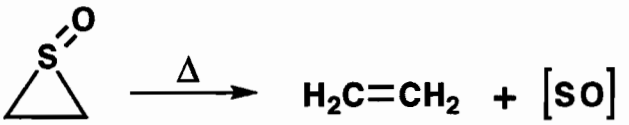
195 W. Moffitt, *Proc. Roy. Soc. (London)*, **A200**, 409 (1950).

196 W. E. Truce, G. H. Birum and E. T. McBee, *J. Am. Chem. Soc.*, **74**, 3594 (1952).

197 S. Patai and F. Bergman, *J. Am. Chem. Soc.*, **72**, 1034 (1950).

198 A. G. Poshkus and J. E. Herweh, *J. Am. Chem. Soc.*, **84**, 555 (1962).

Hartzell and Paige[199] showed that the pyrolysis of thiirane 1-oxides at temperatures over 100 °C yields the corresponding olefins **(Scheme 63)**. Sulfur monoxide was assumed to be a product and the whole process was followed using mass spectrometry.



SCHEME 63

Saito[170] has suggested that sulfur monoxide was generated in the $^3\Sigma^-$ state in this decomposition, but his evidence was not convincing. Maccagnani and coworkers[200] found that in contrast with ethylene episulfoxides and alkyl substituted episulfoxides, the aryl substituted sulfoxides liberate sulfur monoxide at lower temperatures, with respect to ethylene episulfoxide, yielding almost quantitatively and stereospecifically the corresponding olefins. In addition, they[201] demonstrated the transient formation of sulfur monoxide **(Scheme 64)**.

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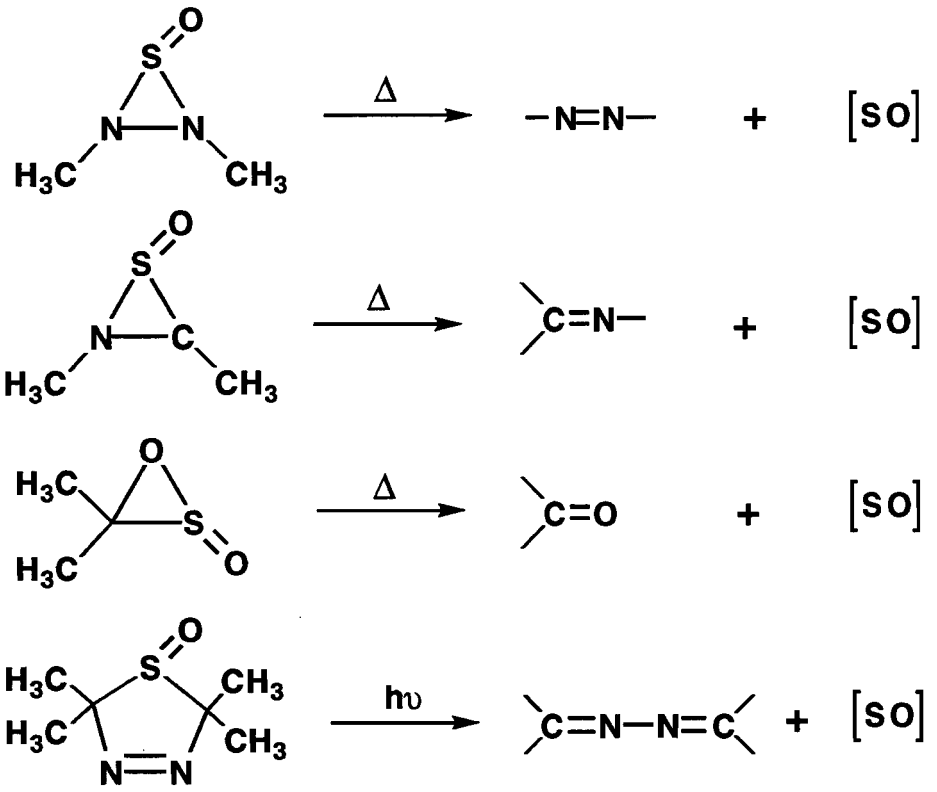
199 a) G. E. Hartzell and J. N. Paige, *J. Am. Chem. Soc.*, **88**, 2616 (1966); b) G. E. Hartzell and J. N. Paige, *J. Org. Chem.*, **32**, 459 (1967).

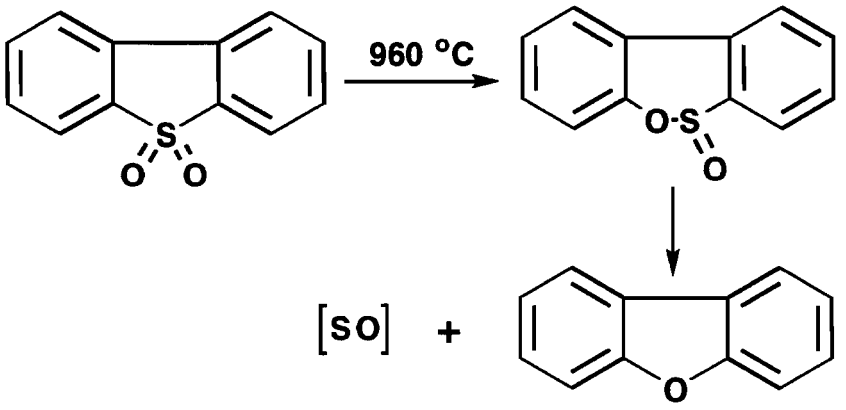
200 a) B. F. Bonini, A. Cappelli, G. Maccagnani and G. Mazzanti, *Gazzatta*, **105**, 827 (1975); b) B. F. Bonini, G. Maccagnani and G. Mazzanti, *J. Chem. Soc., Chem. Commun.*, 431 (1976); c) B. F. Bonini, G. Mazzanti and G. Maccagnani, *Tetrahedron Lett.*, 3585 (1973).

201 L. Benati, G. Deluca, G. Maccagnani and A. Tundo, *J. Chem. Soc., Chem. Commun.*, 702 (1972); b) A. Battaglia, A. Dondoni, G. Maccagnani and G. Mazzanti, *J. Chem. Soc., Perkin Trans. 2*, 609 (1974).



SCHEME 64

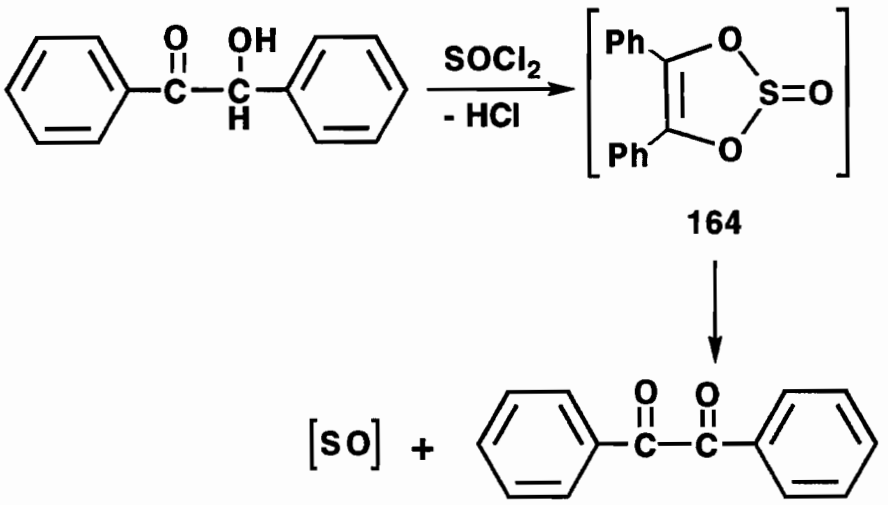
In the pyrolysis of dibenzothiophene 5,5-dioxide resulting in dibenzofuran, a rearrangement with loss of sulfur monoxide was reported (**Scheme 65**).[202]



SCHEME 65

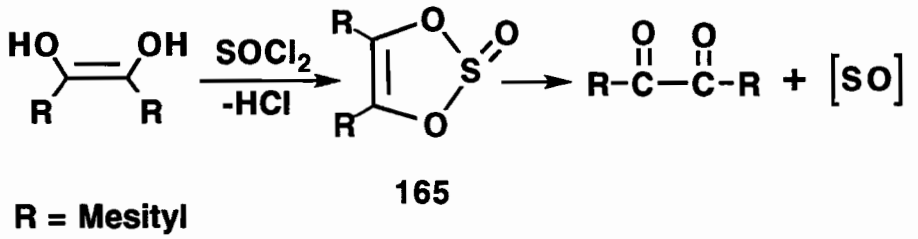
202 E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 2836 (1966).

Also, sulfur monoxide was observed in the roasting of a rare earth sulfide in a nitrogen atmosphere at 300-800 °C.[203] Fieser and Okumura[204] suggested that sulfur monoxide is a product of the reaction of benzoin with thionyl chloride at room temperature giving benzil *via* a cyclic sulfite **164 (Scheme 66)**.



SCHEME 66

Moreover, the closely-related cyclic sulfite **165**[205] has been isolated and found to decompose to give benzil and sulfur monoxide **(Scheme 67)**.



SCHEME 67

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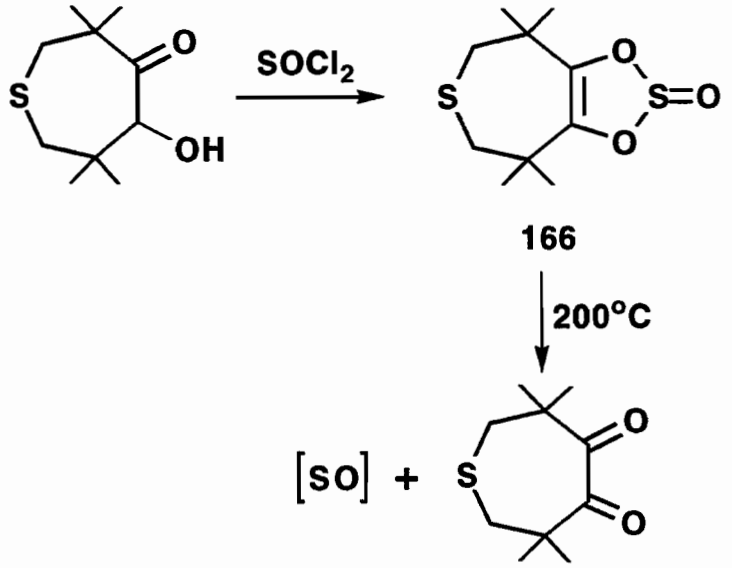
203 C. C. Bisi and A. Clevici, *Gazz. Chim.*, **93**, 1444 (1963).

204 L. F. Fieser and Y. Okumura, *J. Org. Chem.*, **27**, 2247 (1962).

205 Y. Okumura, *J. Org. Chem.*, **28**, 1075 (1963).

DeGroot and coworkers[206] isolated enediol sulfite **166** as a stable solid, subsequently pyrolysis at 200 °C gave the diketone and presumably sulfur monoxide **(Scheme 68)**.



SCHEME 68

In addition, DeJongh and Van Fossen[207] reported that the predominant fragmentation pathway of *o*-phenylene sulfide is the loss of sulfur monoxide on either gas phase pyrolysis or electron-impact. The kinetics of decomposition of trithiol 1-oxide **167** were carefully studied.[208] The generation of sulfur monoxide was postulated and the unstable intermediate dicyano-1,2-dithiete **(168)** led to the formation of dithiin **169 (Scheme 69)**.

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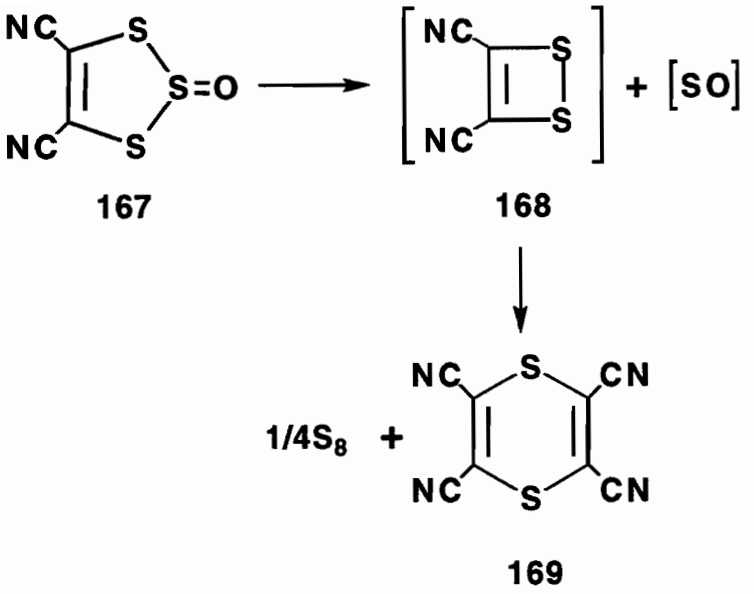
206 A. DeGroot, J. A. Boerma and H. Wynberg, *J. Chem. Soc., Chem. Commun.*, 347 (1968).

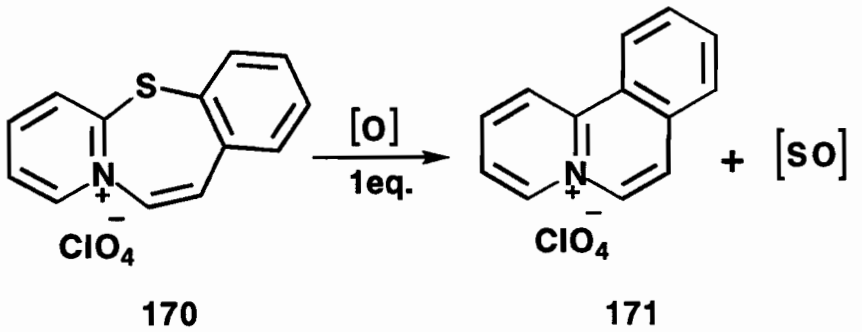
207 D. C. DeJongh and R. Y. Van Fossen, *J. Org. Chem.*, **37**, 1129 (1972).

208 H. E. Simmons, D. C. Blomstrom and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4772 (1962).



SCHEME 69

Oxidation of various thiazepinium salts **170**,[209] with peroxyacetic acid led to the formation of phenanthridizinium salts **171** and sulfur monoxide **(Scheme 70)**.



SCHEME 70

Similarly, Galt and coworkers[210] have also oxidized thiazepin **172** to obtain the oxoacsidin **173** and presumably sulfur monoxide **(Scheme 71)**.

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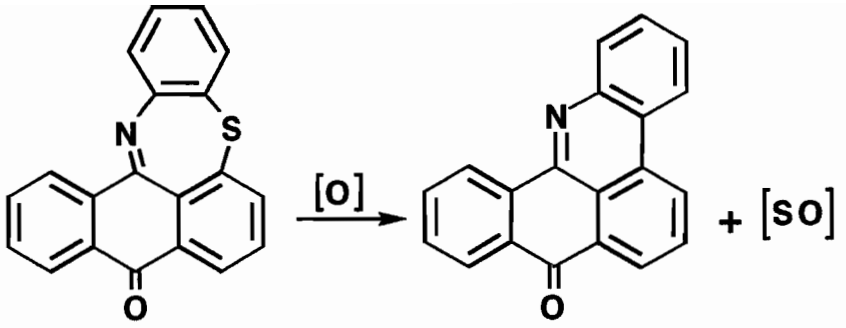
209 a) C. K. Bradsher and J. W. McDonald, *J. Org. Chem.*, **27**, 4475 (1962); b) C. K. Bradsher and J. W. McDonald, *ibid.*, **27**, 4478 (1962); c) C. K. Bradsher and J. W. McDonald, *ibid.*, **27**, 4482 (1962).

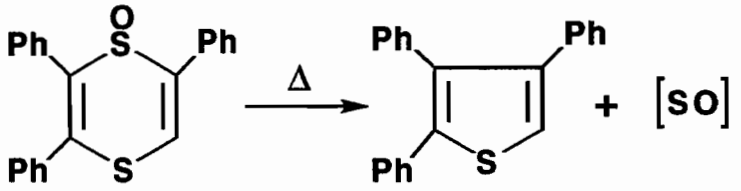
210 R. H. B. Galt, J. D. Loudon and A. D. B. Sloan, *J. Am. Chem. Soc.*, **80**, 1588 (1958).



172 **173**

SCHEME 71

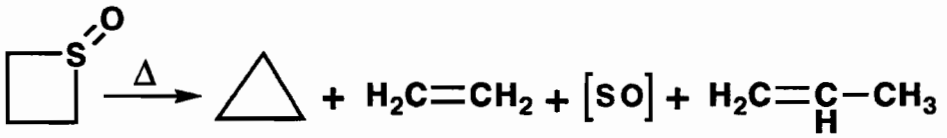
Moreover, the monosulfoxide of 2,3,5-triphenyldithiadiene **174** is unstable at 90 °C in toluene giving 2,3,4-triphenylthiophene and sulfur monoxide **(Scheme 72)**.[211]



174

SCHEME 72

Dorer and Salomon[212] studied the photolysis of trimethylene episulfoxide **175** resulting in formation of ethylene, propylene, cyclopropane and presumably sulfur monoxide **(Scheme 73)**.



175

SCHEME 73

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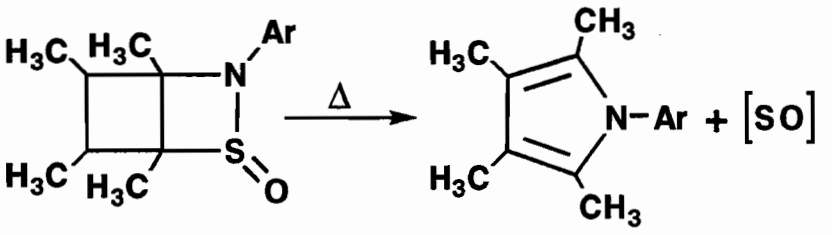
211 H. H. Szmant and L. M. Alfonso, *J. Am. Chem. Soc.*, **79**, 205 (1957).

212 F. H. Dorer and K. E. salomon, *J. Phys. Chem.*, **84**, 3024 (1980).

Sulfinamide **176** is thermally unstable at room temperature and readily loses sulfur monoxide, yielding quantitatively the corresponding pyrole **177 (Scheme 74)**.[213]



176 **177**

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

SCHEME 74

Recently, Glass and Jung[214] reported that thermal decomposition of *cis*- and *trans*-2,3-di(*p*-methoxyphenyl)-2,3-diphenyl thiirane 1-oxide gave the corresponding olefin with moderate stereospecificity and presumably sulfur monoxide. It was also demonstrated[215] rather convincingly that sulfur monoxide is an intermediate species in the dechlorination of thionyl chloride with metals.

In addition, the isolation of simple derivatives of sulfur monoxide was reported in the literature. Meuwsen and Gebhardt[216] isolated a compound which was probably "diethylacetal of sulfur monoxide". Goehring and Messner[217] reported that the material they isolated is the oxime of sulfur monoxide and a compound which is isomeric with it. The isolated compounds are unstable and decompose to a brown material thought to be a polymer. Garcia-Fernandez[218] prepared some inorganic selenium and tellurium compounds

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213 a) H. Hogeveen, R. F. Kingma and D. M. Kok, *J. Org. Chem.*, **47**, 1910 (1982); b) K. S. Fongers, H. Hogeveen and R. F. Kingma, *ibid.*, **48**, 4275 (1983).

214 R. S. Glass and W. Jung, *Sulfur Lett.*, **17**, 183 (1994).

215 a) P. W. Schenk and H. Triebel, *Z. anorg. allg. Chem.*, **229**, 3056 (1956); b) E. Gruner, *ibid.*, **212**, 393 (1933); c) R. A. Hubbard and W. F. Luder, *J. Am. Chem. Soc.*, **73**, 1327 (1951).

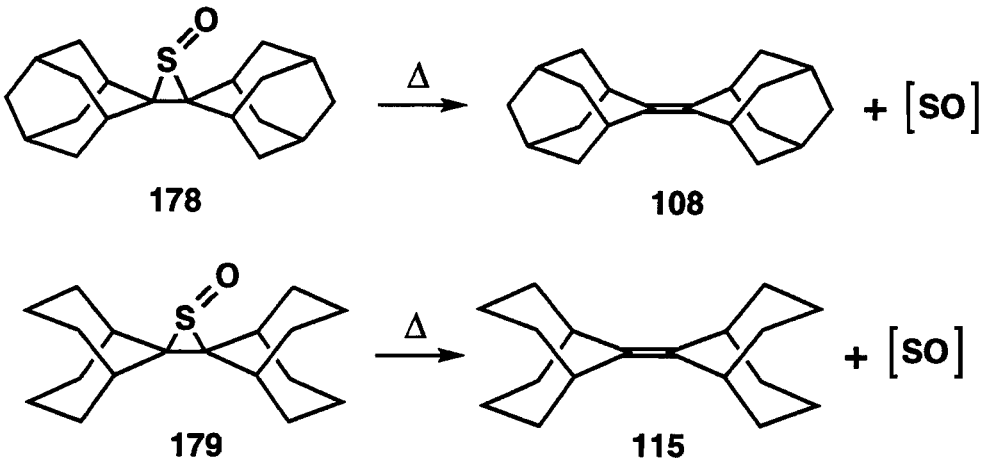
216 A. Meuwsen and H. Gebhardt, *Chem. Ber.*, **69**, 937 (1936).

217 M. Goehring and J. Messner, *Z. anorg. allg. Chem.*, **268**, 47 (1952).

218 H. Garcia-Fernandez, *Compt. Rend.*, **258**, 2579 (1964).

which may contain sulfur monoxide as a ligand (*vide infra* Results and Discussion Section, Chapter 7).

Most recently, we reported that thiirane 1-oxides **178** and **179** derived from adamantylideneadamantane thiirane **(116)**[166] and bicyclo[3.3.1]nonylidenebicyclo-[3.3.1]nonane thiirane **(117)**[167] by the oxidation with *m*-chloroperoxybenzoic acid decomposed completely to the corresponding olefins **108** and **115**, respectively, and sulfur monoxide **(Scheme 75)**.



SCHEME 75

CHAPTER 6

EPISULFOXIDES (THIIRANE 1-OXIDES)

INTRODUCTION

STRUCTURES, SYNTHESIS, REACTIONS AND MECHANISMS

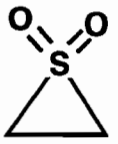
6.1 INTRODUCTION

In general, hetero three-membered ring compounds are highly reactive. This is because these compounds have high molecular strain and consequently, the hetero atom-carbon bond, which has a relatively low bonding energy is easily cleaved.

This principle has been applied to many organic transformations, such as the reactions which extend a carbon chain by the means of an epoxide,[219] synthesis of the compounds which have two functional groups on the β-position using ring-opening of aziridine or episulfides[220] and ring-opening polymerization.[221]

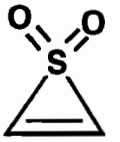
Thiirane 1-oxide (**180**), thiirane 1,1-dioxide (**181**) as well as the unusual compounds thiirene 1-oxide (**182**) and thiirene 1,1-dioxide (**183**) exist.

180



181

182



183

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219 M. S. Kharasch and O. Reinmuth, "Grignard Reagents of Nonmetallic Substances", Prentice-Hall, 1954, p. 961.

220 L. A. Paquette, "Principles of Modern Heterocyclic Chemistry", Benjamin, 1968, p. 25.

221 P. Sigwalt, "Ring-Opening Polymerization", Marcel Dekker, 1969, p. 191.

In these compounds, the oxygen atom is not in the plane of the three-membered ring. Therefore, they show new reactivity which is totally different from that of an epoxide and they are expected to react differently from epoxides.

In these series of compounds, **181** is well-known. It was synthesized by reacting diazo compounds with sulfur dioxide.[222] Later, it received attention as an intermediate of the Ramberg-Bäcklund reaction.[223] Compound **182** was first reported by Carpino.[224] In addition, compound **183** was synthesized by the same group.[225]

Along with this research, the synthesis of compound **180** has been also tried by several groups. However, at the beginning, oxidation could not be stopped at **180** or **181** and only sulfonic acid derivatives[226] or polyethylene sulfone[227] were obtained.

The first synthesis of **180** appeared in a patent in 1955.[228] In 1965, Dittmer and Levy[229] reported the synthesis of dibenzoylstilbene episulfoxide. In the next year, Hartzell and Paige[199a] reported the oxidation of ethylene episulfide by sodium periodate. Since then, these compounds are available.

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222 H. Staudinger and F. Pfenninger, *Chem. Ber.*, **49**, 1941 (1916).

223 L. A. Paquette, *Acc. Chem. Res.*, **1**, 209 (1968).

224 L. A. Carpino and H-W. Chen, *J. Am. Chem. Soc.*, **93**, 786 (1971).

225 L. A. Carpino and L. V. McAdams III, R. H. Rynbrandt and J. W. Spiewak, *J. Am. Chem. Soc.*, **93**, 476 (1971).

226 M. Sander, *Chem Rev.*, **66**, 297 (1966).

227 G. Hesse, E. Reichold and S. Majmudar, *Chem. Ber.*, **90**, 2106 (1957).

228 S. B. Soloway, *U.S. Patent,* 2,694,073, 1954; *Chem. Abstr.*, **49**, 3465 (1955).

229 D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, **30**, 636 (1965).

6.2 STRUCTURES OF EPISULFOXIDES

Ethylene episulfoxide (EESO) has received considerable attention with respect to its characterization because of its simple structure and symmetry. Microwave spectroscopic analysis,[230] NMR, IR and Raman spectra[231] have been reported.

The structural parameters of EESO are shown in **Table 15** with a comparison to dimethyl sulfoxide (DMSO).[232]

Table 15: Molecular Structure of EESO and DMSO

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

230 a) S. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 663 (1969); b) W. F. White and J. E. Wollrab, *Chem. Phys. Lett.*, **3**, 25 (1969).

231 a) R. W. Mitchell, F. A. Hartman and J. A. Merritt, *J. Mol. Spectroscopy*, **32**, 388 (1969); b) M. Ohtsuru, K. Tori, M. Fukuyama, *Tetrahedron Lett.*, 2877 (1970).

232 H. Hreizler and G. Dendl, *Z. Naturforsch.*, **19A**, 512 (1964).

In EESO, the CSC angle is about half of that of DMSO because it is a part of the three-membered ring. The dihedral angle in case of DMSO is 45° and in case of EESO is 67° as shown in **Figure 5**.

DMSO **EESO**

Figure 5: Dihedral Angles of EESO and DMSO

In addition, **Table 16** lists bond lengths and angles for the parent episulfoxide as well as data for its analogs episulfide, oxirane, episulfone, aziridine and phosphorane.

Table 16: Bond Lengths and Bond Angles for the Three-Membered Ring Heterocycles

	X					
	O[233]	NH[234]	P[235]	S[233]	SO[230]	SO_2[236]
C-C	1.472	1.480	1.502	1.492	1.504	1.590
C-X	1.436	1.488	1.807	1.819	1.822	1.731
C-X-C	61°24'	-	47°24'	48°26'	48°26'	54°40'
C-C-X	59°18'	-	66°18'	65°48'	65°48'	62°40'

The sharp difference between the strain energy of cyclopropane and its heteroatom analogs is indicative of the higher degree of stabilization of the heterocyclic compounds by the π-electrons of the heteroatom. The above data shows that the three-membered ring of an episulfoxide is almost same as that of episulfide (*vide infra* Results and Discussion Section, Chapter 7).

Recently, we reported[166] the x-ray crystallographic structure of adamantylidene-adamantane thiirane **(116)** and adamantylideneadamantane thiirane 1-oxide **(178)**.

Bond lengthes and bond angles for thiirane moiety of compound **116** are: S-C_1 = 1.8455(19)Å; S-$C_{1'}$ = 1.8421(20)Å; C_1-$C_{1'}$ = 1.503(3)Å; C_1-S-$C_{1'}$ = 48.09(8)°; S-C_1-$C_{1'}$ = 65.83(10)°; S-$C_{1'}$-C_1 = 66.07(10)°; S-C_1-C_2 = 114.57(13)°; S-$C_{1'}$-$C_{2'}$ = 115.18(14)°.

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233 G. Cunningham, Jr., A. W. Boyd, R. J. Myers, W. D. Gwinn and W. I. LeVan, *J. Chem. Phys.*, **19**, 676, (1951).

234 T. E. Turner, V. C. Fiora, W. M. Kendrick and B. L. Hicks, *J. Chem. Phys.*, **21**, 564, (1953).

235 M. T. Bowers, R. A. Beaudet, H. Goldwhike and R. Tang, *J. Am. Chem. Soc.*, **91**, 17 (1969).

236 Y. Nakano, S. Saito and Y. Morino, *Bull. Chem. Soc. Jpn.*, **43**, 368 (1970).

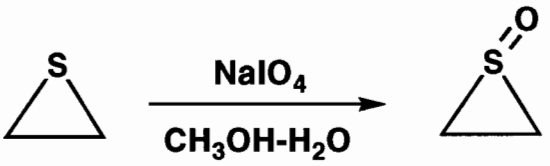
Bond lengthes and bond angles for thiirane 1-oxide moiety of compound **178** are: S_1-O_1 = 1.491(2)Å; S_1-C_1 = 1.865(3)Å; S_1-C_{11} = 1.860(2)Å; C_1-C_{11} = 1.505(3)Å; O_1-S_1-C_1 = 111.2(1)°; O_1-S_1-C_{11} = 111.2(1)°; C_1-S_1-C_{11} = 47.7(1)°; S_1-C_1-C_{11} = 66.0(1)°

6.3 METHODS OF PREPARATION

6.3.1 OXIDATION OF EPISULFIDES

6.3.1.1 With Sodium Periodate

The first episulfoxide clearly described was episulfoxide **184** obtained in 1966 by Hatzell and Paige[199a] through periodate oxidation of the well-known episulfide **185** **(Scheme 76)**.



185 **184**

SCHEME 76

However, it is a low yield reaction because the use of methanol as a solvent makes the extraction difficult. In addition, certain kinds of substituted episulfoxides are so unstable that they can not be isolated. Furthermore, the episulfides of *cis*-, *trans*-9,10-octadecanoic acid and *cis*-13,14-docosanoic acid have been oxidized to the corresponding episulfoxides **186**, **187**, and **188**, respectively, with sodium periodate at room temperature.[237] As a result, this method may be considered as a convenient method for the preparation of long chain fatty acid episulfoxides. Literature reports on the oxidation of short chain episulfoxides reveal the use of only very low temperatures for such a reaction.[199a,238]

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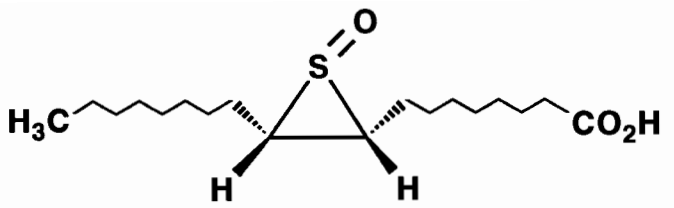
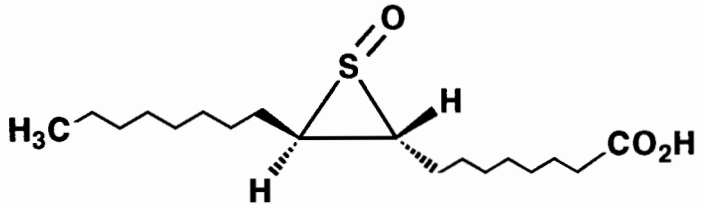
237 B. Y. Rao, C. V. N. Rao and M. R. Subbaram, *J. Oil Technol. Ass. India*, **6(1)**, 19 (1974).

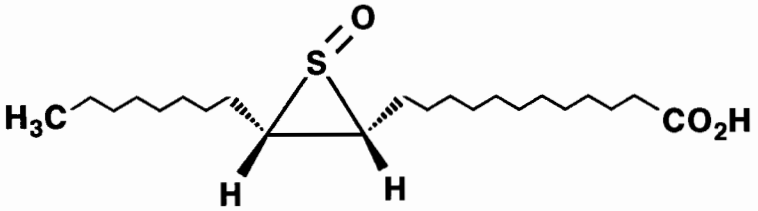
238 N. J. Leonard, C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).



186



187



188

6.3.1.2 With Hydrogen Peroxide

Hardy and coworkers[239] reported that H_2O_2-V_2O_5-*tert*-BuOH system can be used as an oxidizing reagent; however, this method is not good for unstable episulfoxides. In addition, Dittmer and Levy[229] reported that the oxidation of dibenzoylstilbene episulfide with hydrogen peroxide in acetic acid gave the corresponding episulfoxide in good yield.

6.3.1.3 With Peroxy- or *m*-Chloroperoxybenzoic Acid

Kondo and coworkers[240] reported a more general method of oxidation of episulfides. They performed the oxidation with the more versatile peroxybenzoic acid. Moreover, they[241] prepared and characterized several episulfoxides whose stereochemistry

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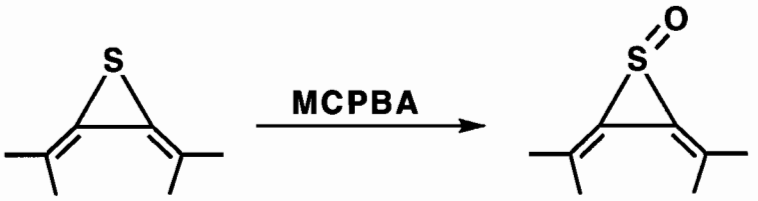
239 F. E. Hardy, P. R. H. Speakman and P. Robson, *J. Chem. Soc., Chem. Commun.*, 2334 (1969).

240 K. Kondo, A. Negishi and M. Fukuyama, *Tetrahedron Lett.*, 2461 (1969).

241 K. Kondo and A. Negishi, *Tetrahedron*, **27**, 4821 (1971).

was assigned. In addition, they noticed that the stereochemical course of the oxidation is very sensitive to steric factors. For instance, they discovered that the oxidation of *cis*-stilbene and styrene episulfides afforded exclusively the corresponding *anti*-episulfoxides, and no trace of the *syn*.

Other authors,[242] found that in the reaction with propylene episulfide, peroxy- or *m*-chloroperoxybenzoic acid is the best oxidizing reagent and methylene chloride is the best solvent. 2,3-Diisopropylidene thiirane 1-oxide **(189)** was also obtained from the oxidation of the corresponding thiirane **190** with *m*-chloroperoxybenzoic acid **(Scheme 77)**.[243]



190 **189**

SCHEME 77

6.3.1.4 With 3,3-Dimethyldioxirane

Recently, it was reported[244] that *cis*- and *trans*-2,3-di(*p*-methoxyphenyl)-2,3-diphenyl thiirane 1-oxides were obtained from the corresponding thiiranes upon the oxidation with 3,3-dimethyldioxirane. Although the products could not be isolated and purified, they could be characterized spectroscopically.

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242 C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 1109 (1965).

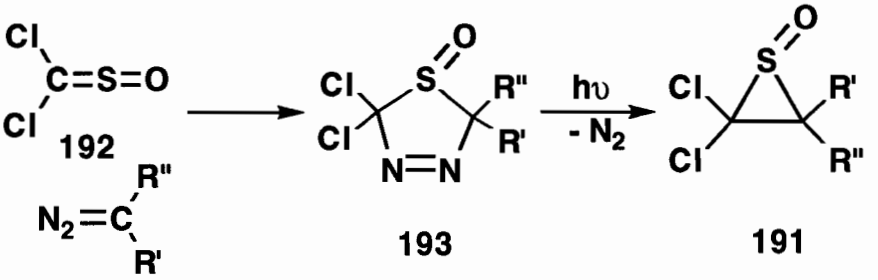
243 W. Ando, Y. Haniu and T. Takata, *Tetrahedron*, **42**, 1989 (1986).

244 a) R. S. Glass and W. Jung, *J. Am. Chem. Soc.*, **116**, 1137 (1994); b) W. Adam and L. Hadjiarapoglou, *Top. Curr. Chem.*, **164**, 45 (1993); c) R. W. Murray, *Chem. Rev.*, **89**, 1187 (1989); d) W. Adam, Y.-Y. Chan, D. Cremer, J. Gauss, D. Scheutzow and M. Schindler, *J. Org. Chem.*, **52**, 2800 (1987); e) R. W. Murray and R. Jeyaraman, *J. Org. Chem.*, **50**, 2847 (1985).

6.3.2 CYCLOADDITION REACTION OF DIAZO COMPOUNDS

6.3.2.1 With Sulfines

The possibility of a [2+3] cycloaddition of sulfines was first suggested by Zwanenburg and coworkers.[245] They obtained relatively stable dichloro episulfoxide **191** from the reaction of sulfine **192** with diazo compounds and proposed that it arises from the initially formed cycloaddition product **193** by nitrogen elimination **(Scheme 78)**.



SCHEME 78

Treatment of diarylsulfines with aryldiazomethanes produces episulfoxide **194** smoothly and in good yield.[246] The formation of **194** takes place by a nucleophilic attack of diazocarbon at the sulfine sulfur providing a zwitterionic diazonium intermediate **195**, *via* an internal 1,3-elimination of nitrogen.

This proposed mechanism bears some analogy with the one that explains the formation of epioxides from ketones and diazo compounds. The above mechanism was also supported

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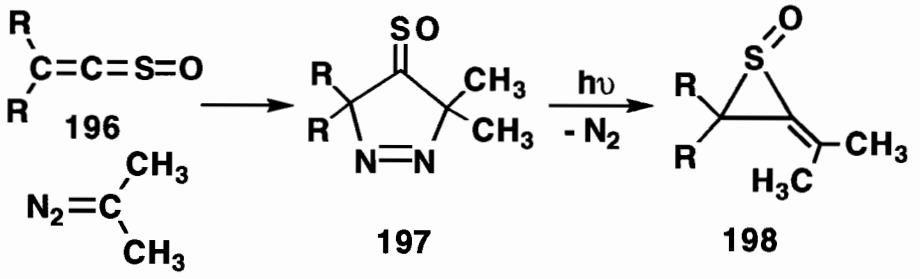
245 a) B. Zwanenburg, L. Thijs and J. Strating, *Tetrahedron Lett.*, 4461 (1969); b) L. Thijs, A. Wagenaar, E. M. M. Van Rens and B. Zwanenburg, *Tetrahedron Lett.*, 3589 (1973).

246 B. F. Bonini and G. Maccagnani, *Gazz. Chim. Ital.*, **105**, 827 (1975).

by different groups.[247] However, the formation of **194** *via* thiadiazoline 1-oxide intermediate **193** cannot be excluded.

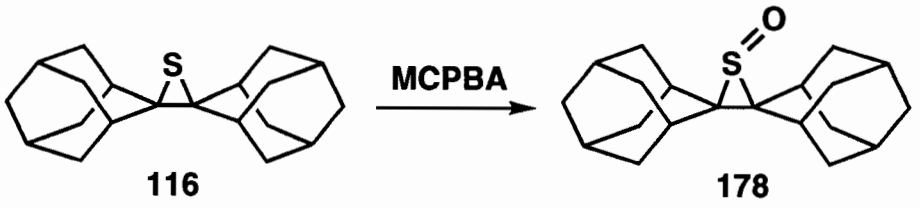
6.3.2.2 With Thioketene 1-Oxides

Thioketene 1-oxides **196** react smoothly with diazopropane to give good yields of adduct **197** resulting from the [2+3] cycloaddition across the carbon-carbon double bond of the heterocumulene. The photolysis of this adduct in benzene or carbon tetrachloride results in rapid elimination of nitrogen and formation of episulfoxide **198 (Scheme 79)**[248] (*vide infra* Results and Discussion Section, Chapter 7).



SCHEME 79

Most recently,[166] we reported that the oxidation of adamantylideneadamantane thiirane **(116)** with equimolar amounts of *m*-chloroperoxybenzoic acid in methylene chloride at 0 °C gave the corresponding adamantylideneadamantane thiirane 1-oxide **(178)**, in high isolated yield (99%) **(Scheme 80)**.



SCHEME 80

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247 B. F. Bonini and G. Maccagnani, *Tetrahedron Lett.*, 3585 (1973).

248 E. Schaumann, H. Behr, G. Adiwidjaja, A. Tangerman, B. H. M. Lammerink and B. Zwanenburg, *Tetrahedron*, **27**, 219 (1981).

In addition, bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide **(179)** was also produced from the reaction of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane **(117)** with *m*-chloroperoxybenzoic acid in methylene chloride. A 98% isolated yield was obtained **(Scheme 81)**.[167]

117 **179**

SCHEME 81

6.4 REACTIONS OF EPISULFOXIDES

6.4.1 With Dienes and Polyenes

There are many reactions which hetero three-membered ring compounds are converted into olefins by thermal elimination.[249] Episulfoxide compounds also can be decomposed by heat and give sulfur monoxide and an olefin. The electronic ground state of sulfur monoxide has been shown to be in the triplet state by microwave optical analysis.[250] The sulfur monoxide molecule can be regarded as an analog of the oxygen molecule.[251] Its half-life is so short that few reactions are known in which it was detected.

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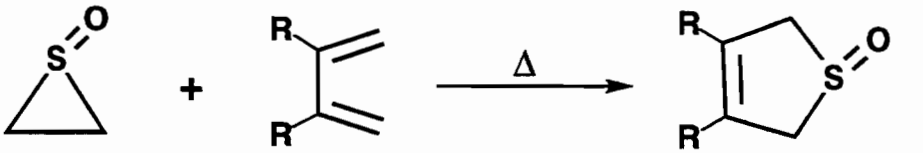
249 a) N. P. Neureiter, F. G. Brodwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963); b) R. D. Clark, G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964); c) N. Tokura, T. Nagai, S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966); d) J. P. Freeman, W. H. Graham, *J. Am. Chem. Soc.*, **89**, 1761 (1967); e) F. G. Brodwell, J. M. Williams, Jr., E. B. Hoyt, Jr., B. B. Jarvis, *J. Am. Chem. Soc.*, **90**, 429 (1968).

250 S. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 667 (1969).

251 P. W. Schenk, R. Steudel, *Angew. Chem., Int. Ed. Engl.*, **4**, 402 (1965).

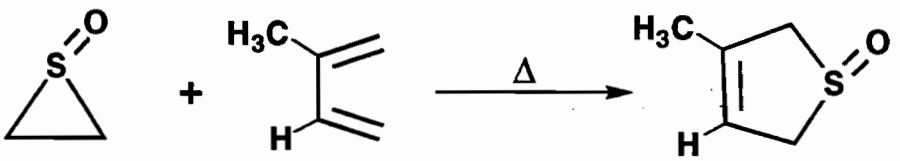
Dodson and Sauers[252] were the first to show that sulfur monoxide generated *in situ* by thermolysis of thiirane 1-oxide **184** could be trapped by 1,3-dienes **62** and **199** in the form of 2,5-dihydrothiophene 1-oxides **200** and **201 (Scheme 82), (Table 17).**



184 **62 ; R = CH_3**
199 ; R = C_6H_5
200 ; R = CH_3
201 ; R = C_6H_5

SCHEME 82

Equimolar amounts of isoprene **(202)** and thiirane 1-oxide **184** in refluxing toluene gave 2,5-dihydro-3-methylthiolene 1-oxide **(203)**,[253] in moderate yield **(Scheme 83), (Table 17).**



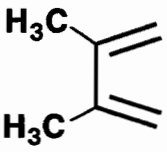
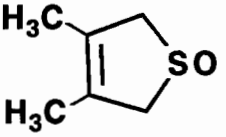
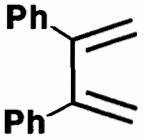
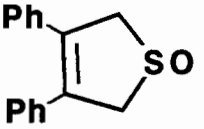
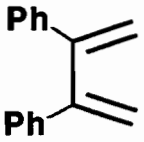
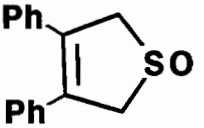
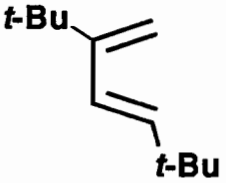
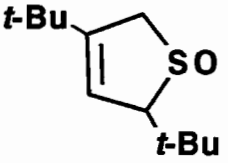
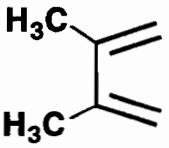
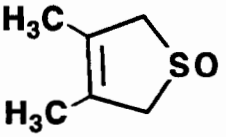
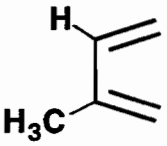
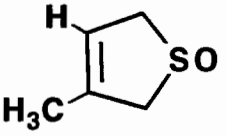
184 **202** **203**

SCHEME 83

252 R. M. Dodson and F. R. Sauers, *J. Chem. Soc., Chem. Commun.*, 1189 (1967).

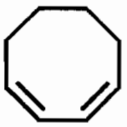
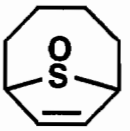
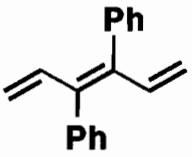
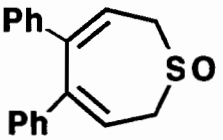
253 P. Chao and D. M. Lemal, *J. Am. Chem. Soc.*, **95**, 920 (1973).

Table 17: Reactions of Conjugated Dienes with Sulfur Monoxide (SO)

conjugated diene	origin of SO	solvent	temp. (°C)	product	yield (%)	ref.
	a	toluene	110		21	252
	a	toluene	110		25	252
	b	benzene	80		30	256
	a	toluene	110		40	252
	c	THF	65		25	257
	a	toluene	110		72	253

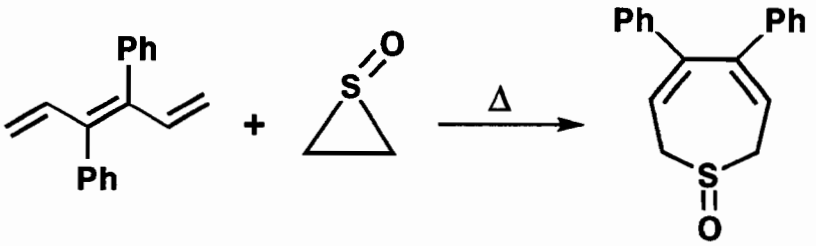
a. ethylene episulfoxide (184); b. dibenzo[*b,f*][1.4.6]thiadiazepin 1-oxide (208)
c. bis(triphenylphosphine)sulfur monoxide palladium (210).

Table 17: continued

conjugated diene	origin of SO	solvent	temp. (°C)	product	yield (%)	ref.
	a	xylene	140		30	255
	b	benzene	80		19	256
	a	toluene	110		35	254

a. ethylene episulfoxide (184); b. dibenzo[*b,f*][1.4.6]thiadiazepin 1-oxide (208)
c. bis(triphenylphosphine)sulfur monoxide palladium (210).

A low yield of 2,7-dihydrothiepin-4,5-diphenyl 1-oxide **(204)** was observed when 3,4-diphenyl-1,3,5-hexatriene **(205)** reacted with thiirane 1-oxide **184 (Scheme 84)**, **(Table 17)**.[254]

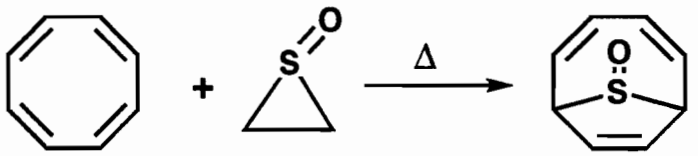


205 **184** **204**

SCHEME 84

254 R. M. Dodson and J. P. Nelson, *J. Chem. Soc., Chem. Commun.*, 1159 (1969).

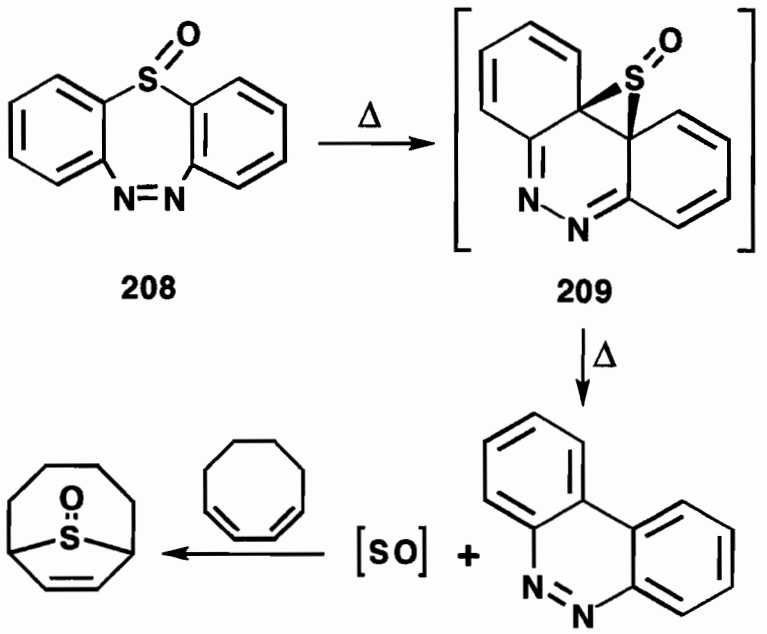
The thermal reaction of cyclooctatetraene **(206)** and thiirane 1-oxide **184** in boiling xylene resulted in the formation of the cyclo adduct product **207** to which the *anti*-configuration was assigned **(Scheme 85)**, **(Table 17)**.[255]



206 **184** **207**

SCHEME 85

Sulfur monoxide was extruded from dibenzo[*b,f*][1.4.6]thiadiazepin 1-oxide **(208)** in refluxing chloroform and trapped with 1,3-dienes to give 2,5-dihydrothiophene 1-oxide **(Scheme 86)**, **(Table 17)**.[256]



208 **209**

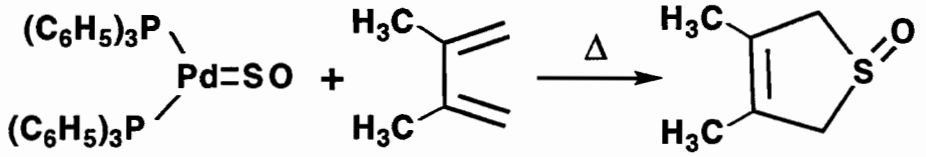
SCHEME 86

255 A. G. Anastassiou and B. Y. H. Chao, *ibid.*, 979 (1971).

256 Y. L. Chow, J. N. S. Tam and J. E. Blier., *J. Chem. Soc., Chem. Commun.*, 1604 (1970).

The same authors[256] suggested that episulfoxide **209** could be a logical intermediate from the thermal decomposition of sulfoxide **208** as shown in **Scheme 86** above.

Recently, Heyke and coworkers[257] reported that the bis(triphenylphosphine)sulfur monoxide palladium complex **(210)** can be used as a SO-source for the formation of 2,5-dihydro-3,4-dimethylthiophene 1-oxide **(200)** from 2,3-dimethyl-1,3-butadiene **(62)** **(Scheme 87)**, **(Table 17)**.



210 **62** **200**

SCHEME 87

6.4.2 With Alcohols and Thiols

6.4.2.1 In the Presence of a Catalyst

Episulfoxides react (acid catalyst)[258] through activation by protonation of the sulfoxide followed by nucleophilic attack on a ring carbon. The sulfinic acid product is unstable and condenses to form various S-S bonded compounds **(Scheme 88)**.

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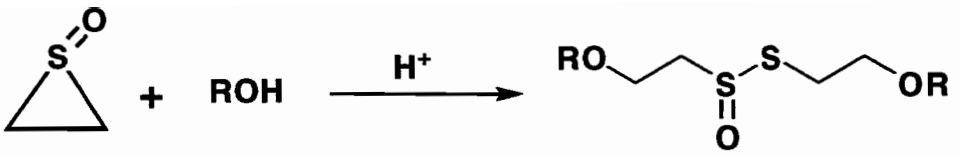
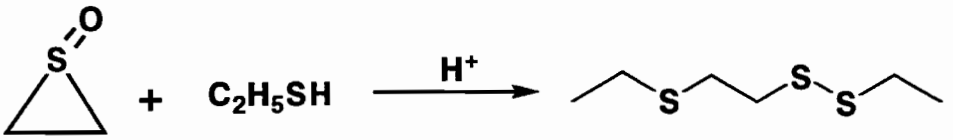
257 O. Heyke, A. Neher and I.-P. Lorenz, *Z. anorg. allg. Chem.*, **23**, 608 (1992).

258 a) A. Saleh and J. G. Tillett, *J. Chem. Soc., Perkin Trans. 2,* 132 (1981); b) K. Kondo, A. Negishi and I. Ojima, *J. Am. Chem. Soc.*, **94**, 5786 (1972); c) K. Kondo, A. Negishi and G. Tsuchihashi, *Tetrahedron Lett.*, 3173 (1969); d) G. E. Manser, A. D. Mesure and J. G. Tillett, *Tetrahedron Lett.*, 3153 (1968); e) J. R. Shelton and K. E. Davis, *J. Am. Chem. Soc.*, **89**, 718 (1967); f) D. Barnard, *J. Chem. Soc., Chem. Commun.*, 4675 (1957).



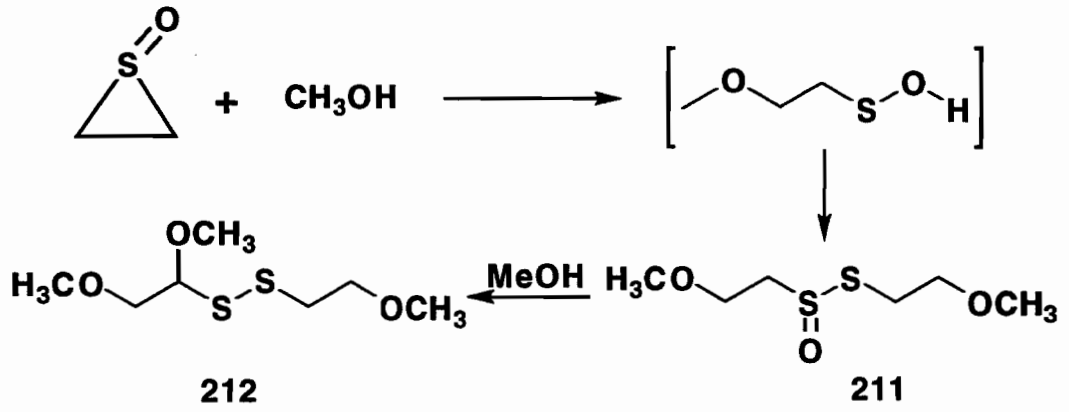
R = Me (97%); Et (65%); *i*-Pr (91%); *tert*-Bu (77%)



SCHEME 88

6.4.2.2 Without a Catalyst

In 1974, Kondo and Negishi[259] discovered that the thermal reaction of ethylene episulfoxide in methanol without an acidic catalyst afforded thiosulfinate **211** as a primary product, which rearranged into the disulfide **212** as a final product (**Scheme 89**).

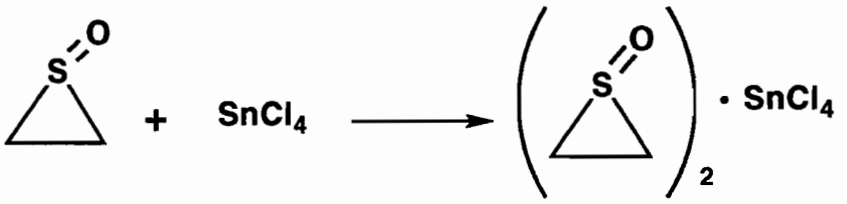


SCHEME 89

259 K. Kondo and A. Negishi, *Chem. Lett.*, 1525 (1974).

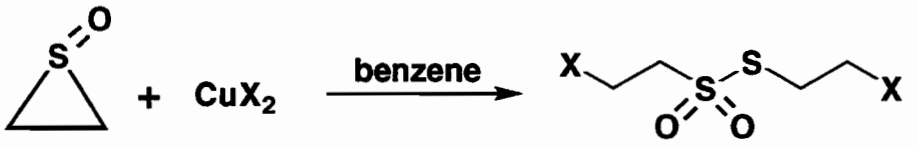
6.4.3 With Copper(II) Halides[260]

In general, sulfoxide compounds form stable complexes with heavy metal salts or transition metal complexes. However, ethylene episulfoxide forms 2:1 addition compounds only with tin(IV) chloride in quantitative yield **(Scheme 90)**.



SCHEME 90

When ethylene episulfoxide **(184)** is added to a suspension of copper(II) halides in benzene solution, thiosulfonate **213** was obtained in good yield **(Scheme 91)**.



184 **213**

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

SCHEME 91

When the reaction was carried out in methylene chloride containing a trace amount of methanol, methyl β-haloethane sulfinate **(214)** was obtained as a sole product, in good yield **(Scheme 92)**.

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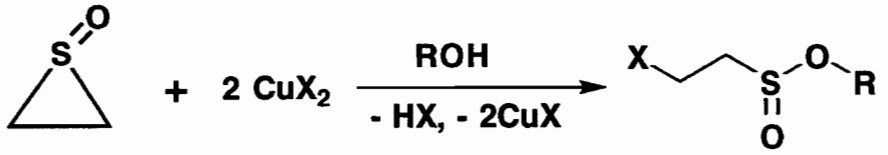
260 a) K. Kondo, A. Negishi and G. Tsuchihashi, *Tetrahedron Lett.*, 2743 (1969); b) R. A. Cotton and F. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960); c) R. M. Topping and N. Kharasch, *J. Org. Chem.*, **27**, 4353 (1962); d) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 212 (1962).

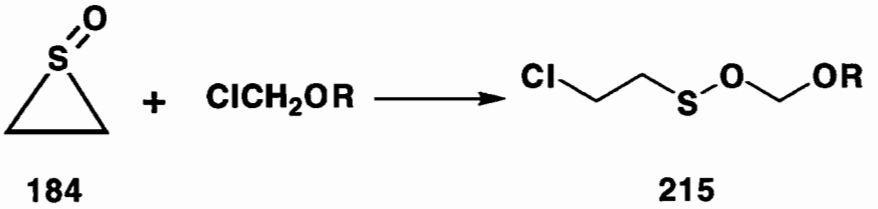


X = Cl, Br; R = Me, Et, *i*-Pr

SCHEME 92

6.4.4 With α-Halo Ethers

Vilsmaier and Hloch[261] reported that the reaction of ethylene episulfoxide **(184)** with α-halo ethers gave only sulfenate **215 (Scheme 93)**.

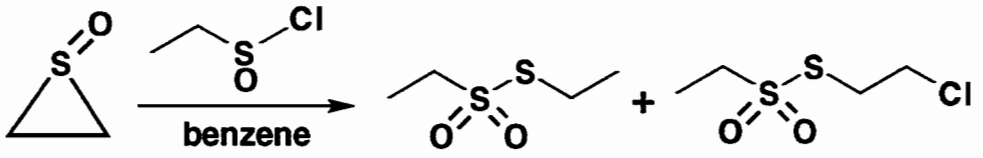


184 215

SCHEME 93

6.4.5 With Sulfenyl Halides

The reaction of ethylene episulfoxide **(184)** with ethanesulfenyl chloride in benzene was undertaken.[260a] The resulting product was a mixture of thiosulfonates **216** (20%) and **217** (80%) **(Scheme 94)**.



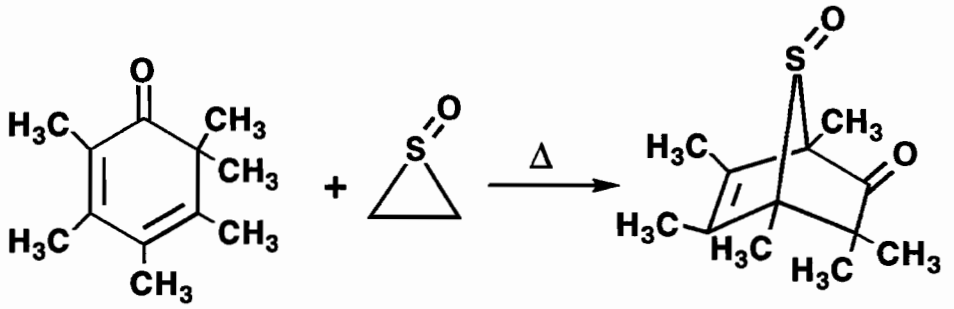
184 216 217

SCHEME 94

261 E. Vilsmaier and B. Hloch, *Synthesis*, 590 (1971).

6.4.6 With Dienone

Murray and coworkers[262] reported that the reaction of ethylene episulfoxide (**184**) with an equimolar amount of 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone (**218**) afforded a good yield of 2,3,4,5,6,6-hexamethyl-7-thiabicyclo[2.2.1]hept-5-en-2-one 7-*anti*-oxide (**219**) (**Scheme 95**).



218 **184** **219**

SCHEME 95

6.4.7 With Organolithium Compounds

The reaction of episulfoxides with organolithium compounds has been studied.[263] For example, the reaction of methyllithium with stilbene episulfoxide (**220**) in the presence of methyl iodide leads to the formation of stilbene (**221**) with complete retention of configuration at the carbon skeleton, methylvinyl sulfoxide (**222**) and dimethyl sulfide (**223**) (**Scheme 96**).

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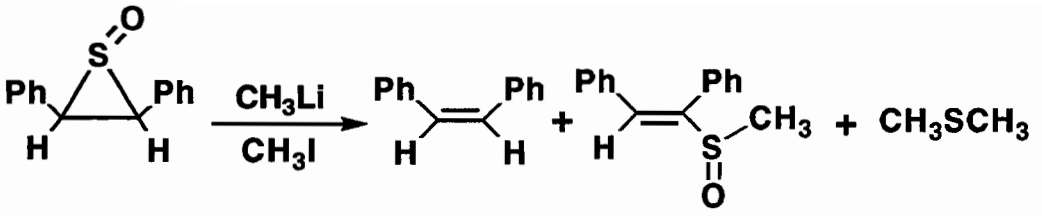
262 R. K. Murray, Jr., J. S. Polley, S. Abdel-Meguid and V. W. Day, *J. Org. Chem.*, **42**, 2127 (1977).

263 a) B. Bonini, G. Maccagnani and G. Mazzanti and P. Piccinelli, *Tetrahedron Lett.*, 3987 (1979); b) B. Bonini, G. Maccagnani and G. Mazzanti and P. Zani, *Gazz. Chim. Ital.*, **120**, 115 (1990).

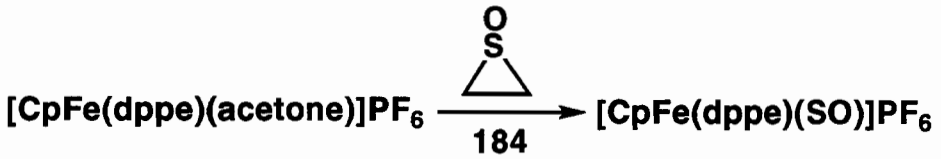


220 221 222 223

SCHEME 96

6.4.8 With Organometallic Compounds

Schenk and Müssig[264] reported that 1,2-bis(diphenylphosphino)ethane-η^5-cyclopentadienyl acetone iron(II) hexafluorophosphate (**224**) reacted with ethylene episulfoxide (**184**) to give 1,2-bis(diphenylphosphino)ethane-η^5-cyclopentadienyl sulfur monoxide iron(II) hexafluorophosphate (**225**) in 63 % yield (**Scheme 97**).



224 225

SCHEME 97

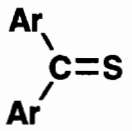
6.4.9 With Thioketones

Thermolysis of stilbene episulfoxide (**220**) in the presence of thioketone **226** resulted in the formation of dithiolane 1-oxides **227** and **228** in good yield.[265]

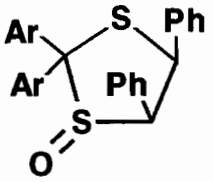
---

264 W. A. Schenk and S. Müssig, *J. Organomet. Chem.*, **320**, C23 (1987).

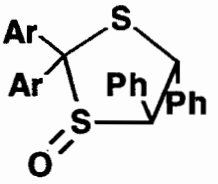
265 K. Kondo, M. Mastsumoto and A. Negishi, *Tetrahedron Lett.*, 2131 (1972).



226



227



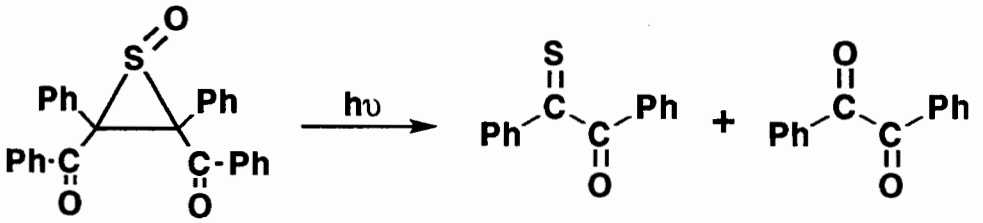
228

On the other hand, thermal decomposition of an alkyl substituted episulfoxide took place easily at room temperature to give a sulfinic acid ester through the formation of the sulfinic acid intermediates.[241]

6.4.10 Other Methods

It was reported[266] that pyridine N-oxide can be deoxygenated by episulfoxides to give the corresponding pyridine, the alkene and sulfur dioxide.

Dittmer and coworkers[267] studied the photolysis and pyrolysis of dibenzoylstilbene episulfoxide **(229)**. They found that benzil **(230)** and monothiobenzil **(231)** can be formed **(Scheme 98)**.



229 231 230

SCHEME 98

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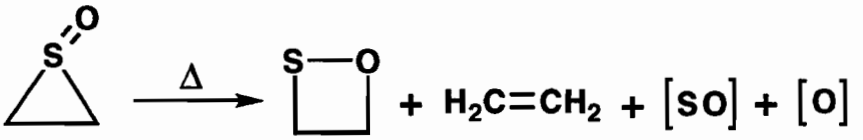
266 B. Bonini, G. Maccagnani and G. Mazzanti and P. Pedrini, *Tetrahedron Lett.*, 1799 (1979).

267 a) D. C. Dittmer, G. C. Levy, G. E. Kuhlmann, *J. Chem. Soc., Chem Commun.*, 2793 (1967); b) D. C. Dittmer, G. E. Kuhlmann and G. C. Levy, *J. Org. Chem.*, **35**, 3676 (1970).

In addition, thermolysis of ethylene episulfoxide (**184**) has been studied[268] by flash vacuum thermolysis field ionization mass spectrometry[269] in the temperature range 1043-1404 °K (**Scheme 99**).



184 **232**

SCHEME 99

Evidence was presented that the ring enlargement product 1,2-oxathietane (**232**) is being formed alongside atomic oxygen extrusion and sulfur monoxide elimination. The extrusion of atomic oxygen from organic sulfoxides has been previously reported.[270]

6.5 MECHANISM OF THERMAL DECOMPOSITION OF EPISULFOXIDES

Hartzell and Paige[199b] favor a two step mechanism in which a dipolar intermediate loses its stereochemical integrity prior to decomposing into sulfur monoxide and an olefin. In contrast Baldwin and coworkers[271] observed that the stereochemistry of the decomposition decreases with increasing temperature and favored a biradical intermediate in the decomposition. Other authors[272] also observed that the temperature of decomposition has a strong influence on the stereochemical course of the elimination of the sulfur monoxide. In addition, Kondo and coworkers[265] concluded that the thermal fragmentation of episulfoxides to afford an olefin and sulfur monoxide proceeds stepwise through a biradical intermediate (**Scheme 100**).

---

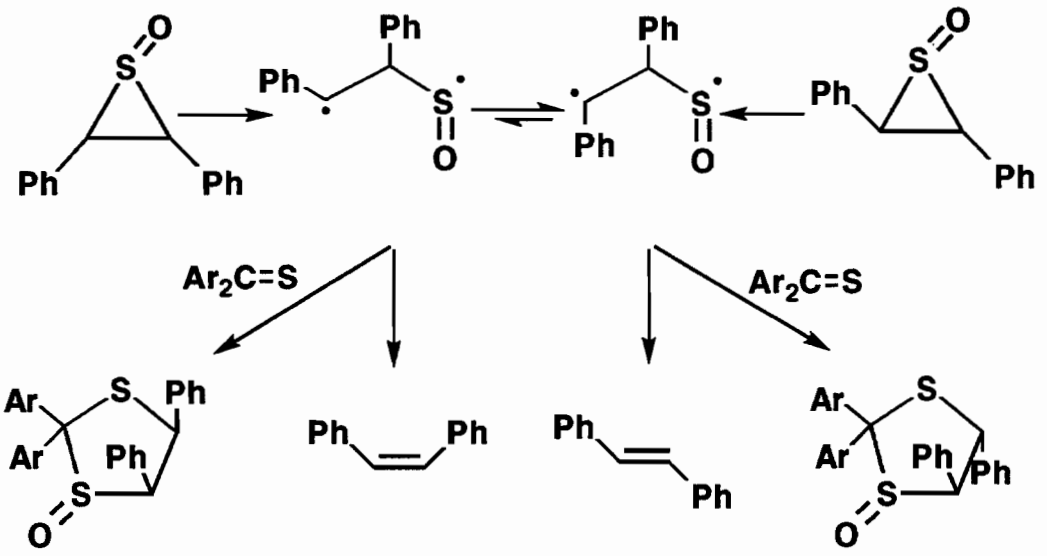
268 L. Carlsen and H. Egsgaard, *J. Chem. Soc., Perkin Trans. 2*, 279 (1982).

269 L. Carlsen and H. Egsgaard, *Thermochim. Acta.*, **38**, 47 (1980).

270 L. Carlsen, H. Egsgaard and D. N. Harpp, *J. Chem. Soc., Perkin Trans. 2*, 116 (1981).

271 J. E. Baldwin, G. Holfe and S. C. Choi, *J. Am. Chem. Soc.*, **93**, 2810 (1971).

272 M. G. L. Aalbersberg and K. P. C. Volhard, *J. Am. Chem. Soc.*, **99**, 2792 (1977).



SCHEME 100

Finally, Lemal and Chao[273] examined the stereochemistry of sulfur monoxide addition to the three isomeric 2,4-hexadienes. With each of the dienes, a mixture of isomeric thiophenes was obtained with a high degree of stereoselectivity and regiospecificity. The authors[273] ruled out a direct attack of thiirane 1-oxide on the diene because they noticed that the rate of decomposition of thiirane 1-oxide is not increased by raising the diene concentration. Because the reaction proceeds at essentially the same rate in acetonitrile as in toluene, the authors favored a biradical mechanism of extrusion of sulfur monoxide **(Scheme 101)**.

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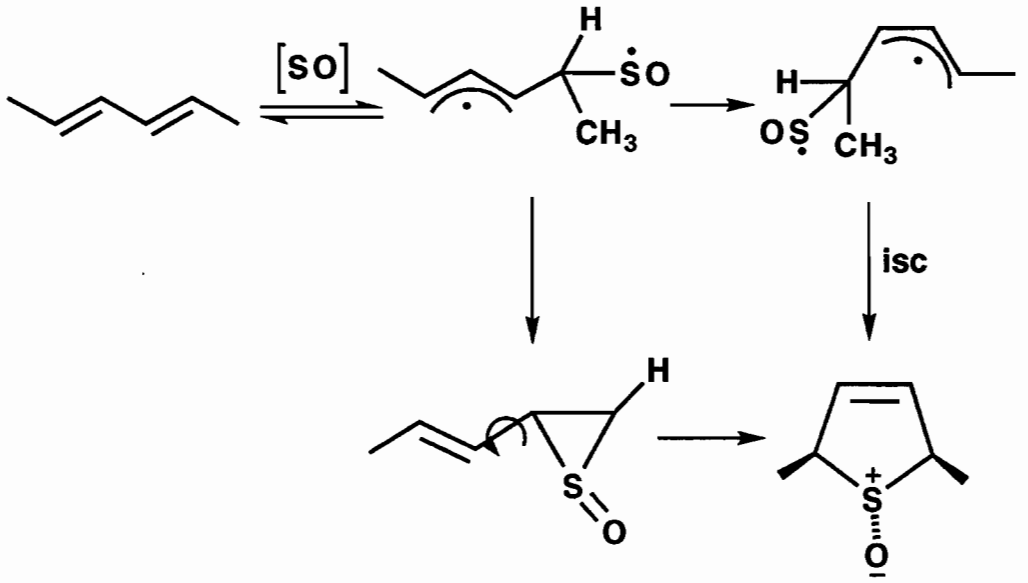
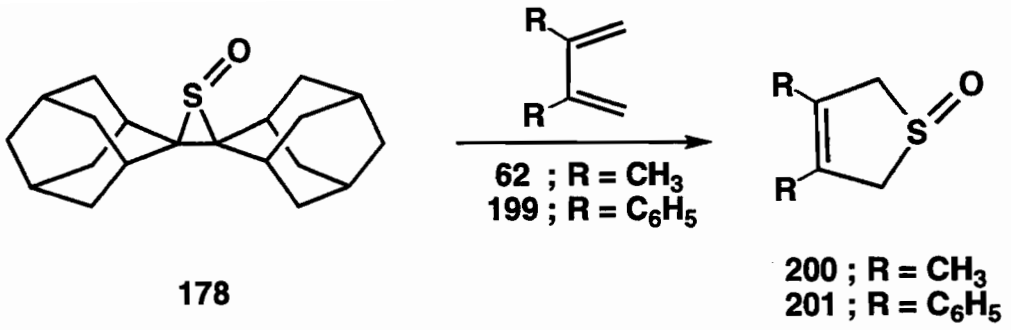
273 D. M. Lemal and P. Chao , *J. Am. Chem. Soc.*, **95**, 922 (1973).



SCHEME 101

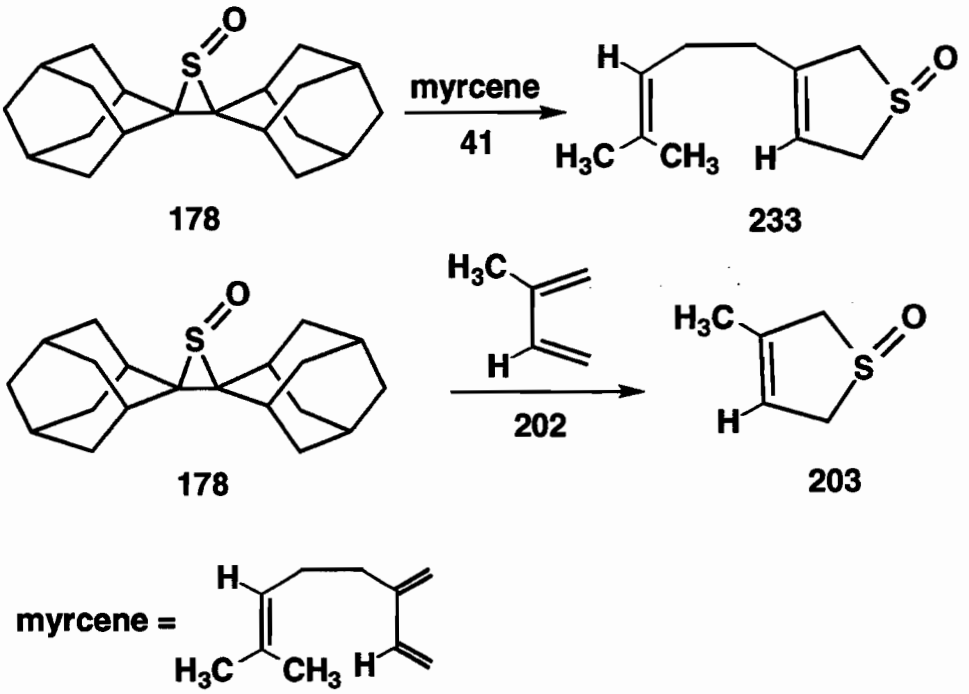
In the above **Scheme**, rotation about the partial double bond C-3 and C-4, and intersystem crossing (isc) must occur before a product can form. They suggested that the stereoselectivity in these reactions may result from the torsional stiffness of the C-2, C-3 bond (estimated 6-10 kcal mole^{-1} barrier) due to the interaction between the C-3 p-orbital and sulfur monoxide group. Such interaction, whether direct[199b,271] or indirect, may lower the torsional barrier for the C-3, C-4 bond. All in all, the literature results generally support a biradical mechanism of extrusion of sulfur monoxide (*vide infra* Results and Discussion Section, Chapter 7).

Most recently, we reported[166] the synthesis of adamantylideneadamantane thiirane 1-oxide **(178)** and studied its thermal decomposition in the presence of 2,3-dimethyl-1,3-butadiene **(62)** or 2,3-diphenyl-1,3-butadiene **(199)** and with variation of solvents, temperature, time and concentration. Sulfur monoxide was trapped and 2,5-dihydrothiophene 1-oxide **200** or **201** was isolated in each case in an optimized yields of 70-80% **(Scheme 102)**, **(Table 18)**. In addition, adamantylideneadamantane **(108)** was also recovered quantitatively.



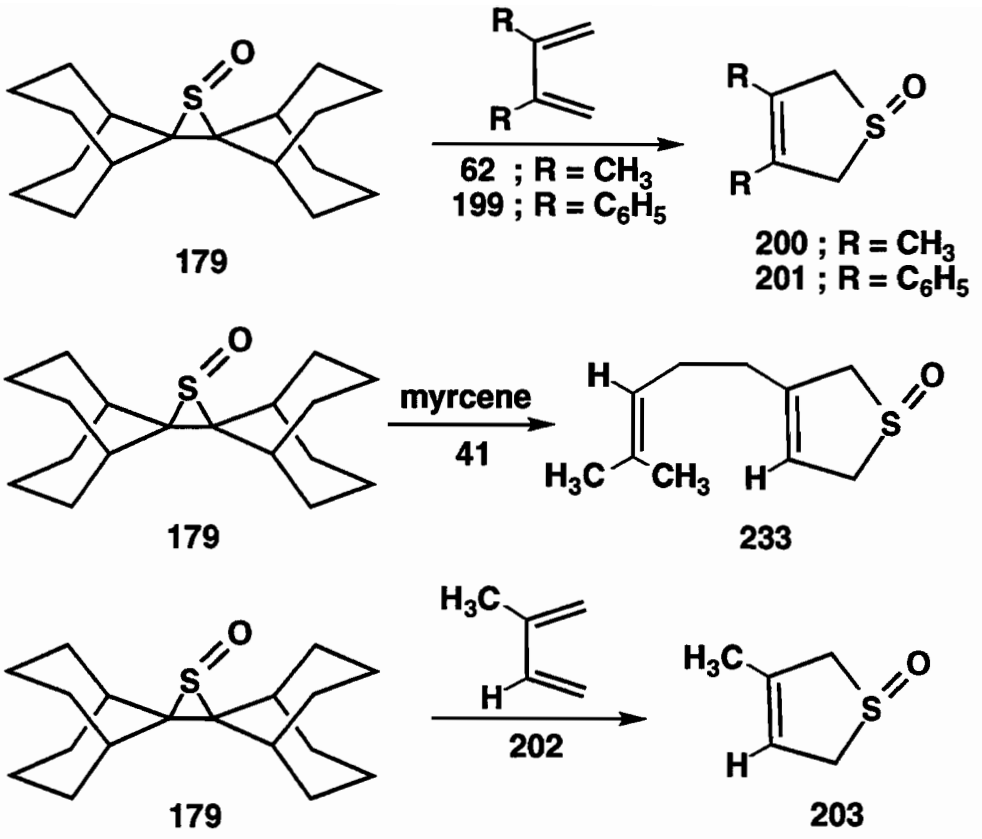
SCHEME 102

Also, we discovered that sulfur monoxide can be trapped from **178** with other dienes (isoprene **202** or myrcene **41**) to give the corresponding 2,5-dihydrothiophene 1-oxide **203** or **233**, respectively, in good isolated yields[167] **(Scheme 103), (Table 18).**



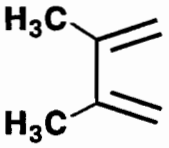
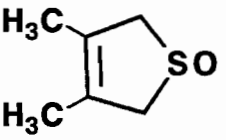
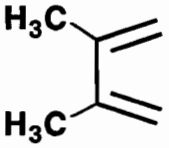
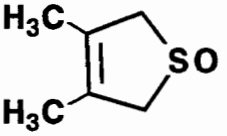
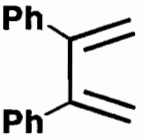
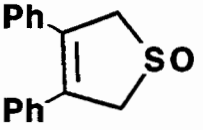
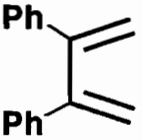
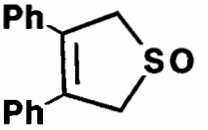
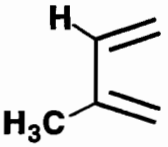
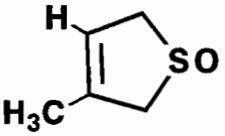
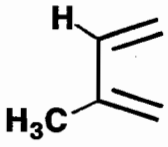
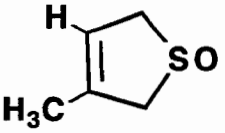
SCHEME 103

Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide **179** was also prepared and used as a SO-source for the trapping of sulfur monoxide with different 1,3-dienes **62, 199, 202** or **41** to give the corresponding 2,5-dihydrothiophene 1-oxides **200, 201, 203** or **233**, respectively, in a variety of solvents, varying temperature, time and concentration[167] **(Scheme 104), (Table 18).**


R
R
62 ; R = CH3
199 ; R = C6H5
R
R
200 ; R = CH3
201 ; R = C6H5
179
myrcene
41
H
H3C
CH3
H
233
179
H3C
H
202
H3C
H
203
179

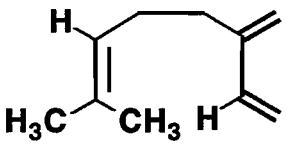
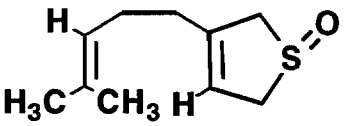
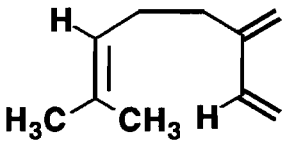
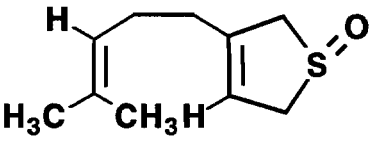
SCHEME 104

Table 18: Reactions of Thiirane 1-Oxides 178 and 179 with 1,3-dienes

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

a = adamantylideneadamantane thiirane 1-oxide (178)
b = bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide (179)

Table 18: continued

conjugated diene	origin of SO	solvent	temp. (°C)	product	yield (%)
	a	toluene	110		52
	b	toluene	110		55

a = adamantylideneadamantane thiirane 1-oxide (178)
b = bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide (179)

CHAPTER 7

RESULTS AND DISCUSSION

There is a considerable interest in finding simple chemical methods to generate and examine the chemistry of reactive diatomic molecules such as singlet diatomic oxygen ($^1O_2$),[274] singlet diatomic sulfur ($^1S_2$),[63] as well as related species such as **R-P=S**,[275] **R-P=Se**,[276] **R-N=S**,[277] **R-N=O**,[278] and **R-N=Se**.[279] Relatively little studied has been carried out on the chemistry of sulfur monoxide (**S=O**).[280]

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274 A. H. Frimer, Singlet O_2, CRC Press, Inc., Boca Raton Florida, 1995

275 a) H. Bock, M. Kremer, B. Solouki, M. Binnewies and M. Meisel, *J. Chem. Soc., Chem. Commun.*, 9 (1992); b) P. L. Folkins, B. R. Vincent and D. N. Harpp, *Tetrahedron Lett.*, **32**, 7009 (1991).

276 D. S. Bohle, C. E. F. Rickard, W. R. Roper and P. Schwerdtfeger, *Organometallics*, **9**, 2068 (1990).

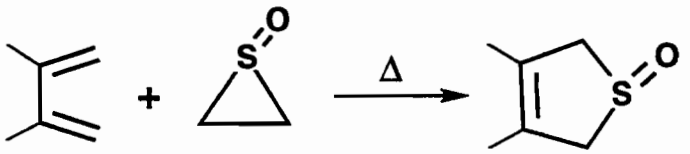
277 a) L. N. Markovskii, A. V. Solov'es, V. V. Pen'kovskii, N. P. Kolesnik, A. V. Borodin, S. V. Iksanova and Y. G. Shermolovich, *Zh. Org. Khim.*, **28**, 1388 (1992); b) M. Takahashi, R. Okazaki, N. Inamoto, T. Sugawara and H. Iwamura, *J. Am. Chem. Soc.*, **114**, 1830 (1992); c) M. R. Bryce and J. N. Heaton, *Tetrahedron Lett.*, **32**, 7459 (1991).

278 a) G. W. Kirby and M. Nazeer, *J. Chem. Soc., Perkin Trans 1*, **13**, 1387 (1993); b) T. Gilchrist and A. Lemons, *J. Chem. Soc., Perkin Trans 1*, **13**, 1391 (1993); c) H. Felber, G. Kresze, F. P. Schmidtchen, R. Prewo and A. Vasella, *Justus Liebigs Ann. Chem.*, **3**, 261 (1993).

279 M. R. Bryce and A. Chesney, *J. Chem. Soc., Chem. Commun.*, 195 (1995).

280 Further references for hetero Diels-Alder reactions are found in D. L. Boger and S. N. Weinreb, "Hetero Diels-Alder Methodology in Organic Synthesis", Academic Press, San Diego, 1987.

The main method of generation of **S=O** is by the pyrolysis of ethylene episulfoxide (**184**) at *ca.* 100 °C.[170,199] Other less-used methods of **S=O** production have involved the thermal decomposition of sulfoxide **175**,[212] and heterocycle **208**.[256] Diene and triene trapping experiments with **S=O** have been carried out by a number of workers;[252,254] the main product is Diels-Alder adduct **234 (Scheme 105)** in yields generally in the 20-40% range **(Table 17)**.



234

SCHEME 105

The work of Lemal focused primarily on the mechanistic features of this trapping process,[253,273] although he indicated isoprene (**202**) can be trapped to give 2,5-dihydro-3-methylthiolene 1-oxide (**203**) in 72% isolated yield.[253] A recent, less direct route for the Diels-Alder trapping of **S=O** has been carried out *via* complex **210**.[257]

In order to further explore this chemistry, a more convenient source of sulfur monoxide (**S=O**) was needed. We found that this can be achieved by thermal decomposition of adamantylideneadamantane thiirane 1-oxide (**178**) and bicyclo[3.3.1]-nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide (**179**).

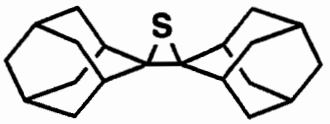
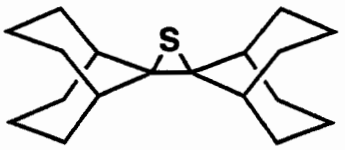
Thiirane 1-oxides **178** and **179** can be prepared from the oxidation of the corresponding thiiranes with *m*-CPBA in high isolated yield (92%). The later can be synthesized from the reaction of triphenylmethanesulfenyl chloride **65** (or its thio **61** and dithio **70** homolog) with the corresponding olefins in high isolated yield (95%).

7.1 SYNTHESIS OF ADAMANTYLIDENEADAMANTANE THIIRANE (116) AND BICYCLO[3.3.1]NONYLIDENEBICYCLO[3.3.1]NONANE THIIRANE (117)

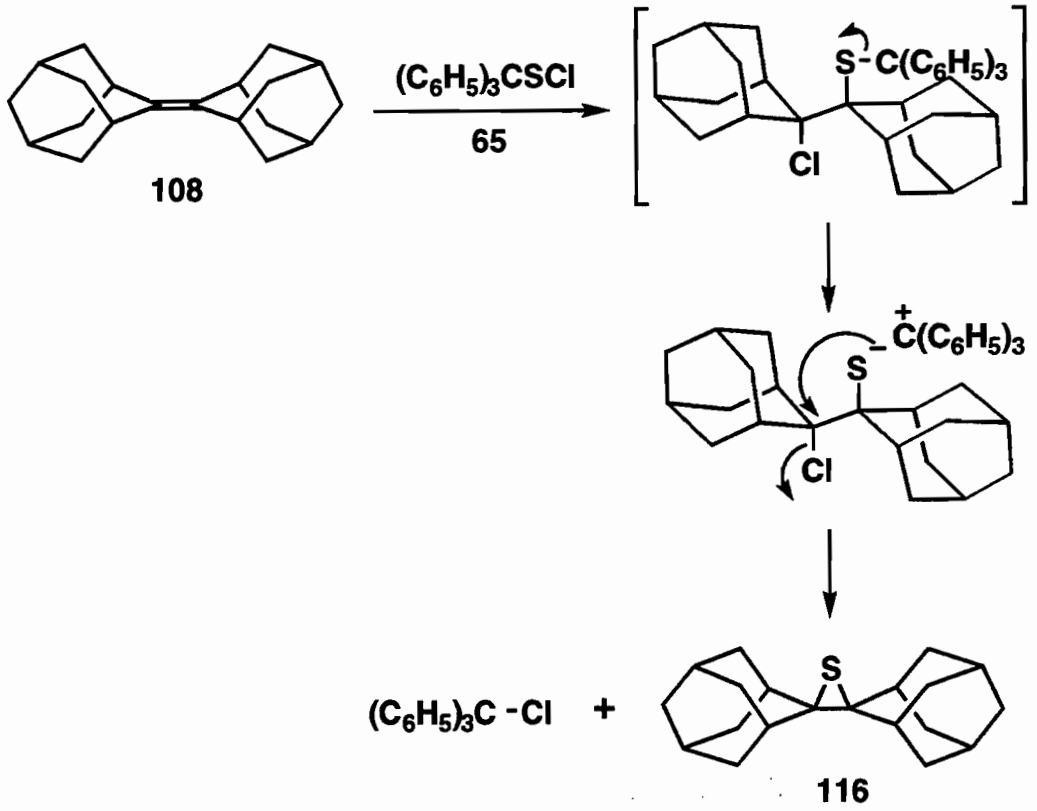
7.1.1 FROM TRIPHENYLMETHANESULFENYL CHLORIDE (65)

Thiiranes **116** and **117** were prepared by the reaction of triphenylmethanesulfenyl chloride **(65)** with the corresponding olefins in methylene chloride (CH_2Cl_2) solution under a nitrogen atmosphere at room temperature. The reaction was stirred for a certain time. Chromatography on silica gel afforded a solid product which upon crystallization from the appropriate solvent gave a pure product of the corresponding thiirane in high, isolated yield **(Table 19)**. In addition, chlorotriphenylmethane was also isolated in each case (*ca.* 58%).

Table 19: Episulfides 116 and 117 From Triphenylmethanesulfenyl Chloride (65): Melting Points, Reaction Times and % Isolated Yields

Entry	Thiirane	Time (h)	%Yield	Mp. (°C)
116		6	88	142-143
117		5	86	166-167

The most probable mechanism for the formation of thiirane **116** in the reaction of sulfenyl chloride **65** with olefin **108** is shown in **Scheme 106.**

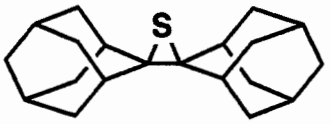
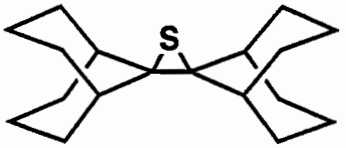


SCHEME 106

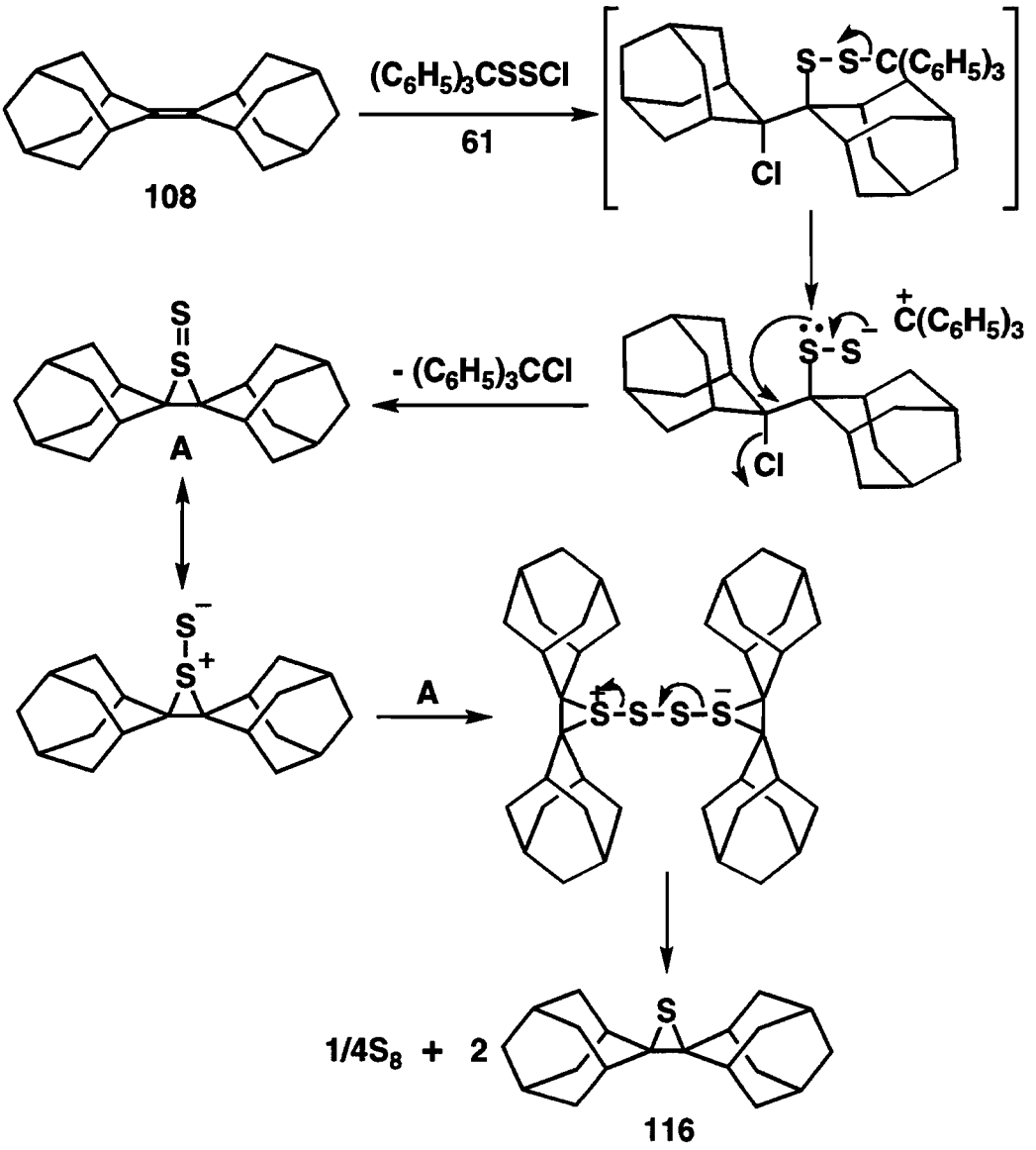
7.1.2 FROM TRIPHENYLMETHANETHIOSULFENYL CHLORIDE (61)

A solution of triphenylmethanethiosulfenyl chloride **(61)** in methylene chloride (CH_2Cl_2) was added dropwise at room temperature to a stirred solution of olefin **108** or **115** in CH_2Cl_2. The reaction was stirred for a certain time under a nitrogen atmosphere. Chromatography on silica gel afforded a solid product which upon crystallization from the appropriate solvent gave a pure product of the corresponding thiirane in high, isolated yield **(Table 20)**. In addition, elemental sulfur was isolated (*ca.* 52%) along with chlorotriphenylmethane (*ca.* 45%).

Table 20: Episulfides 116 and 117 From Triphenylmethanethiosulfenyl Chloride (61): Melting Points, Reaction Times and % Isolated Yields

Entry	Thiirane	Time (h)	%Yield	Mp. (°C)
116		4	92	142-143
117		4	91	166-167

A reasonable pathway explaining the formation of thiirane **116** in the reaction of thiosulfenyl chloride **61** with olefin **108** is shown in **Scheme 107**.

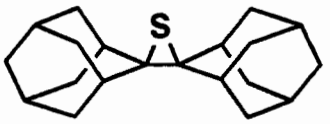
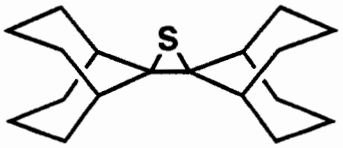


SCHEME 107

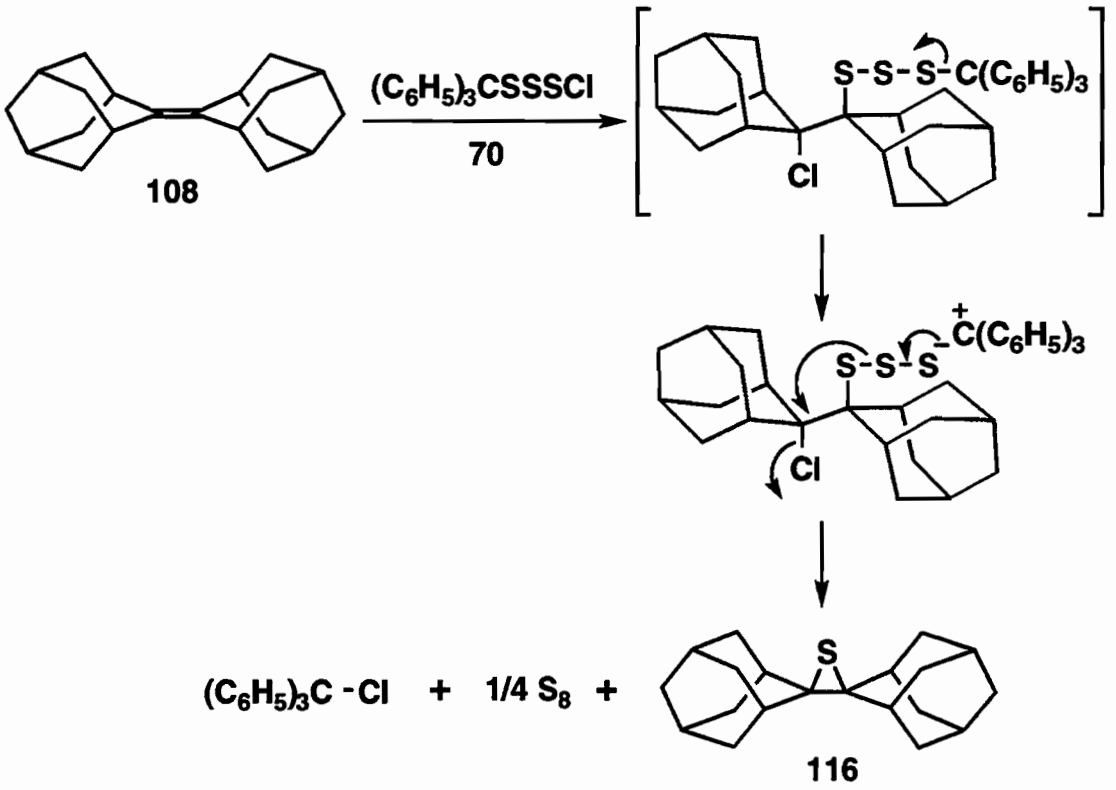
7.1.3 FROM TRIPHENYLMETHANEDITHIOSULFENYL CHLORIDE (70)

A solution of triphenylmethanedithiosulfenyl chloride **(70)** in methylene chloride (CH_2Cl_2) was added dropwise to a stirred solution of olefin **108** or **115** in CH_2Cl_2 at room temperature. The reaction was stirred for a certain time under a nitrogen atmosphere. Chromatography on silica gel afforded a solid product which upon crystallization from the appropriate solvent gave a pure product of the corresponding thiirane in high, isolated yield **(Table 21)**. In addition, elemental sulfur was isolated (*ca.* 55%) along with chlorotriphenylmethane (*ca.* 68%).

Table 21: Episulfides 116 and 117 From Triphenylmethanedithiosulfenyl Chloride (70): Melting Points, Reaction Times and % Isolated Yields

Entry	Thiirane	Time (h)	%Yield	Mp. (°C)
116		3	91	142-143
117		3.5	90	166-167

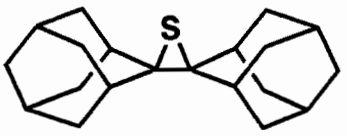
The most probable pathway for the formation of thiirane **116** in the reaction of dithiosulfenyl chloride **70** with olefin **108** is shown in **Scheme 108.**



SCHEME 108

The structure of episulfides **116** and **117** was established by ^{1}H and ^{13}C NMR as well as by mass spectrometry.

In addition, the x-ray crystallographic structure of **116** was reported[166] for the first time. The ORTEP[123] drawing of thiirane **116** is shown in **Figure 6.** Selected bond lengths and angles are given in **Table 22.**



116

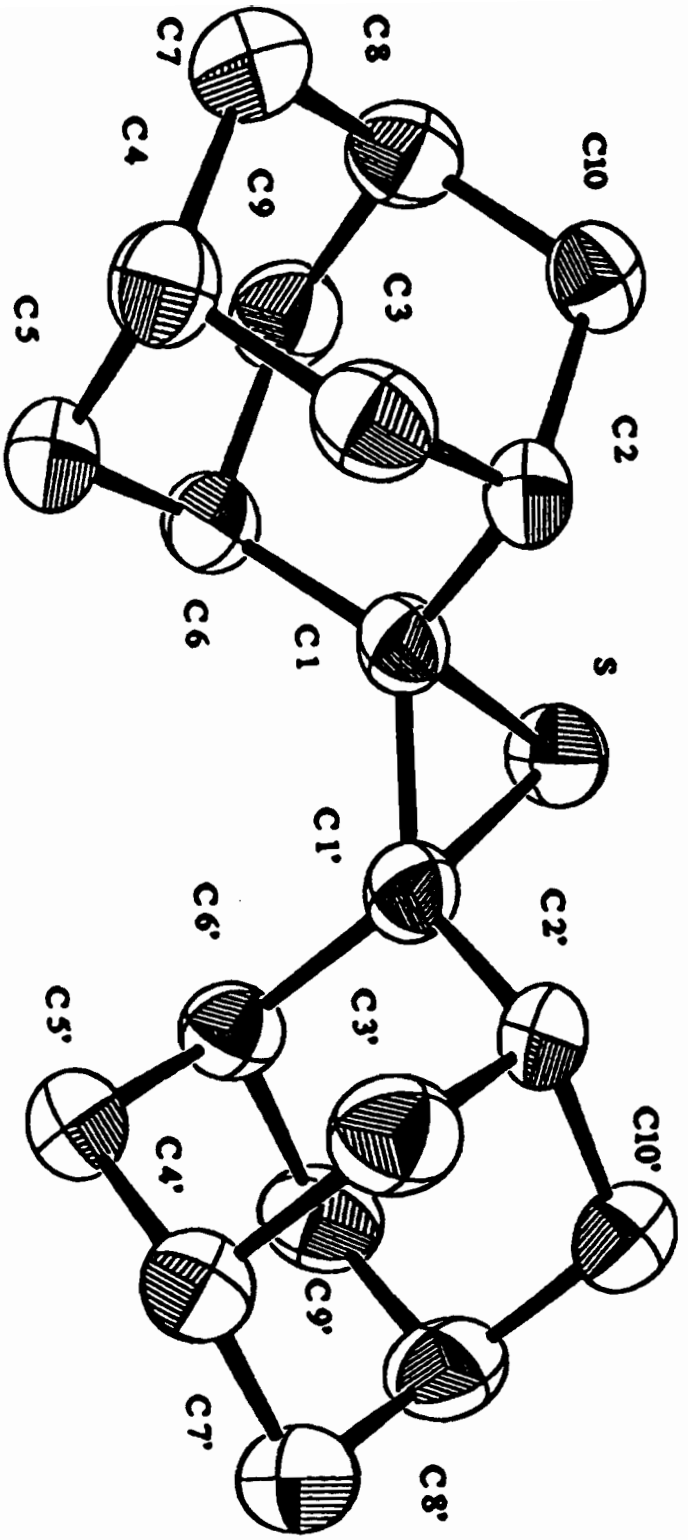


Figure 6: ORTEP Representation of Adamantylideneadamantane Thiirane (116)

Table 22: Selected Bond Lengths and Bond Angles for Adamantylideneadamantane Thiirane (116)

Bond Lengths (Å)	
S-C(1)	1.8455(19)
C(1)-C(2)	1.525(3)
C(1)-C(1')	1.503(3)
Bond Angles (°)	
C(1)-S-C(1')	48.09(8)
S-C(1)-C(2)	114.57(13)
S-C(1)-C(1')	65.83(10)
C(2)-C(1)-C(6)	109.32(16)
C(2)-C(1)-C(1')	122.30(16)
Dihedral Angles (°)	
C(1')-S-C(1)-C(2)	-116.0(1)
S-C(1)-C(2)-C(3)	170.6(2)
S-C(1)-C(1')-C(6')	104.8(1)
S-C(1)-C(2)-C(10)	-70.2(1)

Thiiranes **116** and **117** prepared in this maner can be stored at room temperature for a long time with no apparent decomposition or loss in yields during their oxidation to the corresponding episulfoxides.

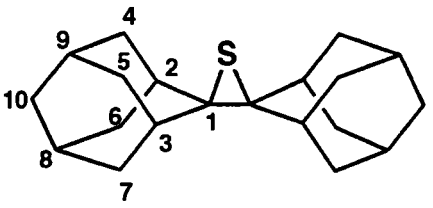
Thermal decomposition of episulfides **116** and **117** in refluxing ethyl acetate for 15 h under a nitrogen atmosphere afforded the corresponding olefins **108** and **115** respectively, in a yield of 98% along with elemental sulfur (68%). In addition, **116** and **117** were completely decomposed when the mixture was refluxed for 2 h in toluene solution .

When the above reactions were carried out in the presence of 2,3-dimethyl-1,3-butadiene **(62)**, the same products were obtained (elemental sulfur and an olefin). No evidence was found for the trapping of diatomic sulfur by diene **62**. It would appear that the concatenation mechanism of sulfur loss from episulfides is operative.[23a]

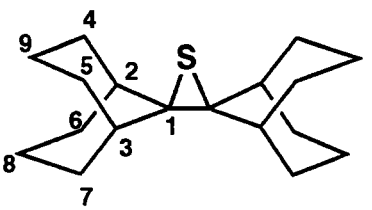
Episulfide **116** was previously prepared by Nakayama and coworkers[160] from the treatment of elemental sulfur with olefin **108**, but the yield was low. The authors[160] reported that, episulfide **116** contained 10 peaks in the ^{13}C NMR spectra and the Mp. was 153-154 °C.

In contrast, we found that thiirane **116** shows only 7 peaks in ^{13}C NMR spectra. This can be explained by the fact, revealed by x-ray analysis, that there is a plane of symmetry passing through S, C_1, C_4, C_7 and C_8 **(Figure 6)**. This symmetry makes C_2 and C_6; C_3 and C_5; C_9 and C_{10} equivalent. In addition, we found that episulfide **116** has lower Mp. (142-143 °C) than previously reported by Nakayama.[160]

The assignments of ^{13}C NMR chemical shifts relative to tetramethylsilane of episulfides are reported in **Table 23**. The carbon atoms were identified using the following numbering system.



116



117

Table 23: Assignments of ^{13}C Chemical Shifts for Episulfide Adducts 116 and 117

Entry	C1	C2,C3	C4,C5	C6,C7	C8	C9	C10
116	71.70	38.62	38.41	37.78	34.95	27.70	27.12
117	70.43	34.76	33.76	31.92	21.26	20.75	-

7.2 SYNTHESIS OF ADAMANTYLIDENEADAMANTANE THIIRANE 1-OXIDE (178)

Thiirane 1-oxide **178** was prepared by *m*-CPBA oxidation of episulfide **116** in methylene chloride solution under a nitrogen atmosphere at -78 °C. Recrystallization from *n*-pentane gave a pure product of thiirane 1-oxide **178** in an isolated yield of 99% **(Scheme 80)**.

116 **178**

SCHEME 80

The structure of thiirane 1-oxide **178** was established by ^{1}H and ^{13}C NMR, mass spectrometry as well as by x-ray analysis.

The electron impact mass spectrum of thiirane 1-oxide **178** is discussed below and the fragmentation pattern is shown in **Figure 7**.

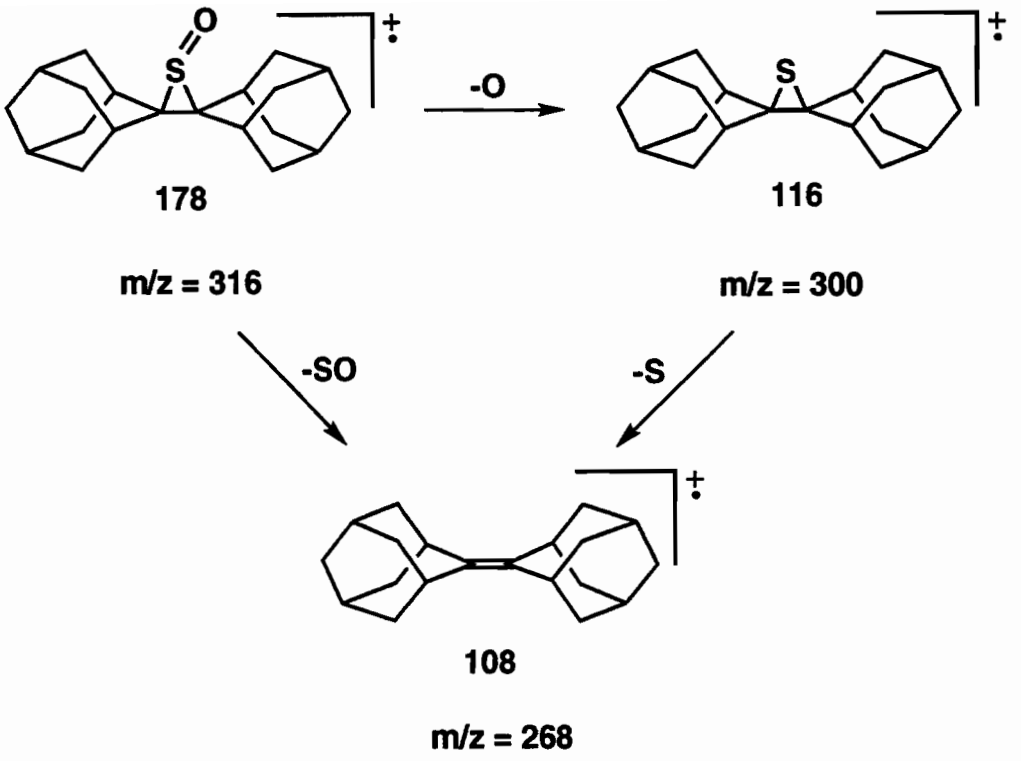
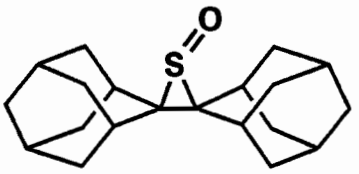


Figure 7: Mass Spectral Fragmentation Pattern for Adamantylideneadamantane Thiirane 1-Oxide (178)

The signal at m/z = 316 corresponds to the molecular ion. When the molecule fragments, the loss of an oxygen atom gives a signal at m/z = 300. Further loss of a sulfur atom results in a signal at m/z = 268, which corresponds to the mass of the starting olefin **108**.

In parent episulfoxides, typical C-C bond lengths fall in the range 1.37Å to 1.60Å and C-S bonds range from 1.37Å to 1.92Å. The C-C bond length in thiirane 1-oxide **178** is 1.505Å, which suggests the presence of a partial double bond character, since a typical sp^3-sp^3 C-C bond length is about 1.55Å and a C=C bond length is 1.34Å. The bond lengths of S-O; C-S and bond angles of C-S-C; C-C-S and O-S-C in the three-membered ring moiety of episulfoxides **178** and **184** where found to be quite similar as can be seen from **Tables 15** and **24**.

The x-ray crystallographic structure of **178** was reported[166] for the first time. The ORTEP[123] drawing of thiirane 1-oxide **178** is shown in **Figure 8.** Selected bond lengths and angles are given in **Table 24.**



178

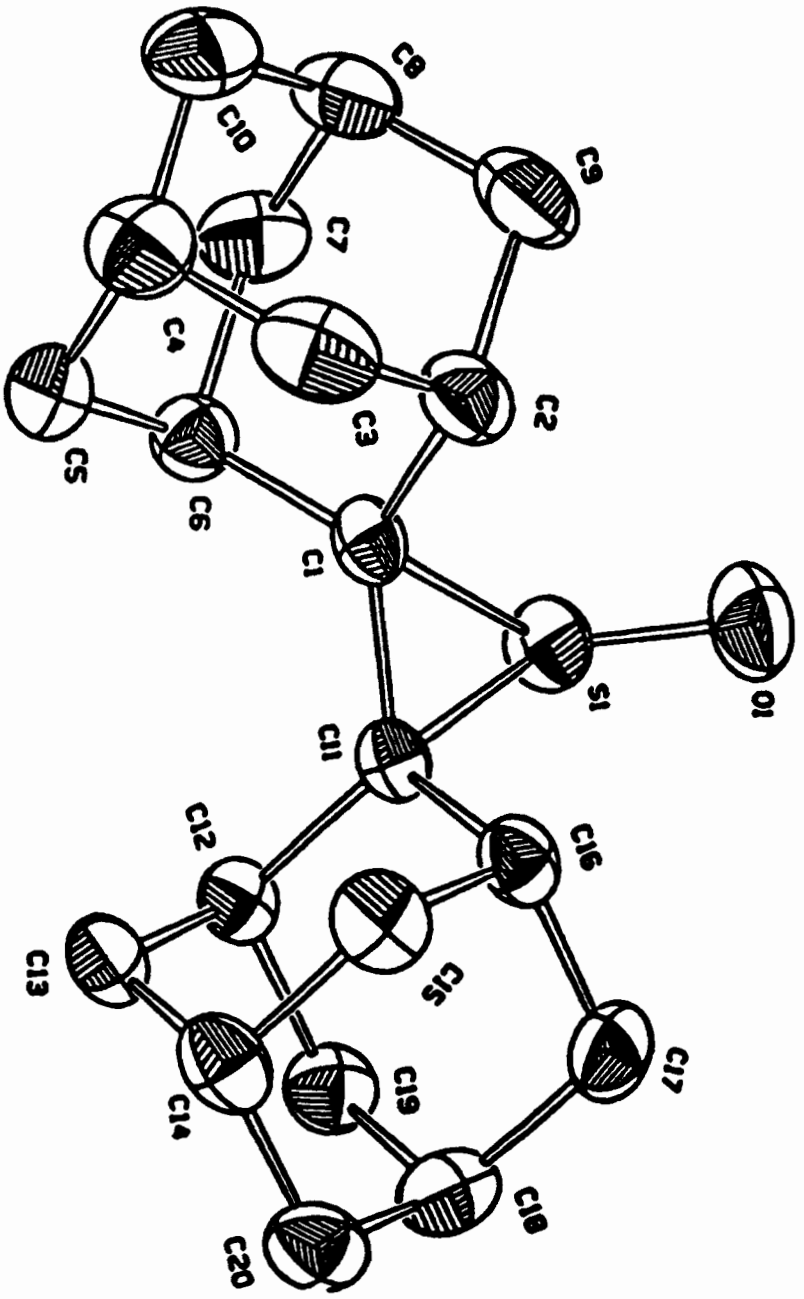
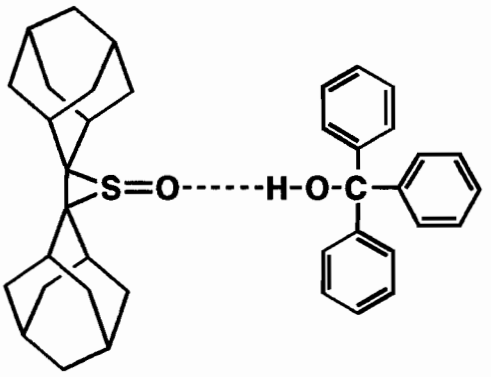


Figure 8: ORTEP Representation of Adamantylideneadamantane Thiirane 1-Oxide (178)

Table 24: Selected Bond Lengths and Bond Angles for Adamantylideneadamantane Thiirane 1-Oxide (178)

Bond Lengths (Å)	
S(1)-O(1)	1.491(2)
S(1)-C(1)	1.865(3)
C(1)-C(11)	1.505(3)
C(1)-C(2)	1.515(4)
Bond Angles (°)	
C(1)-S(1)-C(11)	47.7(1)
S(1)-C(1)-C(11)	66.0(1)
O(1)-S(1)-C(1)	111.2(1)
S(1)-C(1)-C(2)	113.7(2)
Dihedral Angles (°)	
S(1)-C(1)-C(11)-C(16)	102.9(2)
O(1)-S(1)-C(1)-C(2)	16.4(2)
O(1)-S(1)-C(11)-C(1)	99.8(2)
C(1)-S(1)-C(11)-C(16)	-116.7(2)

It is noteworthy to mention that we performed an x-ray analysis of a sample expected to be thiirane 1-oxide **178**. A structure of adduct **235** was observed which formed an interaction between thiirane 1-oxide **178** and triphenylmethanecarbinol through hydrogen-bonding.



235

It would be noted that, ^{13}C NMR shows this product to be pure. We feel that the finding of the triphenylmethanecarbinol was a coincidental choice of crystals containing a small impurity.

Triphenylmethanecarbinol was obtained from the hydrolysis of chlorotriphenyl-methane during the separation of the crude product mixture by column chromatography.

The ORTEP[123] drawing of adduct **235** is shown in **Figure 9**. Selected bond lengths and angles are given in **Table 25**.

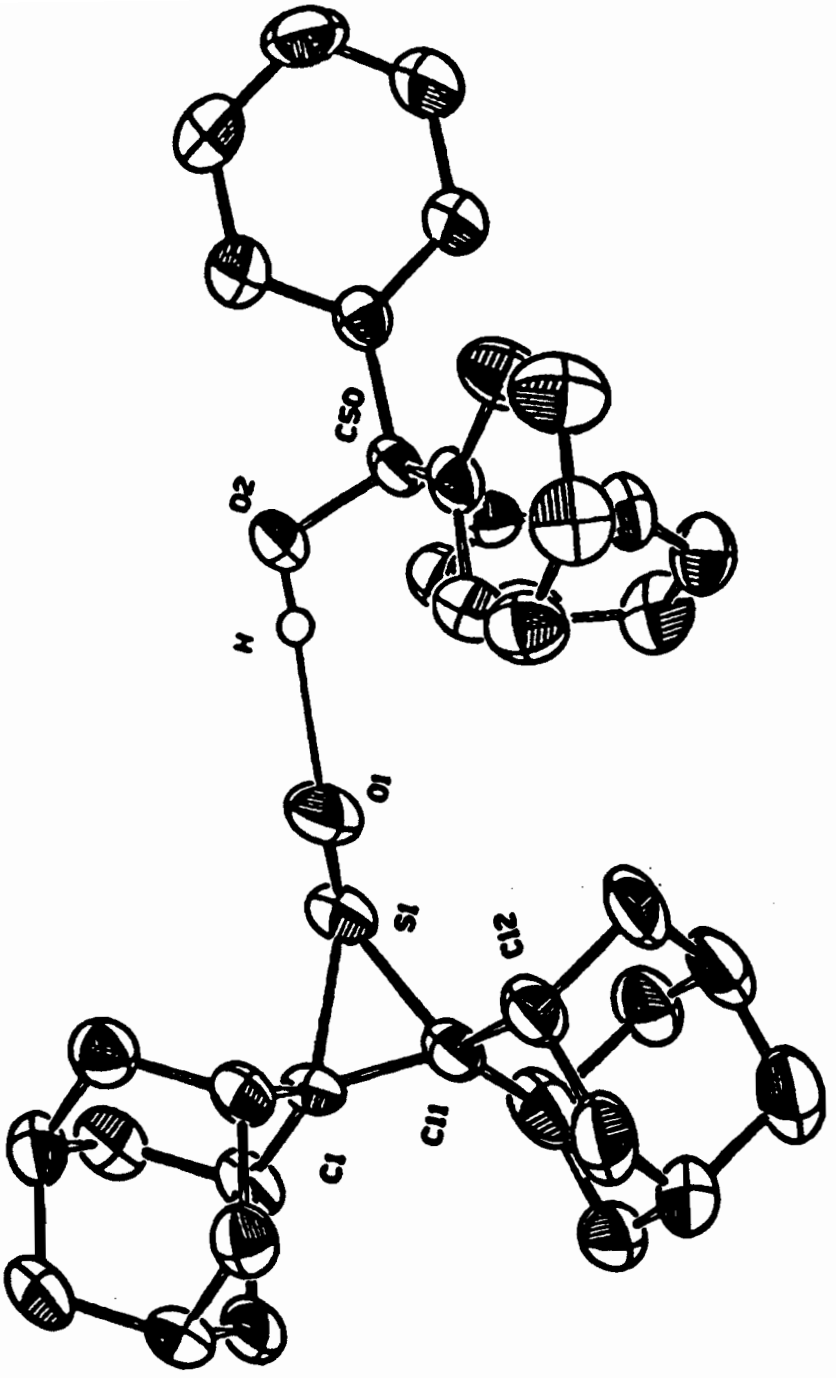


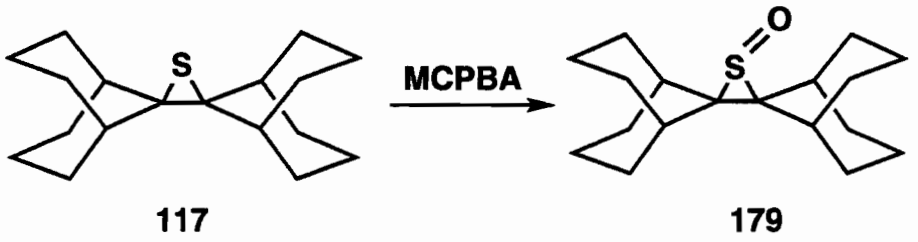
Figure 9: ORTEP Representation of Adduct 235

Table 25: Selected Bond Lengths and Bond Angles for Adduct 235

Bond Lengths (Å)	
S(1)-O(1)	1.509(3)
S(1)-C(1)	1.868(4)
C(1)-C(11)	1.512(5)
O(1)-H	1.91(4)
O(2)-H	0.87(4)
Bond Angles (°)	
C(1)-S(1)-C(11)	47.7(2)
S(1)-C(1)-C(11)	66.1(2)
O(1)-S(1)-C(1)	109.8(2)
S(1)-O(1)-H	133.6(14)
O(1)-H-O(2)	177.0(4)
Dihedral Angles (°)	
S(1)-C(1)-C(11)-C(12)	102.6(4)
O(1)-S(1)-C(1)-C(2)	17.0(3)
O(1)-S(1)-C(11)-C(1)	99.2(2)
C(1)-S(1)-C(11)-C(12)	-116.9(4)

7.3 SYNTHESIS OF BICYCLO[3.3.1]NONYLIDENEBICYCLO[3.3.1]NONANE-THIIRANE 1-OXIDE (179)

Thiirane 1-oxide **179** was prepared in the same way as that of **178**. Thiirane **117** was reacted with *m*-CPBA in methylene chloride solution at -78 °C under a nitrogen atmosphere to give thiirane 1-oxide **179** in high isolated yield (98%) **(Scheme 81)**.



SCHEME 81

The structure of thiirane 1-oxide **179** was established by ^{1}H and ^{13}C NMR as well as by mass spectrometry.

The electron impact mass spectrum of thiirane 1-oxide **179** is discussed below and the fragmentation pattern is shown in **Figure 10**.

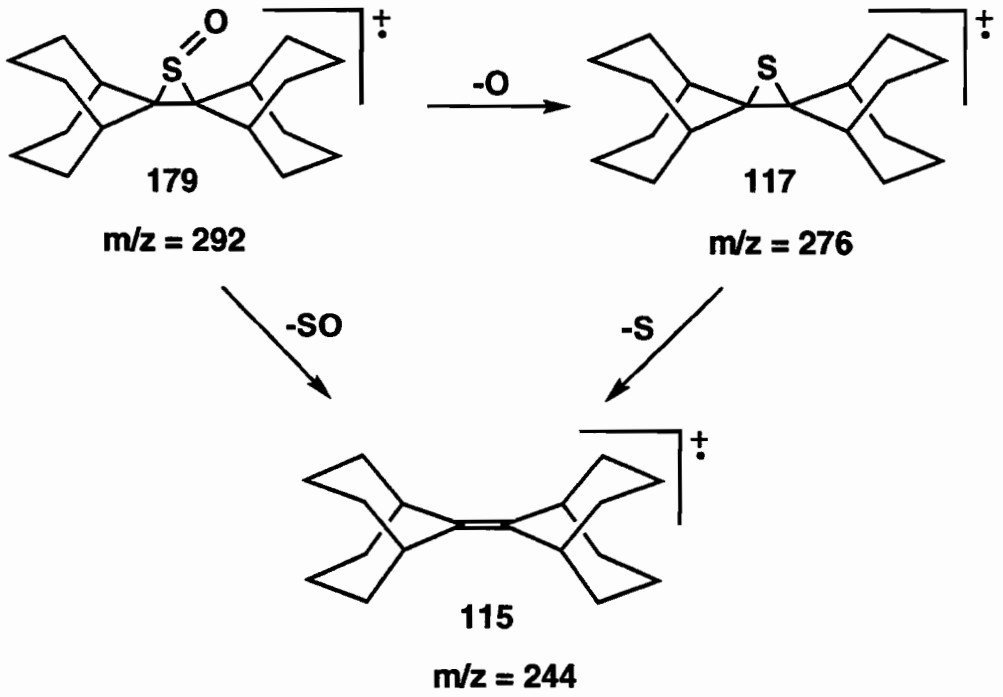
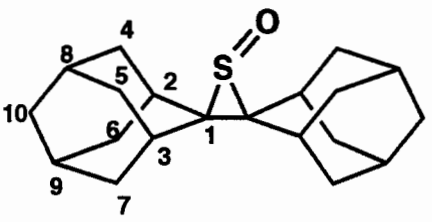


Figure 10: Mass Spectral Fragmentation Pattern for Bicyclo[3.3.1]-nonylidenebicyclo[3.3.1]nonane Thiirane 1-Oxide (179)

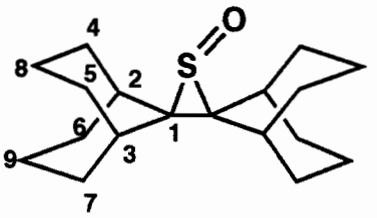
The signal at m/z = 292 corresponds to the molecular ion. When the molecule fragments, the loss of an oxygen atom gives a signal at m/z = 276. Further loss of a sulfur atom results in a signal at m/z = 244, which corresponds to the mass of the starting olefin **115**.

In contrast to thiirane **116**, we found that thiirane 1-oxide **178** shows 10 peaks in ^{13}C NMR spectra. This can be explained by x-ray analysis which revealed that the tetrahedron geometry of the sulfur atom shows the chemical shifts for all of the carbon atoms in the adamantyl-skeleton moiety to be different **(Figure 8)**.

The assignments of ^{13}C NMR chemical shifts relative to tetramethylsilane of thiirane 1-oxides **178** and **179** are reported in **Table 26**. The carbon atoms were identified using the following numbering system.



178



179

Table 26: Assignments of ^{13}C Chemical Shifts for Thiirane 1-Oxides **178** and **179**

Entry	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
178	72.88	37.62	37.56	37.20	37.12	36.16	30.02	27.58	27.39	27.02
179	71.52	32.35	31.31	30.78	30.34	30.07	27.45	21.38	21.28	-

7.4 TRAPPING OF SULFUR MONOXIDE (SO) FROM THERMAL DECOMPOSITION OF THIIRANE 1-OXIDES 178 AND 179

In the literature there are only three reaction systems reported which generate and trap sulfur monoxide in the presence of 1,3-dienes; the yields are low. Moreover, these methods have some limitations.

The major problem in the case of Dodson,[252,254] Lemal,[253] Chao[255] and Heyke[257] procedures is that ethylene episulfoxide (**184**) is unstable at room temperature, has a vile odor and causes burns on contact with the skin.

In the case of the procedure of Chow[256] the most important limitation is in the preparation of sulfoxide **208**; in addition, the authors could not isolate the corresponding episulfoxide **209** which they thought could have been obtained from the thermolysis of sulfoxide **208 (Scheme 86)**. The yield of the trapped adduct was low in each case. It is noteworthy to mention that *trans*-2,3-diphenyl thiirane 1-oxide has been shown to transfer sulfur monoxide to ylides in low (11-19%) yield.[281]

In contrast, thiirane 1-oxides **178** and **179** are very stable even if they are exposed to the atmospheric moisture for several days. They are crystalline and easy to prepare. In addition, we found that sulfur monoxide can be easily generated and trapped smoothly in high, isolated yields to form 2,5-dihydrothiophene 1-oxide through thermal decomposition of **178** and **179** in the presence of 1,3-dienes.

7.4.1 GENERAL PROCEDURE

The general procedure used for the reaction of thiirane 1-oxides with 1,3-dienes is as follows: a solution of the diene and thiirane 1-oxide in an appropriate solvent was refluxed for a certain time under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 15 to 25% ethyl acetate in hexane as eluent.

The first fraction was isolated in near quantitative yield by the same eluent and was identified as the corresponding olefin (**108** from **178**; **115** from **179**). By eluting with

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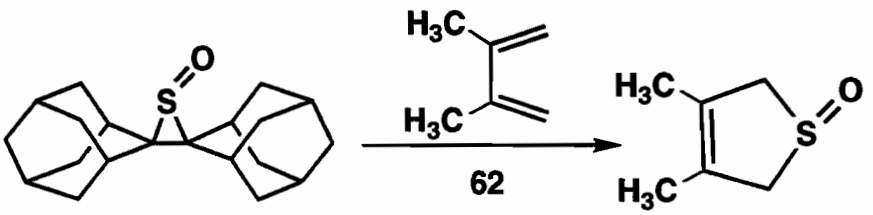
281 B. F. Bonini, G. Maccagnani, G. Mazzanti, P. Pedrini and P. Piccinelli, *J. Chem. Soc., Perkin Trans 1*, 1720 (1979).

methanol, the second fraction was isolated and identified as the corresponding 2,5-dihydrothiophene 1-oxides as oily, pure products. The yields are quite high compared to those in the literature.

7.4.2 2,3-DIMETHYL-1,3-BUTADIENE (62): FORMATION OF 2,5-DIHYDRO-3,4-DIMETHYLTHIOPHENE 1-OXIDE (200)

7.4.2.1 FROM ADAMANTYLIDENEADAMANTANE THIIRANE 1-OXIDE (178)

The reaction of equimolar amounts of 2,3-dimethyl-1,3-butadiene **(62)** and thiirane 1-oxide **178** in toluene solution gave an oily product of 2,5-dihydro-3,4-dimethyl-thiophene 1-oxide **(200)** in 74% isolated yield **(Scheme 109)**. The identity of sulfoxide **200** was confirmed by ^{1}H and ^{13}C NMR as well as by mass spectrometry.



178 **200**

SCHEME 109

The decomposition was further investigated by varying the reaction conditions hoping to maximize the yield of the trapped adduct **200**. When the reaction was repeated in a variety of solvents, varying temperature, time and concentration, adduct **200** was trapped and isolated in an optimized yield of 80% **(Table 27)**.

Table 27: Summary of Sulfur Monoxide Trapping Experiments of 2,3-Dimethyl-1,3-butadiene (62) with Adamantylidene-adamantane Thiirane 1-Oxide (178)

R[e]	Solvent	Temp. (°C)	Time	%Yield*
1 : 1	$CHCl_3$	61	10 days	N. R.
1 : 1	EtOAc	77	10 days	N. R.
1 : 1	CH_3CN	81	10 days	N. R.
1 : 1	Toluene	80	10 days	N. R.
1 : 3	Toluene	110	12 h	73
1 : 1	Toluene	110	12 h	74
3 : 1	Toluene	110	12 h	80
1 : 3	C_6H_5Cl	132	8 h	30
1 : 1	C_6H_5Cl	132	8 h	30
3 : 1	C_6H_5Cl	132	8 h	33
1 : 3	Xylene	138	8 h	32
1 : 1	Xylene	138	8 h	34
3 : 1	Xylene	138	8 h	37

Table 27: continued

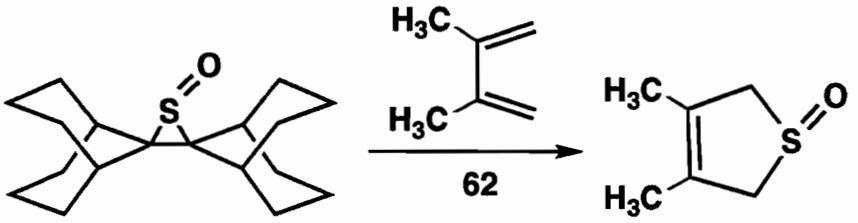
R^e	Solvent	Temp. (°C)	Time	%Yield*
1 : 3	Decane	135	8 h	33
1 : 1	Decane	135	8 h	34
3 : 1	Decane	135	8 h	36
1 : 1	Decane	174	5 h	12
3 : 1	Toluene	110	8 h	70
3 : 1	Toluene	110	16 h	76
3 : 1	Xylene	110	12 h	69
3 : 1	Xylene	138	12 h	35
3 : 1	Xylene	138	20 h	10
3 : 1	Xylene	138	35 h	0
3 : 1	Decane	110	12 h	67

R^e refers to the molar ratio of thiirane 1-oxide **178** to 2,3-dimethyl-1,3-butadiene **(62)**.

* refers to 2,5-dihydro-3,4-dimethylthiophene 1-oxide **(200)**.

7.4.2.2 FROM BICYCLO[3.3.1]NONYLIDENEBICYCLO[3.3.1]NONANE THIIRANE 1-OXIDE (179)

The reaction of 2,3-dimethyl-1,3-butadiene **(62)** with an equimolar amount of thiirane 1-oxide **179** in toluene solution gave an oily product of 2,5-dihydro-3,4-dimethylthiophene 1-oxide **(200)** in 71% isolated yield **(Scheme 110)**. The structure of sulfoxide **200** was established by ^{1}H and ^{13}C NMR as well as by mass spectrometry.



179 **200**

SCHEME 110

The decomposition was further investigated by varying the reaction conditions hoping to maximize the yield of the trapped adduct **200**. When the reaction was repeated in a variety of solvents, varying temperature, time and concentration, adduct **200** was trapped and isolated in an optimized yield of 82% **(Table 28)**.

Table 28: Summary of Sulfur Monoxide Trapping Experiments of 2,3-Dimethyl-1,3-butadiene (62) with Bicyclo[3.3.1]-nonylidenebicyclo[3.3.1]nonane Thiirane 1-Oxide (179)

R^f	Solvent	Temp. (°C)	Time	%Yield*
1 : 1	$CHCl_3$	61	7 days	N. R.
1 : 1	EtOAc	77	7 days	N. R.
1 : 1	Toluene	80	8 days	N. R.
1 : 3	Toluene	110	8 h	75
1 : 1	Toluene	110	8 h	71
3 : 1	Toluene	110	8 h	82
1 : 3	C_6H_5Cl	132	5 h	39
1 : 1	C_6H_5Cl	132	5 h	34
3 : 1	C_6H_5Cl	132	5 h	45
1 : 3	Xylene	138	5 h	40
1 : 1	Xylene	138	5 h	36
3 : 1	Xylene	138	5 h	46
1 : 1	Decane	174	4 h	17

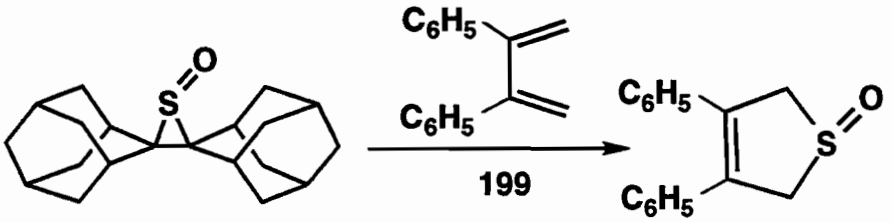
R^f refers to the molar ratio of thiirane 1-oxide **179** to 2,3-dimethyl-1,3-butadiene **(62)**.

* refers to 2,5-dihydro-3,4-dimethylthiophene 1-oxide **(200)**.

7.4.3 2,3-DIPHENYL-1,3-BUTADIENE (199): FORMATION OF 2,5-DIHYDRO-3,4-DIPHENYLTHIOPHENE 1-OXIDE (201)

7.4.3.1 FROM ADAMANTYLIDENEADAMANTANE THIIRANE 1-OXIDE (178)

The reaction of 2,3-diphenyl-1,3-butadiene **(199)** with an equimolar amount of thiirane 1-oxide **178** was carried out in toluene solution. Chromatography of the crude product gave 64% of pure 2,5-dihydro-3,4-diphenylthiophene 1-oxide **(201)** **(Scheme 111)**. The structure of sulfoxide **201** was established by ^{1}H and ^{13}C NMR as well as by mass spectrometry.



178 **201**

SCHEME 111

The decomposition was further investigated by varying the reaction conditions in a variety of ways **(Table 29)**.

Table 29: Summary of Sulfur Monoxide Trapping Experiments of 2,3-Diphenyl-1,3-butadiene (199) with Adamantylidene-adamantane Thiirane 1-Oxide (178)

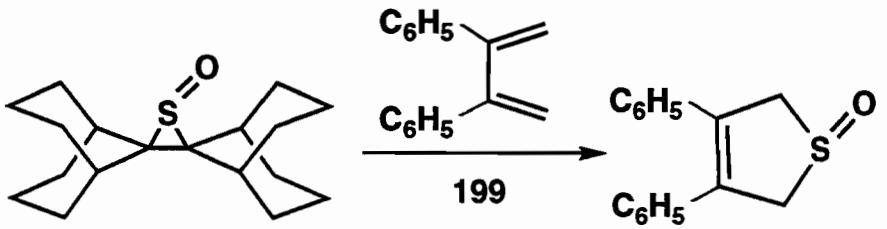
Rg	Solvent	Temp. (°C)	Time	%Yield*
1 : 1	$CHCl_3$	61	10 days	N. R.
1 : 1	EtOAc	77	10 days	N. R.
1 : 1	CH_3CN	81	10 days	N. R.
1 : 1	Toluene	80	10 days	N. R.
1 : 1	Toluene	110	24 h	64
1 : 3	Toluene	110	24 h	65
3 : 1	Toluene	110	24 h	70
3 : 1	Toluene	110	72 h	70
1 : 1	C_6H_5Cl	132	15 h	25
3 : 1	C_6H_5Cl	132	15 h	27
1 : 1	Xylene	138	15 h	26
3 : 1	Xylene	138	15 h	29

Rg refers to the molar ratio of thiirane 1-oxide **178** to 2,3-diphenyl-1,3-butadiene **(199)**.

* refers to 2,5-dihydro-3,4-diphenylthiophene 1-oxide **(201)**.

7.4.3.2 FROM BICYCLO[3.3.1]NONYLIDENEBICYCLO[3.3.1]NONANE THIIRANE 1-OXIDE (179)

The reaction of 2,3-diphenyl-1,3-butadiene **(199)** with an equimolar amount of thiirane 1-oxide **179** was carried out in toluene solution. Chromatography of the crude product gave 68% of pure 2,5-dihydro-3,4-diphenylthiophene 1-oxide **(201)** **(Scheme 112)**. The identity of sulfoxide **201** was confirmed by ^{1}H and ^{13}C NMR as well as by mass spectrometry.



179 **201**

SCHEME 112

The decomposition was further investigated by varying the reaction conditions in a variety of ways **(Table 30)**.

Table 30: Summary of Sulfur Monoxide Trapping Experiments of 2,3-Diphenyl-1,3-butadiene (199) with Bicyclo[3.3.1]-nonylidenebicyclo[3.3.1]nonane Thiirane 1-Oxide (179)

R^h	Solvent	Temp. (°C)	Time	%Yield*
1 : 1	$CHCl_3$	61	8 days	N. R.
1 : 1	EtOAc	77	8 days	N. R.
1 : 1	Toluene	80	8 days	N. R.
1 : 3	Toluene	110	12 h	70
1 : 1	Toluene	110	12 h	68
3 : 1	Toluene	110	12 h	73
3 : 1	Toluene	110	36 h	75
1 : 1	C_6H_5Cl	132	8 h	32
3 : 1	C_6H_5Cl	132	8 h	38
1 : 1	Xylene	138	8 h	33
3 : 1	Xylene	138	8 h	40

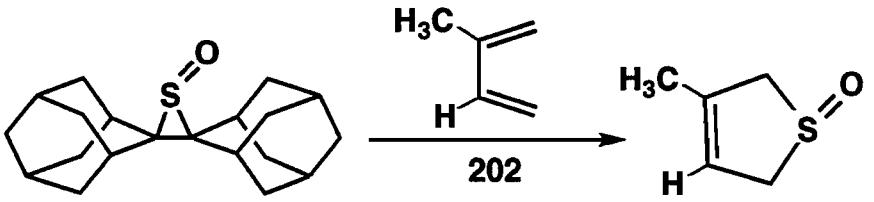
R^h refers to the molar ratio of thiirane 1-oxide **179** to 2,3-diphenyl-1,3-butadiene **(199)**.

* refers to 2,5-dihydro-3,4-diphenylthiophene 1-oxide **(201)**.

7.4.4 ISOPRENE (202): FORMATION OF 2,5-DIHYDRO-3-METHYL-THIOLENE 1-OXIDE (203)

7.4.4.1 FROM ADAMANTYLIDENEADAMANTANE THIIRANE 1-OXIDE (178)

Equimolar amounts of isoprene (**202**) and thiirane 1-oxide **178** were boiled in toluene solution for 25 h under a nitrogen atmosphere. Chromatography of the crude product gave 58% of pure 2,5-dihydro-3-methylthiolene 1-oxide (**203**) (**Scheme 113**). The identity of sulfoxide **203** was confirmed by ^{1}H and ^{13}C NMR as well as by mass spectrometry.



178 **203**

SCHEME 113

When the reaction was repeated in a variety of solvents, varying temperature, time and concentration, adduct **203** was trapped and isolated in an optimized yield of 69% (**Table 31**).

Table 31: Summary of Sulfur Monoxide Trapping Experiments of Isoprene (202) with Adamantylideneadamantane Thiirane 1-Oxide (178)

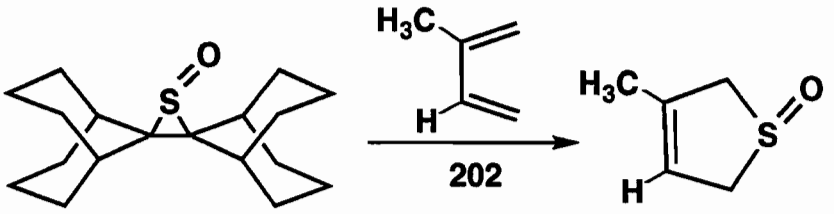
R^i	Solvent	Temp. (°C)	Time	% Yield*
1 : 1	Toluene	80	10 days	N. R.
1 : 3	Toluene	110	36 h	62
1 : 1	Toluene	110	36 h	58
3 : 1	Toluene	110	36 h	69
1 : 1	C_6H_5Cl	132	20 h	30
3 : 1	C_6H_5Cl	132	20 h	35
1 : 1	Xylene	138	20 h	33
3 : 1	Xylene	138	20 h	40
3 : 1	Xylene	110	36 h	64
3 : 1	Decane	135	20 h	37
3 : 1	Decane	174	20 h	12

R^i refers to the molar ratio of thiirane 1-oxide **178** to isoprene **(202)**.

* refers to 3-methyl-2,5-dihydrothiolene 1-oxide **(203)**.

7.4.4.2 FROM BICYCLO[3.3.1]NONYLIDENEBICYCLO[3.3.1]NONANE THIIRANE 1-OXIDE (179)

Equimolar amounts of isoprene (**202**) and thiirane 1-oxide **179** were boiled in toluene solution for 20 h under a nitrogen atmosphere. Chromatography of the crude product gave 61% of pure 2,5-dihydro-3-methylthiolene 1-oxide (**203**) **(Scheme 114)**. The structure of sulfoxide **203** was established by ^{1}H and ^{13}C NMR as well as by mass spectrometry.



179 **203**

SCHEME 114

When the reaction was repeated in a variety of solvents, varying temperature, time and concentration, adduct **203** was trapped and isolated in an optimized yield of 72% **(Table 32)**.

Table 32: Summary of Sulfur Monoxide Trapping Experiments of Isoprene (202) with Bicyclo[3.3.1]nonylidenebicyclo-[3.3.1]nonane Thiirane 1-Oxide (179)

R^j	Solvent	Temp. (°C)	Time	%Yield*
1 : 1	Toluene	80	6 days	N. R.
1 : 3	Toluene	110	20 h	66
1 : 1	Toluene	110	20 h	61
3 : 1	Toluene	110	20 h	72
1 : 1	C_6H_5Cl	132	15 h	32
3 : 1	C_6H_5Cl	132	15 h	38
1 : 1	Xylene	138	15 h	36
3 : 1	Xylene	138	15 h	43
3 : 1	Xylene	110	20 h	65
3 : 1	Decane	135	15 h	40
3 : 1	Decane	174	15 h	15

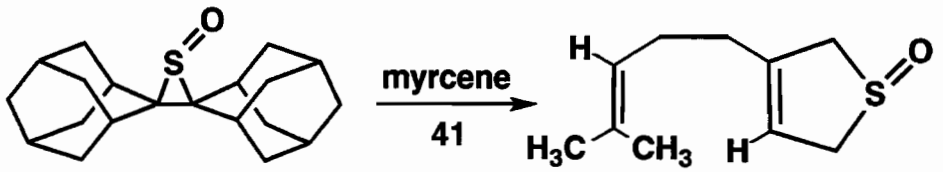
R^j refers to the molar ratio of thiirane 1-oxide **179** to isoprene **(202)**.

* refers to 3-methyl-2,5-dihydrothiolene 1-oxide **(203)**.

7.4.5 MYRCENE (41): FORMATION OF 3-(4'-METHYL-3'-PENTENYL)-2,5-DIHYDROTHIOPHENE 1-OXIDE (233)

7.4.5.1 FROM ADAMANTYLIDENEADAMANTANE THIIRANE 1-OXIDE (178)

Equimolar amounts of myrcene (**41**) and thiirane 1-oxide **178** were carried out in toluene solution under reflux for 16 h. Chromatography on silica gel afforded 40% of pure 3-(4'-methyl-3'-pentenyl)-2,5-dihydrothiophene 1-oxide (**233**) as an oily product (**Scheme 115**). The identity of sulfoxide **233** was confirmed by ^{1}H and ^{13}C NMR as well as by mass spectrometry.



178 **233**

SCHEME 115

When the reaction was repeated in a variety of solvents, varying temperature, time and concentration, adduct **233** was trapped and isolated in an optimized yield of 52% (**Table 33**).

Table 33: Summary of Sulfur Monoxide Trapping Experiments of Myrcene (41) with Adamantylideneadamantane Thiirane 1-Oxide (178)

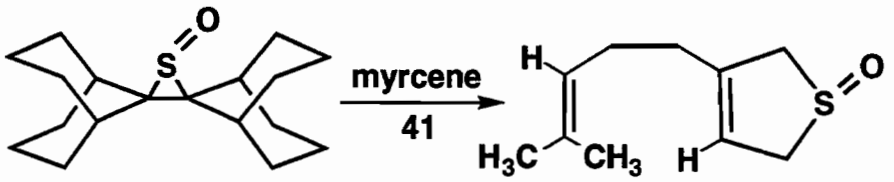
R^k	Solvent	Temp. (°C)	Time	%Yield*
1 : 1	$CHCl_3$	61	10 days	N. R.
1 : 1	EtOAc	77	10 days	N. R.
1 : 1	CH_3CN	81	10 days	N. R.
1 : 1	Toluene	80	10 days	N. R.
1 : 3	Toluene	110	16 h	46
1 : 1	Toluene	110	16 h	40
3 : 1	Toluene	110	16 h	52
1 : 1	C_6H_5Cl	132	12 h	23
3 : 1	C_6H_5Cl	132	12 h	27
1 : 1	Xylene	138	12 h	22
3 : 1	Xylene	138	12 h	28
3 : 1	Xylene	110	16 h	48
3 : 1	Decane	135	12 h	30
3 : 1	Decane	174	8 h	15

R^k refers to the molar ratio of thiirane 1-oxide **178** to myrcene **(41)**.

* refers to 3-(4'-methyl-3'-pentenyl)-2,5-dihydrothiophene 1-oxide **(233)**.

7.4.5.2 FROM BICYCLO[3.3.1]NONYLIDENEBICYCLO[3.3.1]NONANE THIIRANE 1-OXIDE (179)

Equimolar amounts of myrcene **(41)** and thiirane 1-oxide **179** were carried out in toluene solution under reflux for 14 h. Chromatography on silica gel afforded 47% of pure 3-(4'-methyl-3'-pentenyl)-2,5-dihydrothiophene 1-oxide **(233)** as an oily product **(Scheme 116)**. The structure of sulfoxide **233** was established by ^{1}H and ^{13}C NMR as well as by mass spectrometry.



179 **233**

SCHEME 116

When the reaction was repeated in a variety of solvents, varying temperature, time and concentration, adduct **233** was trapped and isolated in an optimized yield of 55% **(Table 34)**.

Table 34: Summary of Sulfur Monoxide Trapping Experiments of Myrcene (41) with Bicyclo[3.3.1]nonylidenebicyclo-[3.3.1]nonane Thiirane 1-Oxide (179)

R^1	Solvent	Temp. (°C)	Time	%Yield*
1 : 1	$CHCl_3$	61	8 days	N. R.
1 : 1	EtOAc	77	8 days	N. R.
1 : 1	CH_3CN	81	8 days	N. R.
1 : 1	Toluene	80	8 days	N. R.
1 : 3	Toluene	110	14 h	52
1 : 1	Toluene	110	14 h	47
3 : 1	Toluene	110	14 h	55
1 : 1	C_6H_5Cl	132	10 h	26
3 : 1	C_6H_5Cl	132	10 h	30
1 : 1	Xylene	138	10 h	27
3 : 1	Xylene	138	10 h	34
3 : 1	Xylene	110	15 h	51
3 : 1	Decane	135	10 h	32
3 : 1	Decane	174	6 h	17

R^1 refers to the molar ratio of thiirane 1-oxide **179** to myrcene **(41)**.

* refers to 3-(4'-methyl-3'-pentenyl)-2,5-dihydrothiophene 1-oxide **(233)**.

The assignments of relevant ^{13}C NMR chemical shifts relative to tetramethylsilane of 2,5-dihydrothiophene 1-oxide adducts are reported in **Table 35.** The carbon atoms were identified using the following numbering system.

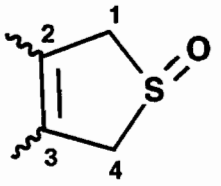


Table 35: Assignments of Relevant ^{13}C Chemical Shifts for 2,5-Dihydrothiophene 1-Oxide Adducts

Entry	C1	C2	C3	C4
200	64.32	126.07	-	-
201	64.46	125.01	-	-
203	62.92	135.55	119.07	59.99
233	61.61	139.87	123.93	59.68

As mentioned earlier, ethylene episulfoxide **(184)** has been shown to decompose at a temperature of 110 °C to ethylene and sulfur monoxide.[199] This fact was used in a system designed to add sulfur monoxide to unsaturated hydrocarbons.[252] Episulfoxide **184** and substituted dienes when refluxed in toluene (110-112 °C) were found to transfer sulfur monoxide *in situ* and to produce the appropriately substituted 2,5-dihydrothiophene 1-oxide as a major product but the yields were quite low (*ca.* 40%).

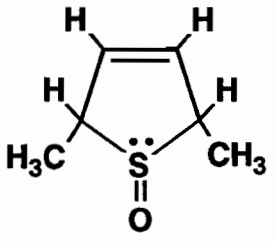
In contrast, we found that thiirane 1-oxides **178** and **179** transfer sulfur monoxide to 1,3-dienes smoothly to give the corresponding 2,5-dihydrothiophene 1-oxide adducts in high isolated yields. Ratios of thiirane 1-oxides **178** or **179** to diene were varied from 1:3

to 3:1 with relatively little change in yields (**Table 27-34**). Interestingly, the choice of solvent is critical; no decomposition either of **178** nor of **179** took place over 10 days in refluxing chloroform, ethyl acetate or acetonitrile (T = 61 °C, 77 °C, 81 °C respectively).

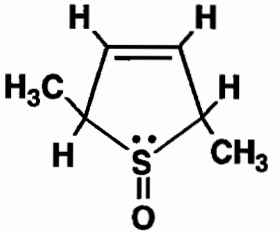
The best conditions for the release of sulfur monoxide and its subsequent trapping (*ca.* 82% isolated) appear to be in refluxing toluene (110 °C) for 12 h in the case of 2,3-dimethyl-1,3-butadiene **(62)** with thiirane 1-oxide **178 (Table 27)** and 8 h in the case of thiirane 1-oxide **179 (Table 28)**.

At 110 °C in decane and xylene, yields of the trapping adduct **200** were *ca.* 68% **(Table 27)**. In refluxing xylene (138 °C), the yield diminished to 35% implying decomposition of the diene adduct **200**. When a pure sample of **200** was heated in refluxing xylene for 20 h, only 10% remained. This confirms the retro chelotropic decomposition; diene adduct **200** decomposed completely in 35 h in refluxing xylene (*ca.* 138 °C) **(Table 27)**.

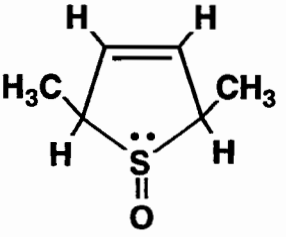
It is noteworthy to mention that, Lemal[273] found that when ethylene episulfoxide **(184)** was reacted with each of the three 2,4-hexadiene isomers, mixtures of *cis,cis-*, *cis,trans-*, and *trans,trans*-2,5-dihydro-2,5-dimethylthiophene 1-oxides **(236, 237, 238** respectively) were formed. While there was significant stereoselectivity, Lemal concluded that because of the formation of multiple sulfoxide isomers in each reaction, the thermal decomposition of episulfoxide **184** proceeds *via* a biradical intermediate in the triplet state.



236



237



238

We found that thiirane 1-oxide **178** reacts with 2,4-hexadiene (a mixture of isomers, Aldrich), and gives a 85% yield of the *trans,trans*-2,5-dihydro-2,5-dimethyl-thiophene 1-oxide **(238)**; there appears to be the only one product. Therefore, we conclude this lack of stereospecificity strongly implicates a triplet, biradical intermediate and full isomerization has taken place.

CONCLUSIONS AND ORIGINAL CONTRIBUTIONS TO KNOWLEDGE

The synthesis of a new series of di- and trithio compounds *via* triphenylmethanesulfenyl chloride **65** (or its thio **61** and dithio **70** homolog) has been investigated.

It was concluded that the triphenylmethanesulfenyl chloride (**65**) addition to bicyclo[2.2.1]heptene (**66**) proceeds *via* initial formation of an episulfonium ion intermediate, which is then opened to a dithio adduct **68**.

The stereochemistry of 1,2-addition products [*endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane (**68**) and *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane (**69**)] has been determined by x-ray analysis and revealed the regiochemistry of adduct **68**; the symmetry of adduct **69** permits only one isomer.

We discovered that pyrolysis of di- and trithio reagents *trans*-2-chloro-1-(triphenylmethyldithio)cyclohexane (**74**) and *trans*-2-chloro-1-(triphenylmethyltrithio)cyclohexane (**76**) in the presence of 2,3-dimethyl-1,3-butadiene (**62**), affords products that are consistent with the trapping of diatomic sulfur in the form of cyclic tetrasulfide 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene (**64**). Adduct **64** was formed in good, overall yield.

Tetrasulfide **64** can be converted quantitatively to disulfide adduct 1,2-dithia-4,5-dimethyl-4-cyclohexene (**63**) by an *in situ* treatment with triphenylphosphine (**141**); as a result, this methodology serves to a transfer two sulfur unit to a diene in over 50% isolated yield.

The x-ray crystal structure of compounds **68**, **69**, **75** and **76** was reported[64,65] for the first time.

We discovered that triphenylmethanesulfenyl chloride **65** (or its thio **61** and dithio **70** homolog) are a versatile reagents for synthesis of stable episulfides, adamantylideneadamantane thiirane (**116**) and bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane (**117**) in high isolated yields (92%).

Oxidation of episulfides **116** and **117** with *m*-CPBA gave novel episulfoxides, adamantylideneadamantane thiirane 1-oxide **(178)** and bicyclo[3.3.1]nonylidenebicyclo-[3.3.1]nonane thiirane 1-oxide **(179)**, respectively in 99% isolated yield. Thiirane 1-oxides **178** and **179** are crystalline, stable and easy to prepare compared to what is known in the literature.

Thermal decomposition of thiirane 1-oxides **178** and **179** in refluxing toluene provides a convenient method for the generation and trapping of sulfur monoxide in the presence of various 1,3-diene [2,3-dimethyl-1,3-butadiene **(62)**, 2,3-diphenyl-1,3-butadiene **(199)**, isoprene **(202)** and myrcene **(41)**]; to give the corresponding 2,5-dihydrothiophene 1-oxide adducts in high isolated yields (*ca.* 80%).

The x-ray crystal structures of adamantylideneadamantane thiirane **(116)** and adamantylideneadamantane thiirane 1-oxide **(178)** were reported[166] for the first time. The identity of compounds **116**, **117**, **178**, **179**, **200**, **201**, **203** and **233** was determined by ^{1}H and ^{13}C NMR as well as by mass spectrometry.

CHAPTER 8

EXPERIMENTAL

8.1 GENERAL PROCEDURES

Commercially available reagents were obtained from Aldrich Chemical Company (Milwaukee, Wl 53233 USA) and used directly except as indicated.

2,3-Dimethyl-1,3-butadiene and isoprene were stored at -15 °C over molecular sieves. The *m*-chloroperoxybenzoic acid (*m*-CPBA) was purified by washing the commercial 80-85% or 50-60% material with a phosphate buffer, drying, filtering and evaporating at reduced pressure. The solid was then recrystalized from methylene chloride to afford 99% *m*-CPBA.[282] Sulfur dichloride (SCl_2) was purified according to Fieser and Fieser.[283] Sulfur dichloride was distilled twice over 0.1% phosphorus pentachloride (PCl_5) and the fraction boiling at 58-60 °C (lit.[283] 59 °C) was collected. The red liquid was used immediately. Sulfur monochloride (S_2Cl_2) was also purified according to Fieser and Fieser.[283] Sulfur monochloride was distilled twice from a mixture of sulfur and charcoal and the fraction boiling at 137-139 °C was collected. The orange liquid was used immediately. Sulfuryl chloride (SO_2Cl_2) was distilled immediately before use.

Hexanes were distilled from concentrated sulfuric acid (H_2SO_4) and passed through an alumina column before use. Tetrahydrofuran (THF) was distilled from the blue sodium-benzophenone ketyl and used directly. Methylene chloride (CH_2Cl_2) was distilled from anhydrous phosphorus pentoxide (P_2O_5) and stored over 3Å molecular sieves.[284] Benzene

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282 N. N. Shartz and J. H. Blumberg, *J. Org. Chem.*, **29**, 1496 (1976).

283 L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", John Wiley and Sons, Pub., New York, Vol. 1, 1967, p. 1121.

284 D. R. Burfield, G.-H. Gan and R. H. Smithers, *J. Appl. Chem. Biotechnol.*, **28**, 23 (1978).

and toluene were stored over metallic sodium. All other solvents were stored over 3Å molecular sieves. Molecular sieves were activated by heating at 400 °C overnight and cooled in a desiccator before use. Petroleum ether was low boiling 35-60 °C unless otherwise stated. Ether in all cases refers to anhydrous diethyl ether ($C_2H_5OC_2H_5$).

Column chromatography was performed using Merck Kieselgel 60 (230-400 mesh) and Fisher Scientific Neutral Alumina (80-200 mesh). In both cases, flash column procedures[285] were used. Chromatographic solvent mixtures are volume/volume (v/v) percentages. Experiments requiring inert atmosphere were done under nitrogen.

Thin Layer Chromatography (TLC) was performed on 0.25 mm Merck silica gel plates (60F-254) with polyester backing and visualized by UV light and/or dipping in a solution of ammonium molybdate (2.5 g) and cerium sulfate (1.0 g) in 10% v/v aqueous sulfuric acid (100 mL).

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded at 200 MHz (Varian XL-200, Varian Gemini-200), at 300 MHz (Varian XL-300), or at 270 MHz (JEOL 270-CPF) spectrometers. ^{13}C-NMR spectra were recorded on the same instruments (50.3, 67.9, and 75.4 MHz, respectively). In both cases, deuteriochloroform ($CDCl_3$) was used as the reference solvent unless otherwise indicated. ^{1}H- and ^{13}C-NMR chemical shifts are quoted in parts per million, δ (ppm), relative to tetramethylsilane (TMS, 0 δ) used as an internal standard. The spectra are recorded as: shift, multiplicity and integration. Multiplicity assignments are recorded using the following abbreviations: s for singlet; d for doublet; t for triplet; q for quartet; m for multiplet and br. for broad.

Melting points (Mp.) were obtained in open capillaries on a Gallenkamp melting point apparatus and are uncorrected.

Low resolution impact (EI) mass spectra were obtained using a Dupont Instrument 21-492B equipped with a 70-eV ionizing energy source and used in direct-inlet mode. The analysis of the spectra was reported according to the following: mass of charge ratio (m/z); relative intensity; assignment.

Elemental analysis were carried out by Guelph Chemical Laboratories Ltd. (Guelph, Ontario, Canada).

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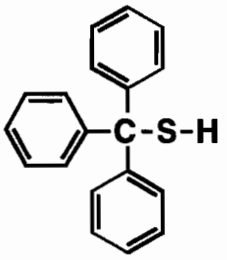
285 W. C. Still, M. Khan and A. Mitra, *J. Org. Chem.*, **43**, 2923 (1978).

The x-ray crystallography of compounds **68**, **69** and **116** was performed by Dr. Rosemary C. Hynes; the x-ray crystallography of compounds **75**, **76**, **178** and **235** was performed by Dr. Anne-Marie Lebuis at the Department of Chemistry, McGill University, Montreal, Quebec, Canada. ORTEP drawings were obtained using the ORTEP - A Fortran Thermal Ellipsoid Plot Program.[123]

8.2 EXPERIMENTAL PROCEDURES

8.2.1 Preparation of Triphenylmethanethiol (85)



85

Triphenylmethanethiol was prepared from triphenylmethanol.[72] Hydrogen sulfide gas was passed through a suspension of triphenylmethanol (60 g, 0.23 mol) in 200 mL of glacial acetic acid containing 1 mL of concentrated sulfuric acid. Hydrogen sulfide gas addition was stopped when no yellow color remained. The resulting mixture was flushed with nitrogen and treated with 350 mL of distilled water to precipitate the product. The solution was filtered and the solid was washed twice with 200 mL of water. Recrystallization from acetone gave a white crystalline solid of triphenylmethanethiol **(85)** (50 g, 79%). Mp. 106-107 °C (lit.[72] Mp. 107 °C). ^{1}H-NMR ($CDCl_3$) δ: 3.1 (s, 1H) and 7.22-7.30 (m, aryl-H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 62.75, 126.80, 127.70, 129.28 and 147.01 ppm.

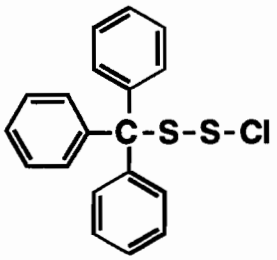
8.2.2 Preparation of Triphenylmethanesulfenyl Chloride (65)

65

Sulfuryl chloride (19.5 g, 145 mmol) was added slowly by a syringe to a stirred solution of triphenylmethanethiol **(85)** (20 g, 72.5 mmol) in 50 mL of toluene and 225 mL of anhydrous ether. The solution was maintained near 0 °C. The reaction vessel was sealed and as the solution was stirred for 2 h at 0 °C; a yellow solid crystallized. The

heterogeneous mixture was treated with toluene (300 mL) leading to a homogeneous solution which was washed with water (600 mL), a 1:1 mixture of saturated $NaHCO_3/H_2O$ and saturated $NaCl/H_2O$ (200 mL). The solution was dried with $MgSO_4$ and upon the removal of the volatile solvents under reduced pressure, a yellow solid resulted. Recrystallization from a chloroform *tert*-butanol mixture afforded 18 g, 76% of pure triphenylmethanesulfenyl chloride **(65)**. Mp. 136-137 °C (lit.[72] Mp. 137 °C). ^{1}H-NMR ($CDCl_3$) δ: 7.30 (m, aryl-H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 72.12, 127.86, 128.20, 129.92 and 141.78 ppm.

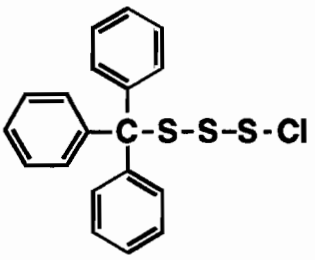
8.2.3 Preparation of Triphenylmethanethiosulfenyl Chloride (61)



61

A solution of triphenylmethanethiol **(85)** (12 g, 44.1 mmol) in 100 mL of anhydrous ether was slowly added to a stirred solution of sulfur dichloride (6.14 g, 60.15 mmol) in 75 mL of anhydrous ether under a nitrogen atmosphere at -78 °C. The addition time was 1.5 h during which an orange-yellow precipitate formed in the reaction flask. The mixture was warmed to ambient temperature, concentrated to 30 mL under reduced pressure and the solid was separated by filtration and stored at -15 °C. Recrystallization from *n*-hexane gave an orange solid of pure triphenylmethanethiosulfenyl chloride **(61)** (6.54 g, 73%). Mp. 91-92 °C (lit.[73] Mp. 91-93 °C). ^{1}H-NMR ($CDCl_3$) δ: 7.36 (m, aryl-H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 77.62, 127.66, 128.10, 130.55 and 142.23 ppm.

8.2.4 Preparation of Triphenylmethanedithiosulfenyl Chloride (70)



70

Triphenylmethanethiol **(85)** (5.47 g, 20 mmol) was dissolved in 100 mL of anhydrous ether to form a yellow solution which was added dropwise during 1 h to a stirred solution of disulfur dichloride (3.35 g, 25 mmol) in 75 mL anhydrous ether under a nitrogen atmosphere at -78 °C. The mixture was warmed to ambient temperature and concentrated to 30 mL under reduced pressure. Crystallization took place upon cooling at -15 °C for 48 h. After filtration an orange solid was recovered and identified as triphenylmethanedithiosulfenyl chloride **(70)** (4.92 g, 65%). Mp. 76-77 °C (lit.[74] Mp. 76-78 °C). ^{1}H-NMR ($CDCl_3$) δ: 7.18 (m, aryl-H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 74.70, 127.21, 128.13, 130.08 and 142.45 ppm.

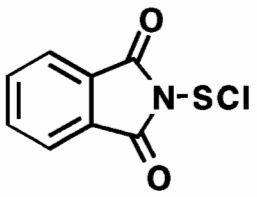
8.2.5 Preparation of N,N'-Dithiobis(phthalimide) (239)

239

A solution of sulfur monochloride (3.35 g, 25 mmol) in 10 mL of methylene chloride was added dropwise to a stirred suspension of potassium phthalimide (8.8 g, 50 mmol) in 50 mL of CH_2Cl_2 under a nitrogen atmosphere at 0 °C. Removal of the solvent under reduced pressure afforded a colorless precipitate. After recrystalization of the crude product from chloroform, large colorless needles of N,N'-dithiobis(phthalimide) **(239)**

were obtained in a yield of 81%. Mp. 228-230 °C (lit.[286] Mp. 230 °C). ^{1}H-NMR ($CDCl_3$) δ: 7.95-8.13 (m, aryl-H) ppm.

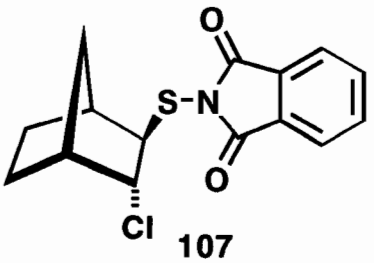
8.2.6 Preparation of Phthalimido-N-Sulfenyl Chloride (105)



105

Chlorine gas was bubbled for 2.5 h (until the yellow color was discharged) through a stirred solution of N,N'-dithiobis(phthalimide) **(239)** (7.12 g, 20 mmol) in 40 mL of chloroform. The temperature was maintained between 50-60 °C. Nitrogen gas was passed through the mixture to remove any excess of chlorine. Removal of the solvent under reduced pressure afforded yellow crystals of phthalimido-N-sulfenyl chloride **(105)** in a yield of 97%. Mp. 117-118 °C (lit.[287] Mp. 117 °C). ^{1}H-NMR ($CDCl_3$) δ: 7.75-8.15 (m, aryl-H) ppm.

8.2.7 Preparation of *endo*-2-Chloro-*exo*-1-(N-phthalimidothio)bicyclo-[2.2.1]heptane (107)



107

Phthalimido-N-sulfenyl chloride **(105)** (3.0 g, 14 mmol) was dissolved in 10 mL of methylene chloride to form a yellow solution which was added dropwise at room temperature to a solution of bicyclo[2.2.1]heptene **(66)** (1.60 g, 17 mmol) in 25 mL of

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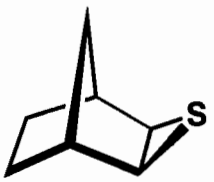
286 M. V. Kalnins, *Can. J. Chem.*, **44**, 2111 (1966).

287 A. B. Sullivan and K. Boustany, *Int. J. Sulfur. Chem. (A)*, **1**, 207 (1971).

CH_2Cl_2. The mixture was stirred until no yellow color remained. Removal of the solvent under reduced pressure yielded 4.39 g, 100% of *endo*-2-chloro-*exo*-1-(N-phthalimidodithio)bicyclo[2.2.1]heptane **(107)** as colorless crystals. Mp. 113-114 °C (lit.[110] Mp. 113 °C). ^{1}H-NMR ($CDCl_3$) δ: 1.2-2.6 (m, 8H), 3.15-3.25 (m, 1H), 4.15-4.30 (m, 1H) and 7.65-7.95 (m, 4H) ppm. MS (m/z, rel. int., assignment): 307, 9%, $M^{+\cdot}$; 271, 10%, $M^{+\cdot}$-Cl; 179, 59%, $M^{+\cdot}$-C_7H_8Cl; 160, 88%, $M^{+\cdot}$-$C_8H_5O_2N$; 147, 65%, $M^{+\cdot}$-C_7H_8SCl; 129, 36%, $M^{+\cdot}$-$C_8H_5O_2NS$; 93, 100%, $M^{+\cdot}$-$C_8H_6O_2NSCl$.

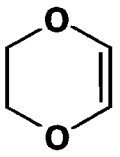
8.2.8 Preparation of *exo*-2,3-Epithionorbornane (102)



102

exo-2,3-Epithionorbornane **(102)**[110] was prepared from *endo*-2-chloro-*exo*-1-(N-phthalimidodithio)bicyclo[2.2.1]heptane **(107)**. A mixture of 1 mL of ethanol in 4 mL of tetrahydrofuran (THF) was added dropwise to a stirred suspension of lithium aluminum hydride (0.9 g) in 25 mL of dry THF at 0 °C under a nitrogen atmosphere. The mixture was subsequently cooled to -78 °C and *endo*-2-chloro-*exo*-1-(N-phthalimidodithio)bicyclo-[2.2.1]heptane **(107)** (4.2 g, 14 mmol) in 10 mL of THF was added dropwise to the stirred reducing agent for over 1.5 h. After stirring for an additional 10 min, the mixture was allowed to warm to room temperature and then quenched with water. Episulfide **102** was extracted with ether and dried with $MgSO_4$. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 5% chloroform in hexane as eluent gave 0.95 g, 56% of *exo*-2,3-epithionorbornane **(102)** as a pure, oily product. ^{1}H-NMR ($CDCl_3$) δ: 0.63 (d, 1H, J=10.26 Hz, anti-7H), 1.18 (d, 1H, J=10 Hz, syn-7H), 1.23-1.63 (m, 4H), 2.42 (br., 2H), 2.71 (m, 2H) ppm. MS (m/z, rel. int., assignment): 126, 77%, $M^{+\cdot}$; 93, 100%, $M^{+\cdot}$-H_2S.

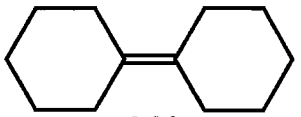
8.2.9 Preparation of 1,4-Dioxene (240)



240

1,4-Dioxene (**240**) was prepared by the procedure of Moss and Paige.[288] The spectral data are included here for completeness. ^{1}H-NMR ($CDCl_3$) δ: 4.05 (s, 4H) and 5.93 (s, 2H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 64.83 and 126.35 ppm. MS (m/z, rel. int., assignment): 86, 100%, $M^{+\cdot}$; 58, 5%, $M^{+\cdot}$ -C_2H_4.

8.2.10 Preparation of Cyclohexylidenecyclohexane (241)



241

Cyclohexylidenecyclohexane (**241**) was prepared by the procedure of McMurry, Fleming, Kees and Krepski.[289] Potassium metal (1.82 g, 49 mmol) was added to a stirred slurry of $TiCl_3$ (2.15 g, 14 mmol) in 75 mL of dry THF under a nitrogen atmosphere at room temperature. After refluxing for 40 min, the black mixture was cooled and a solution of cyclohexanone (0.343 g, 3.5 mmol) in 5 mL of THF was added. After the mixture was further refluxed for 24 h, the reaction was cooled to room temperature and filtered under an inert atmosphere. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with hexane as eluent, afforded a solid product of cyclohexylidene-cyclohexane (**241**) (0.482 g, 83%). Mp. 53-54 °C (lit. Mp. 52-53 °C[289], 53.5-54.5 °C[290]). ^{1}H-NMR ($CDCl_3$) δ: 2.18-2.12 (m, 8H) and 1.49-1.45 (m, 12H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 27.65, 29.20, 30.75 and 130.50 ppm. MS (m/z, rel. int., assignment): 164, 99%, $M^{+\cdot}$; 82, 100%, $M^{+\cdot}$ -C_6H_{10}.

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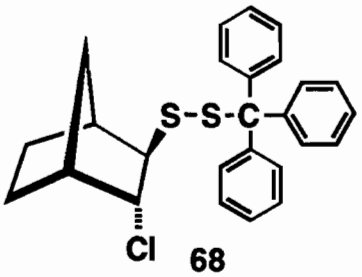
288 R. D. Moss and J. Paige, *J. Chem. Eng. Data,* **12**, 452 (1967).

289 J. E. McMurry, M. P. Fleming, K. L. Kees and L. R. Krepski, *J. Org. Chem.*, **43**, 3255 (1978).

290 R. Griegee, E. Vogel and H. Hoger, *Chem. Ber.*, **85**, 144 (1952).

8.2.11 Reaction of Triphenylmethanesulfenyl Chloride (65) with Bicyclo-[2.2.1]heptene (66)



68

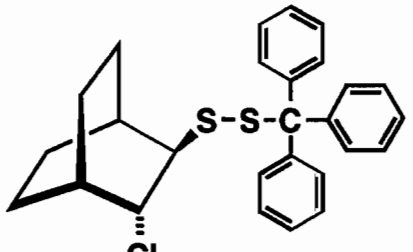
A solution of triphenylmethanesulfenyl chloride **(65)** (1.97 g, 12.5 mmol) in 25 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo[2.2.1]-heptene **(66)** (1.177 g, 12.5 mmol) in 25 mL of dry CH_2Cl_2 under a nitrogen atmosphere at room temperature. The mixture was stirred for 20 h. Removal of the solvent under reduced pressure and chromatography 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 3.45 g, 63% of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane **(68)**. 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: 21.83, 28.28, 35.11, 42.57, 44.82, 58.76, 66.41, 71.26, 126.94, 127.91, 130.18 and 143.74 ppm. Anal. calc'd 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 **68** was reported for the first time **(Figure 1)**.

8.2.12 Production of *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo-[2.2.1]heptane (68) using *exo*-2,3-Epithionorbornane (102) as a Precursor

A solution of triphenylmethanesulfenyl chloride **(65)** (1.97 g, 6.35 mmol) in 25 mL of dry methylene chloride was added dropwise to a stirred solution of *exo*-2,3-epithionorbornane **(102)** (0.8 g, 6.35 mmol) in 25 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 3.5 h. Removal of the solvent under reduced pressure and chromatography 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 2.0 g, 90% of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane **(68)**. Mp. 114-115 °C. ^{1}H-NMR ($CDCl_3$) δ: 0.94-1.61 (m, 7H), 2.02-2.03 (m, 1H), 2.29-2.31 (m, 1H), 3.62-3.64 (m, 1H) and 7.20-7.47 (m, 15H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 21.83, 28.29, 35.11, 42.56, 44.81, 58.76, 66.41, 71.26, 126.95, 127.91, 130.18 and 143.74 ppm.

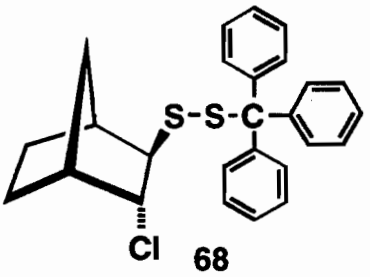
8.2.13 Reaction of Triphenylmethanesulfenyl Chloride (65) with Bicyclo-[2.2.2]octene (67)



69

A solution of triphenylmethanesulfenyl chloride **(65)** (1.94 g, 6.25 mmol) in 25 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo[2.2.2]-octene **(67)** (0.67 g, 6.25 mmol) in 25 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 22 h. Removal of the solvent under reduced pressure and chromatography 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*-hexane gave 1.70 g, 60% of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane **(69)**. 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: 18.61, 18.78, 24.98, 25.26, 28.71, 33.99, 55.86, 65.00, 71.16, 127.41, 128.32, 130.17 and 143.76 ppm. Anal. calc'd 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 **69** was reported for the first time **(Figure 2)**.

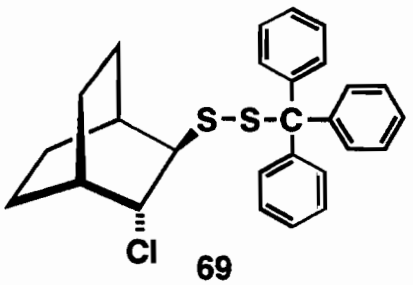
8.2.14 Reaction of Triphenylmethanethiosulfenyl Chloride (61) with Bicyclo[2.2.1]heptene (66)



68

A solution of triphenylmethanethiosulfenyl chloride **(61)** (4.29 g, 12.5 mmol) in 30 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo-[2.2.1]heptene **(66)** (1.18 g, 12.5 mmol) in 20 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 6 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 upon treatment with 35-60 °C petroleum ether. Recrystallization from *n*-pentane gave 4.74 g, 87% of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane **(68)**. Mp. 114-115 °C. ^{1}H-NMR ($CDCl_3$) δ: 0.91-1.62 (m, 7H), 2.02-2.04 (m, 1H), 2.29-2.32 (m, 1H), 3.61-3.64 (m, 1H) and 7.20-7.46 (m, 15H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 21.85, 28.28, 35.10, 42.58, 44.83, 58.82, 66.40, 71.49, 126.94, 127.89, 130.16 and 143.73 ppm.

8.2.15 Reaction of Triphenylmethanethiosulfenyl Chloride (61) with Bicyclo[2.2.2]octene (67)

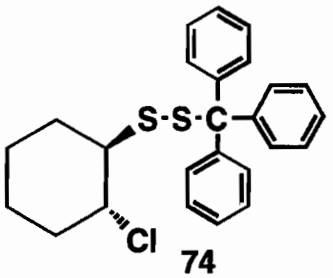


69

A solution of triphenylmethanethiosulfenyl chloride **(61)** (2.143 g, 6.25 mmol) in 25 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo-[2.2.2]octene **(67)** (0.676 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 upon treatment with 35-60 °C petroleum ether. Recrystallization from *n*-hexane gave 2.31 g, 82% of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane **(69)**. Mp. 118-119 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.93-1.19 (m, 11H), 3.59 (m, 1H) and 7.18-7.56 (m, 15H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 18.59, 18.77, 25.0, 25.26, 28.70, 34.0, 55.87, 65.01, 71.16, 127.40, 128.34, 130.17 and 143.78 ppm.

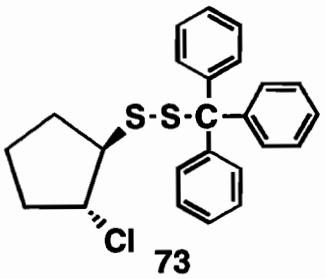
8.2.16 Reaction of Triphenylmethanethiosulfenyl Chloride (61) with Cyclohexene (72)



74

A solution of triphenylmethanethiosulfenyl chloride **(61)** (2.143 g, 6.25 mmol) in 25 mL of dry methylene chloride was added dropwise to a stirred solution of cyclohexene **(72)** (0.513 g, 6.25 mmol) in 25 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 5 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 20% chloroform in hexane, afforded an oily product which solidified under vacuum overnight. Recrystallization from *n*-hexane gave 2.38 g, 90% of *trans*-2-chloro-1-(triphenylmethyldithio)cyclohexane **(74)**. 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: 22.54, 22.75, 28.62, 32.76, 52.78, 62.26, 71.44, 127.00, 127.95, 130.18 and 143.77 ppm. Anal. calc'd 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.

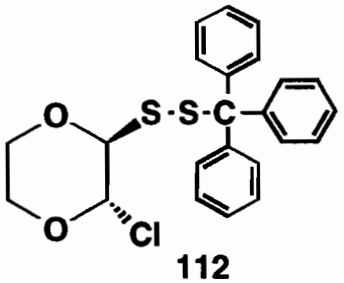
8.2.17 Reaction of Triphenylmethanethiosulfenyl Chloride (61) with Cyclopentene (71)



73

A solution of triphenylmethanethiosulfenyl chloride **(61)** (2.143 g, 6.25 mmol) in 20 mL of dry methylene chloride was added dropwise to a stirred solution of cyclopentene **(71)** (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 **(73)**. 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: 22.02, 28.89, 33.66, 55.25, 65.79, 71.38, 126.95, 127.85, 130.04 and 143.57. Anal. calc'd 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.

8.2.18 Reaction of Triphenylmethanethiosulfenyl Chloride (61) with 1,4-Dioxene (240)

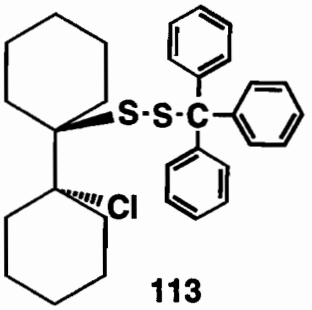


112

A solution of triphenylmethanethiosulfenyl chloride **(61)** (0.477 g, 1.395 mmol) in 25 mL of dry methylene chloride was added dropwise to a stirred solution of 1,4-dioxene **(240)** (0.12 g, 1.395 mmol) in 20 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 8 h. Removal of the solvent

under reduced pressure and chromatography of the residue on silica gel with 30% ethyl acetate in hexane, afforded an oily product of *trans*-2-chloro-3-(triphenylmethyldithio)-1,4-dioxane **(112)** (0.365 g, 61%). ^{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: 59.09, 59.73, 71.92, 88.16, 89.99, 127.66, 127.98, 130.01 and 143.23 ppm.

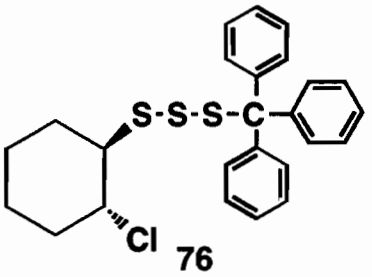
8.2.19 Reaction of Triphenylmethanethiosulfenyl Chloride (61) with Cyclohexylidenecyclohexane (241)



113

A solution of triphenylmethanethiosulfenyl chloride **(61)** (0.208 g, 0.609 mmol) in 25 mL of dry methylene chloride was added dropwise to a stirred solution of cyclohexylidenecyclohexane **(241)** (0.10 g, 0.609 mmol) in 20 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 10 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 30% chloroform in hexane, afforded a solid product of *trans*-1'-chloro-1-(triphenylmethyldithio)bicyclohexyl **(113)** (0.208 g, 68%). Mp. 43-44 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.04-1.28 (m, 20H) and 7.29-7.15 (m, 15H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 22.72, 22.80, 23.88, 24.32, 25.39, 25.72, 26.06, 26.19, 33.73, 34.02, 59.81, 60.72, 72.74, 127.73, 127.84, 130.34 and 143.78 ppm.

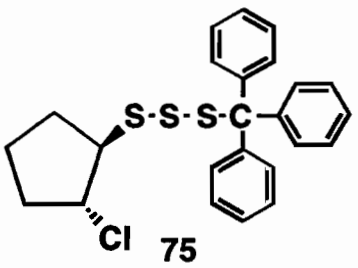
8.2.20 Reaction of Triphenylmethanedithiosulfenyl Chloride (70) with Cyclohexene (72)



76

A solution of triphenylmethanedithiosulfenyl chloride (**70**) (2.34 g, 6.25 mmol) in 20 mL of dry methylene chloride was added dropwise to a stirred solution of cyclohexene (**72**) (0.512 g, 6.25 mmol) in 25 mL of dry CH_2Cl_2 under a nitrogen atmosphere at room temperature. The mixture was stirred for 3 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 25% chloroform in hexane, afforded an oily product which solidified upon treatment with 35-60 °C petroleum ether. Recrystallization from *n*-hexane afforded 2.64 g, 92% of *trans*-2-chloro-1-(triphenylmethyltrithio)cyclohexane (**76**). 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. calc'd 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 **76** was reported for the first time (**Figure 3**).

8.2.21 Reaction of Triphenylmethanedithiosulfenyl Chloride (70) with Cyclopentene (71)

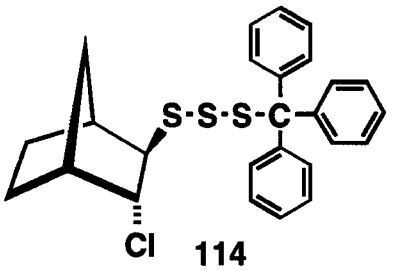


75

A solution of triphenylmethanedithiosulfenyl chloride (**70**) (2.34 g, 6.25 mmol) in 20 mL of dry methylene chloride was added dropwise to a stirred solution of cyclopentene

(71) (0.426 g, 6.25 mmol) in 20 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 4 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 25% chloroform in hexane, afforded an oily product which solidified upon treatment with 35-60 °C petroleum ether. Recrystallization from *n*-pentane gave 2.54 g, 90% of *trans*-2-chloro-1-(triphenylmethyltrithio)cyclopentane **(75)**. 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: 22.07, 29.69, 34.33, 59.39, 65.08, 73.29, 127.21, 127.96, 130.34 and 143.23 ppm. Anal. calc'd 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 **75** was reported for the first time **(Figure 4)**.

8.2.22 Reaction of Triphenylmethanedithiosulfenyl Chloride (70) with Bicyclo[2.2.1]heptene (66)

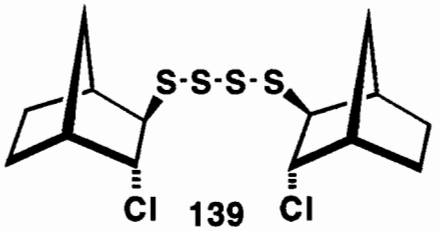


114

A solution of triphenylmethanedithiosulfenyl chloride **(70)** (3.748 g, 10.0 mmol) in 20 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo[2.2.1]heptene (0.94 g, 10.0 mmol) in 30 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 10 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 15% chloroform in hexane, permitted three fractions to be isolated and identified. The first fraction was isolated in a yield of 68% as an oily product of *endo*-2-chloro-*exo*-1-(triphenylmethyltrithio)bicyclo[2.2.1]heptane **(114)**. ^{1}H-NMR ($CDCl_3$) δ: 0.94-2.10 (m, 7H), 2.30-2.45 (m, 1H), 2.65-2.72 (m, 1H), 4.0-4.10 (m, 1H) and 7.25-7.60 (m, 15H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 21.81, 28.77, 35.64, 43.15, 44.52, 62.58, 66.38, 73.22, 126.88, 127.89, 130.32 and 143.26 ppm.

The second fraction was isolated as an oily product and identified as *exo*-2,3-epithionorbornane **(102)** (0.25 g, 20%). ^{1}H-NMR ($CDCl_3$) δ: 0.63 (d, 1H, J=10.26 Hz, anti-7H), 1.19 (d, 1H, J=10 Hz, syn-7H), 1.24-1.63 (m, 4H), 2.42 (br., 2H), 2.71 (m, 2H) ppm. MS (m/z, rel. int., assignment): 126, 77%, $M^{+\cdot}$; 93, 100%, $M^{+\cdot}$ -H_2S. The third fraction was isolated and identified as chlorotriphenylmethane (22%).

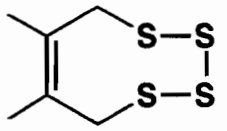
8.2.23 Thermal Chemistry of *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane (68)



139

A solution of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane **(68)** (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 eluent. After evaporating the solvent 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 (0.12 g, 68%) as an oily product and identified as di[(2-chloro)-1-norbornyl] tetrasulfide **(139)**. ^{1}H-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. calc'd for $C_{14}H_{18}Cl_2S_4$: C, 43.44; H, 5.17; S, 33.10. Found: C, 43.58; H, 4.92; S, 33.04. Chlorotriphenylmethane was isolated (19%) along with starting material (15%), elemental sulfur (18%) and triphenylmethanethiol (21%). In addition, bicyclo[2.2.1] heptene **(66)** was detected by ^{1}H NMR (*ca.* 7%).

8.2.24 Trapping of Diatomic Sulfur From the Decomposition of *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane (68) with 2,3-Dimethyl-1,3-butadiene (62)



64

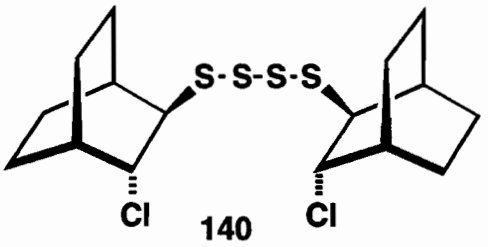
2,3-Dimethyl-1,3-butadiene **(62)** (0.0125 g, 0.153 mmol) was added to a mixture of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane **(68)** (0.20 g, 0.458 mmol) in 35 mL of dry ethyl acetate. The solution was refluxed for 36 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 25% $CHCl_3$ in hexane as eluent. After evaporating the solvent 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 (35 mg, 59%) as an oily product and identified as the acyclic di[(2-chloro)-1-norbornyl] tetrasulfide **(139)**. ^{1}H-NMR ($CDCl_3$) δ: 1.22-2.09 (m, 6H), 2.52 (m, 2H), 3.14 (m, 1H) and 4.15 (m, 1H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 21.88, 28.89, 35.85, 43.48, 44.75, 62.60 and 66.77 ppm. The second fraction was isolated and identified as the cyclic tetrasulfide adduct **(64)** (7.72 mg, 24%). ^{1}H-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%, $M^{+\cdot}$; 146, 45%, $M^{+\cdot}$ -S_2; 82, 90%, $M^{+\cdot}$ -S_4; 67, 100%, $M^{+\cdot}$ -CH_3S_4. Cyclic disulfide **63** was detected by ^{1}H NMR in low yield (*ca.* 6%). Starting material was isolated (10%) along with triphenylmethanethiol (25%), elemental sulfur (14%) and chlorotriphenylmethane (23%). In addition, bicyclo[2.2.1]heptene **(66)** was detected by ^{1}H NMR (*ca.* 5%).

8.2.25 Trapping of Diatomic Sulfur From the Decomposition of *endo*-2-Chloro-*exo*-1-(triphenylmethyltrithio)bicyclo[2.2.1]heptane (114) in the Presence of 2,3-Dimethyl-1,3-butadiene (62)

2,3-Dimethyl-1,3-butadiene **(62)** (0.087 g, 1.06 mmol) was added to a mixture of *endo*-2-chloro-*exo*-1-(triphenylmethyltrithio)bicyclo[2.2.1]heptane **(114)** (0.50 g, 1.08 mmol) in 30 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 10% $CHCl_3$ in hexane as eluent. After evaporating the solvent under reduced pressure, the products

were separated by column chromatography using the same eluent (10% $CHCl_3$ in hexane), in which the first fraction was isolated (60%) as an oily product and identified as the acyclic di[(2-chloro)-1-norbornyl] tetrasulfide **(139)**. ^{1}H-NMR ($CDCl_3$) δ: 1.21-2.09 (m, 6H), 2.53 (m, 2H), 3.14 (m, 1H) and 4.15 (m, 1H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 21.87, 28.89, 35.85, 43.48, 44.74, 62.61 and 66.77 ppm. Anal. calc'd for $C_{14}H_{18}Cl_2S_4$: S , 33.10. Found: S, 33.26. The second fraction was isolated and identified as cyclic tetrasulfide adduct **64** in a yield of 15%. Cyclic disulfide **63** was detected by ^{1}H NMR in low yield (*ca.* 4%). Starting material was isolated (16%) along with triphenylmethanethiol (27%), chlorotriphenylmethane (19%) and elemental sulfur (17%). In addition, bicyclo[2.2.1]-heptene **(66)** was detected by ^{1}H NMR (*ca.* 7%).

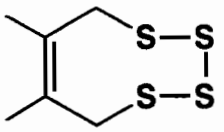
8.2.26 Thermal Chemistry of *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane (69)



140

A solution of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane **(69)** (0.6 g, 1.33 mmol) in 20 mL of dry ethyl acetate was refluxed for 42 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% $CHCl_3$ in hexane as eluent. After evaporating the solvent 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 (0.11 g, 60%) as an oily product and identified as the acyclic di[(2-chloro)-1-bicyclo[2.2.2]octyl] tetrasulfide **(140)**. ^{1}H-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. calc'd for $C_{16}H_{22}Cl_2S_4$: C, 46.29; H, 5.79; S, 30.86. Found: C, 46.10; H, 5.65; S, 30.63. Starting material was isolated (15%) along with triphenylmethanethiol (25%), chloro-triphenylmethane (21%) and elemental sulfur (15%). In addition, bicyclo[2.2.2]octene **(67)** was detected by ^{1}H NMR (*ca.* 6%).

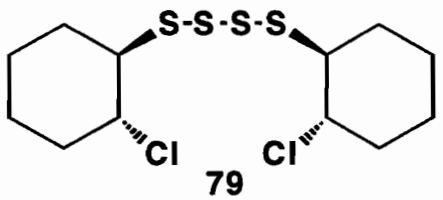
8.2.27 Trapping of Diatomic Sulfur From the Decomposition of *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane (69) with 2,3-Dimethyl-1,3-butadiene (62)



64

2,3-Dimethyl-1,3-butadiene **(62)** (0.0273 g, 0.333 mmol) was added to a mixture of *endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane **(69)** (0.45 g, 0.995 mmol) in 40 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 30% $CHCl_3$ in hexane as eluent. After evaporating the solvent under reduced pressure, the products were separated by column chromatography using the same eluent (30% $CHCl_3$ in hexane), in which the first fraction was isolated (0.070 g, 51%) as an oily product and identified as the acyclic di[(2-chloro)-1-bicyclo[2.2.2]octyl] tetrasulfide **(140)**. ^{1}H-NMR ($CDCl_3$) δ: 1.20-2.13 (m, 10H), 3.58 (m, 1H) and 4.03 (m, 1H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 19.27, 19.50, 25.36, 26.17, 30.62, 34.46, 61.54 and 64.96 ppm. Cyclic tetrasulfide adduct **64** was isolated in a yield of 19%. Cyclic disulfide **63** was detected by ^{1}H NMR but in low yield (*ca.* 5%). Triphenylmethanethiol was isolated (23%) along with starting material (14%), chlorotriphenylmethane (21%) and elemental sulfur (18%). In addition, bicyclo-[2.2.2] octene **(67)** was detected by ^{1}H NMR (*ca.* 7%).

8.2.28 Thermal Chemistry of *trans*-2-Chloro-1-(triphenylmethyldithio)-cyclohexane (74)

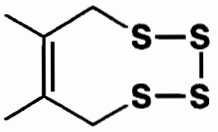


79

A solution of *trans*-2-chloro-1-(triphenylmethyldithio)cyclohexane **(74)** (1.83 g, 4.0 mmol) in 20 mL of dry ethyl acetate was refluxed for 13 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% $CHCl_3$ in hexane as eluent. After evaporating the solvent 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 (69%) as an oily product and identified as the acyclic di[(2-chloro)-1-cyclohexyl] tetrasulfide **(79)**. ^{1}H-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. Starting material was isolated (15%) along with triphenylmethanethiol (26%), chlorotriphenylmethane (23%) and elemental sulfur (18%). In addition, cyclohexene **(72)** was detected by ^{1}H-NMR (*ca.* 9%).

8.2.29 Trapping of Diatomic Sulfur From the Decomposition of *trans*-2-Chloro-1-(triphenylmethyldithio)cyclohexane (74) with 2,3-Dimethyl-1,3-butadiene (62)

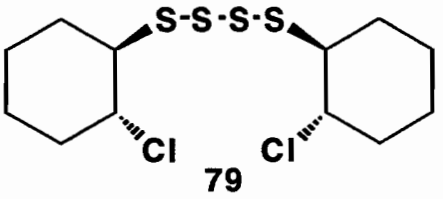


64

2,3-Dimethyl-1,3-butadiene **(62)** (0.106 g, 1.20 mmol) was added to a mixture of *trans*-2-chloro-1-(triphenylmethyldithio)cyclohexane **(74)** (1.65 g, 3.60 mmol) in 30 mL of dry ethyl acetate. The solution was refluxed for 10 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% $CHCl_3$ in hexane as eluent. After evaporating the solvent 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 (16%) as an oily product and identified as the acyclic di[(2-chloro)-1-cyclohexyl] tetrasulfide **(79)**. ^{1}H-NMR ($CDCl_3$) δ: 1.29-1.95 (m, 6H), 2.19-2.40 (m, 2H), 3.18-3.32 (m, 1H) and 4.19-4.25 (m, 1H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 23.87, 24.29, 30.60, 35.07, 56.99 and 61.71 ppm. Anal. calc'd for $C_{12}H_{22}Cl_2S_4$: C, 39.70; H, 5.51; S, 35.29. Found: C, 40.08; H, 5.33; S, 35.00. The second fraction was isolated and identified as cyclic tetrasulfide adduct **64** (58%). ^{1}H-NMR ($CDCl_3$) δ: 3.63 (s, 4H) and 1.79 (s, 6H); ^{13}C-NMR ($CDCl_3$) δ: 18.13 (CH_3); 42.76 (CH_2) and 130.33 (C=C) ppm. MS (m/z, rel. int., assignment): 210, 7%, $M^{+\cdot}$; 146, 40%, $M^{+\cdot}$ -S_2; 82, 93%, $M^{+\cdot}$ -S_4; 67, 100%, $M^{+\cdot}$ -CH_3S_4. Cyclic disulfide **63** was detected by ^{1}H NMR in low yield (*ca.* 10%). Starting material was isolated (10%) along with triphenylmethanethiol (28%), chlorotriphenylmethane (18%) and elemental sulfur (17%). In addition, cyclohexene **(72)** was detected by ^{1}H-NMR (*ca.* 8%).

The above reaction was repeated in a variety of solvents, varying temperature, time and concentration using the above procedure. The same products were isolated in each case but in varying yields (**Table 10**).

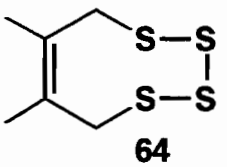
8.2.30 Thermal Chemistry of *trans*-2-Chloro-1-(triphenylmethyltrithio)-cyclohexane (76)



79

A solution of *trans*-2-chloro-1-(triphenylmethyltrithio)cyclohexane (**76**) (0.923 g, 2.0 mmol) in 25 mL of dry ethyl acetate was refluxed for 8 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 25% $CHCl_3$ in hexane as eluent. After evaporating the solvent 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 (65%) as an oily product and identified as the acyclic di[(2-chloro)-1-cyclohexyl] tetrasulfide (**79**). ^{1}H-NMR ($CDCl_3$) δ: 1.29-1.94 (m, 6H), 2.19-2.40 (m, 2H), 3.18-3.33 (m, 1H) and 4.19-4.24 (m, 1H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 23.87, 24.29, 30.61, 35.06, 56.99 and 61.71 ppm. Chlorotriphenylmethane was isolated (21%) along with starting material (13%), triphenylmethanethiol (28%) and elemental sulfur (23%). In addition, cyclohexene (**72**) was detected by ^{1}H NMR (*ca.* 8%).

8.2.31 Trapping of Diatomic Sulfur From the Decomposition of *trans*-2-Chloro-1-(triphenylmethyltrithio)cyclohexane (76) with 2,3-Dimethyl-1,3-butadiene (62)



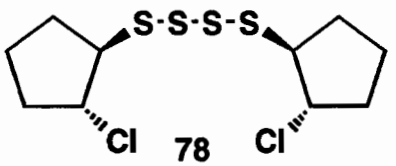
64

2,3-Dimethyl-1,3-butadiene (**62**) (0.037 g, 0.44 mmol) was added to a mixture of *trans*-2-chloro-1-(triphenylmethyltrithio)cyclohexane (**76**) (0.609 g, 1.32 mmol) in 20 mL

of dry ethyl acetate. The solution was refluxed for 10 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 15% $CHCl_3$ in hexane as eluent. After evaporating the solvent under reduced pressure, the products were separated by column chromatography using the same eluent (15% $CHCl_3$ in hexane), in which the first fraction was isolated (12%) as an oily product and identified as the acyclic di[(2-chloro)-cyclohexyl] tetrasulfide **(79)**. ^{1}H-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: 23.87, 24.29, 30.61, 35.08, 56.99 and 61.71 ppm. The second fraction was isolated and identified as cyclic tetrasulfide adduct **64** (63%). ^{1}H-NMR ($CDCl_3$) δ: 3.63 (s, 4H) and 1.79 (s, 6H); ^{13}C-NMR ($CDCl_3$) δ: 18.12 (CH_3); 42.75 (CH_2) and 130.32 (C=C) ppm. Cyclic disulfide **63** was detected by ^{1}H NMR in low yield (*ca.* 8%). Starting material was isolated (9%) along with triphenylmethanethiol (29%), elemental sulfur (24%) and chlorotriphenyl-methane (17%). In addition, cyclohexene **(72)** was detected by ^{1}H-NMR (*ca.* 7%).

The decomposition was further investigated by varying the reaction conditions in a variety of ways **(Table 11)**.

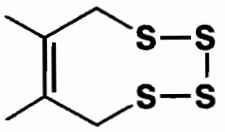
8.2.32 Thermal Chemistry of *trans*-2-Chloro-1-(triphenylmethyldithio)-cyclopentane (73)



78

A solution of *trans*-2-chloro-1-(triphenylmethyldithio)cyclopentane **(73)** (1.045 g, 2.50 mmol) in 35 mL of dry ethyl acetate was refluxed for 8 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% $CHCl_3$ in hexane as eluent. After evaporating the solvent 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 (65%) as an oily product and identified as the acyclic di[(2-chloro)-1-cyclopentyl] tetrasulfide **(78)**. ^{1}H-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. Chlorotriphenylmethane was isolated (20%) along with starting material (12%), elemental sulfur (26%) and triphenylmethanethiol (24%). In addition, cyclopentene **(71)** was detected by ^{1}H NMR (*ca.* 8%).

8.2.33 Trapping of Diatomic Sulfur From the Decomposition of *trans*-2-Chloro-1-(triphenylmethyldithio)cyclopentane (73) with 2,3-Dimethyl-1,3-butadiene (62)

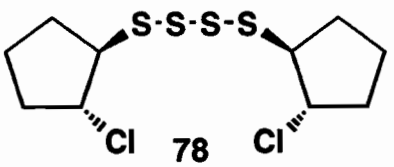


64

2,3-Dimethyl-1,3-butadiene **(62)** (0.12, 1.46 mmol) was added to a mixture of *trans*-2-chloro-1-(triphenylmethyldithio)cyclopentane **(73)** (1.80 g, 4.38 mmol) in 50 mL of dry ethyl acetate. The solution was refluxed for 15 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 15% $CHCl_3$ in hexane as eluent. After evaporating the solvent under reduced pressure, the products were separated by column chromatography using the same eluent (15% $CHCl_3$ in hexane), in which the first fraction was isolated (24%) as an oily product and identified as the acyclic di[(2-chloro)-1-cyclopentyl] tetrasulfide **(78)**. ^{1}H-NMR ($CDCl_3$) δ: 1.56-2.08 (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, 30.22, 34.79, 59.59 and 65.35 ppm. Anal. calc'd 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. The second fraction was identified as the cyclic tetrasulfide adduct **64** in a yield of 40%. ^{1}H-NMR ($CDCl_3$) δ: 3.64 (s, 4H) and 1.79 (s, 6H); ^{13}C-NMR ($CDCl_3$) δ: 18.12 (CH_3); 42.76 (CH_2) and 130.34 (C=C) ppm. Cyclic disulfide **63** was detected by ^{1}H NMR in low yield (*ca.* 8%). Starting material was isolated (12%) along with triphenylmethanethiol (26%), chlorotriphenylmethane (21%) and elemental sulfur (18%). In addition, cyclopentene **(71)** was detected by ^{1}H-NMR (*ca.* 9%).

The above reaction was repeated in a variety of solvents, varying temperature, time and concentration using the above procedure. The same products were isolated in each case but in varying yields **(Table 12)**.

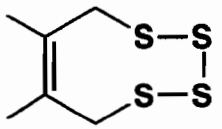
8.2.34 Thermal Chemistry of *trans*-2-Chloro-1-(triphenylmethyltrithio)-cyclopentane (75)



78

A solution of *trans*-2-chloro-1-(triphenylmethyltrithio)cyclopentane **(75)** (0.884 g, 2.0 mmol) in 30 mL of dry ethyl acetate was refluxed for 7 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 15% $CHCl_3$ in hexane as eluent. After evaporating the solvent under reduced pressure, the products were separated by column chromatography using the same eluent (15% $CHCl_3$ in hexane), in which the first fraction was isolated (67%) as an oily product and identified as the acyclic di[(2-chloro)-1-cyclopentyl] tetrasulfide **(78)**. ^{1}H-NMR ($CDCl_3$) δ: 1.56-2.08 (m, 4H), 2.26-2.58 (m, 2H), 3.73-3.89 (m, 1H) and 4.52-4.69 (m, 1H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 22.59, 30.21, 34.79, 59.59 and 65.34 ppm. Chlorotriphenylmethane was isolated (19%) along with starting material (10%), elemental sulfur (23%) and triphenylmethanethiol (27%). In addition, cyclopentene **(71)** was detected by ^{1}H NMR (*ca.* 6%).

8.2.35 Trapping of Diatomic Sulfur From the Decomposition of *trans*-2-Chloro-1-(triphenylmethyltrithio)cyclopentane (75) with 2,3-Dimethyl-1,3-butadiene (62)



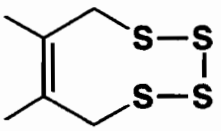
64

2,3-Dimethyl-1,3-butadiene **(62)** (0.0353 g, 0.43 mmol) was added to a mixture of *trans*-2-chloro-1-(triphenylmethyltrithio)cyclopentane **(75)** (0.57 g, 1.29 mmol) in 20 mL of dry ethyl acetate. The solution was refluxed for 24 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 25% $CHCl_3$ in hexane as eluent. After evaporating the solvent 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 (22%) as an oily product and identified as the acyclic di[(2-chloro)-1-cyclopentyl] tetrasulfide **(78)**. ^{1}H-NMR ($CDCl_3$) δ: 1.55-2.08 (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 65.34 ppm. Anal. calc'd for $C_{10}H_{16}Cl_2S_4$: C, 35.85; H, 4.78; S, 38.24. Found: C, 35.88; H, 4.40; S, 38.53. The second fraction was isolated and identified as cyclic tetrasulfide adduct **64** (45%). ^{1}H-NMR ($CDCl_3$) δ: 3.63 (s, 4H) and 1.79 (s, 6H); ^{13}C-NMR ($CDCl_3$) δ: 18.13 (CH_3); 42.75 (CH_2) and 130.32 (C=C) ppm. Cyclic disulfide **63** was detected by ^{1}H NMR in low yield (*ca.* 9%). Starting material was isolated (8%) along with triphenylmethanethiol (30%), chlorotriphenylmethane (20%) and elemental sulfur (25%). In addition, cyclopentene (**71**) was detected by ^{1}H-NMR (*ca.* 6%).

The above reaction was repeated in a variety of solvents, varying temperature, time and concentration using the above procedure. The same products were isolated in each case but in varying yields (**Table 13**).

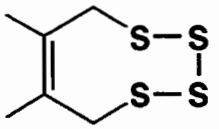
8.2.36 Trapping of Diatomic Sulfur From the Decomposition of *trans*-2-Chloro-3-(triphenylmethyldithio)-1,4-dioxane (112) with 2,3-Dimethyl-1,3-butadiene (62)



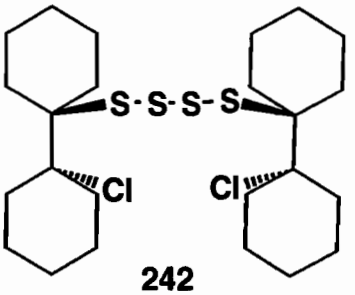
64

2,3-Dimethyl-1,3-butadiene (**62**) (0.0128 g, 0.0117 mmol) was added to a mixture of *trans*-2-chloro-3-(triphenylmethyldithio)-1,4-dioxane (**112**) (0.20 g, 0.0467 mmol) in 20 mL of dry ethyl acetate. The solution was refluxed for 30 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 35% ethyl acetate in hexane as eluent. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel using the same eluent (35% EtOAc in hexane) afforded an oily product which was identified as the cyclic tetrasulfide adduct **64** (30%). ^{1}H-NMR ($CDCl_3$) δ: 3.64 (s, 4H) and 1.79 (s, 6H); ^{13}C-NMR ($CDCl_3$) δ: 18.13 (CH_3); 42.76 (CH_2) and 130.32 (C=C) ppm. Cyclic disulfide **63** was detected by ^{1}H NMR in low yield (*ca.* 4%). Starting material was isolated (14%) along with triphenylmethanethiol (24%), chlorotriphenylmethane (20%) and elemental sulfur (12%). In addition, 1,4-dioxene (**240**) was detected by ^{1}H-NMR (*ca.* 6%)

8.2.37 Trapping of Diatomic Sulfur From the Decomposition of *trans*-1'-Chloro-1-(triphenylmethyldithio)bicyclohexyl (113) in the Presence of 2,3-Dimethyl-1,3-butadiene (62)



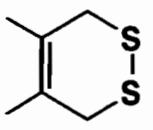
64



242

2,3-Dimethyl-1,3-butadiene **(62)** (0.0135 g, 0.165 mmol) was added to a mixture of *trans*-1'-chloro-1-(triphenylmethyldithio)bicyclohexyl **(113)** (0.25 g, 0.494 mmol) in 25 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 20% $CHCl_3$ in hexane as eluent. After evaporating the solvent 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 (23%) as an oily product and identified as the acyclic di[(1'-chloro)-1-bicyclohexyl] tetrasulfide **(242)**. ^{1}H-NMR ($CDCl_3$) δ: 2.32-1.39 (m, 20H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 22.20, 22.89, 22.93, 23.01, 24.46, 24.49, 25.74, 26.19, 33.65, 34.18, 50.11 and 60.70 ppm. The second fraction was isolated and identified as cyclic tetrasulfide adduct **64** (28%). ^{1}H-NMR ($CDCl_3$) δ: 3.63 (s, 4H) and 1.78 (s, 6H); ^{13}C-NMR ($CDCl_3$) δ: 18.12 (CH_3); 42.76 (CH_2) and 130.33 (C=C) ppm. Cyclic disulfide **63** was detected by ^{1}H NMR in low yield (*ca.* 4%). In addition, starting material was isolated (12%) along with triphenylmethanethiol (27%), elemental sulfur (14%) and chlorotriphenylmethane (22%).

8.2.38 Thermal Chemistry of Cyclic Tetrasulfide 64 in the Presence of Triphenylphosphine (141)

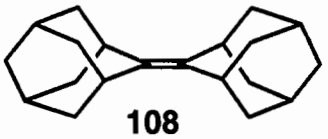


63

Triphenylphosphine **(141)** (0.142 g, 0.542 mmol) was added to a mixture of cyclic tetrasulfide **64** (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 eluent. After evaporating the solvent under reduced pressure, the products were isolated by column chromatography using the same eluent (15% $CHCl_3$ in hexane) afforded cyclic disulfide **63** as an oily product (91%). ^{1}H-NMR ($CDCl_3$) δ: 1.74 (s, 6H) and 3.19 (s, 4H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 20.81, 34.15 and 125.15 ppm. MS (m/z, rel. int., assignment): 146, 75%, $M^{+\cdot}$; 82, 100%, $M^{+\cdot}$ -S_2; 67, 82%, $M^{+\cdot}$ -CH_3S_2. In addition, triphenylphosphine sulfide was isolated in a yield of 98%.

8.2.39 Preparation of Adamantylideneadamantane (108)



108

Adamantylideneadamantane was prepared by the procedure of McMurry, Fleming, Kees and Krepski.[289] Potassium metal (3.84 g, 49 mmol) was added to a stirred slurry of titanium trichloride ($TiCl_3$) (4.30 g, 28 mmol) in 150 mL of dry tetrahydrofuran (THF) under a nitrogen atmosphere at room temperature. After refluxing for 40 min the black mixture was cooled and a solution of adamantanone (1.05 g, 7.0 mmol) in 10 mL of THF was added and the mixture was further refluxed for 16 h. The mixture was cooled to room temperature and filtered under an inert atmosphere. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with hexane, afforded a solid product which upon crystallization from *n*-hexane gave 0.75 g, 80% of adamantylideneadamantane **(108)**. Mp. 184-186 °C (lit. Mp. 183-185 °C[289], 184-187 °C[291]). ^{1}H-NMR ($CDCl_3$) δ: 1.58-1.98 (m, 24H) and 2.91 (br., 4H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 28.89, 32.21, 37.68, 39.95 and 133.48 ppm . MS (m/z, rel. int., assignment): 268, 100%, $M^{+\cdot}$.

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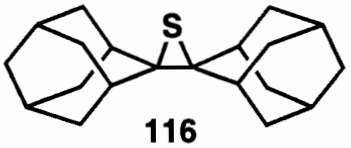
291 H. W. Geluk, *Synthesis*, 652 (1970).

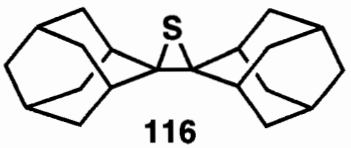
8.2.40 Reaction of Adamantylideneadamantane (108) with Triphenylmethanesulfenyl Chloride (65)



116

A solution of triphenylmethanesulfenyl chloride **(65)** (0.116 g, 0.373 mmol) in 25 mL of dry methylene chloride was added dropwise to a stirred solution of adamantylideneadamantane **(108)** (0.10 g, 0.373 mmol) in 20 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 6 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 20% chloroform in hexane, afforded a solid product which upon crystallization from *n*-hexane gave 0.096 g, 88% of adamantylideneadamantane thiirane **(116)**. Mp. 142-143 °C (lit. Mp. 153-154 °C[160], 131-132 °C[292]). ^{1}H-NMR ($CDCl_3$) δ: 2.08-1.56 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 27.12, 27.70, 34.95, 37.78, 38.41, 38.62 and 71.70 ppm. MS (m/z, rel. int., assignment): 268, 100%, $M^{+\cdot}$-S; 300, 14%, $M^{+\cdot}$. In addition, chlorotriphenylmethane was isolated in a yield of 58%. The x-ray crystallographic structure of episulfide **116** was reported for the first time **(Figure 6)**.

8.2.41 Reaction of Adamantylideneadamantane (108) with Triphenylmethanethiosulfenyl Chloride (61)



116

A solution of triphenylmethanethiosulfenyl chloride **(61)** (0.155 g, 0.45 mmol) in 20 mL of dry methylene chloride was added dropwise to a stirred solution of adamantylideneadamantane **(108)** (0.12 g, 0.45 mmol) in 20 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 4 h. Removal of the solvent under reduced pressure and chromatography of the residue on

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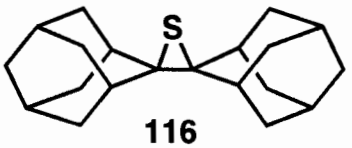
292 G. A. Tolstikov, B. M. Lerman, L. I. Umanskaya, Yu. T. Struchkov, A. A. Espenbetov and A. L. Yanovsky, *Tetrahedron Lett.*, **21**, 4189 (1980).

silica gel with 20% chloroform in hexane, afforded a solid product which upon crystallization from *n*-hexane gave 0.115 g, 92% of adamantylideneadamantane thiirane **(116)**. Mp. 142-143 °C (lit. Mp. 153-154 °C[160], 131-132 °C[292]). ^{1}H-NMR ($CDCl_3$) δ: 2.09-1.56 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 27.13, 27.70, 34.96, 37.78, 38.41, 38.64 and 71.71 ppm. MS (m/z, rel. int., assignment): 268, 64%, $M^{+\cdot}$-S; 300, 100%, $M^{+\cdot}$. In addition, elemental sulfur was isolated in a yield of 52% along with chlorotriphenylmethane (45%).

8.2.42 Reaction of Adamantylideneadamantane (108) with Triphenylmethanedithiosulfenyl Chloride (70)



116

A solution of triphenylmethanedithiosulfenyl chloride **(70)** (0.139 g, 0.373 mmol) in 20 mL of dry methylene chloride was added dropwise to a stirred solution of adamantylideneadamantane **(108)** (0.10 g, 0.373 mmol) in 20 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 3 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 25% chloroform in hexane, afforded a solid product which upon crystallization from *n*-hexane gave 0.095 g, 91% of adamantylideneadamantane thiirane **(116)**. Mp. 142-143 °C (lit. Mp. 153-154 °C[160], 131-132 °C[292]). ^{1}H-NMR ($CDCl_3$) δ: 2.09-1.56 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 27.13, 27.70, 34.94, 37.77, 38.41, 38.62 and 71.70 ppm. In addition, elemental sulfur was isolated in a yield of 55% along with chlorotriphenylmethane (68%).

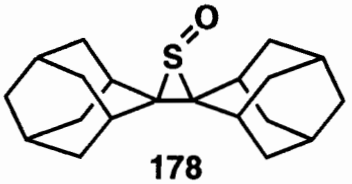
8.2.43 Thermal Chemistry of Adamantylideneadamantane Thiirane (116) in the Presence of 2,3-Dimethyl-1,3-butadiene (62)

2,3-Dimethyl-1,3-butadiene **(62)** (0.073 g, 0.90 mmol) was added to a mixture of adamantylideneadamantane thiirane **(116)** (0.18 g, 0.60 mmol) in 15 mL of dry ethyl acetate. The solution was refluxed for 15 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 15% $CHCl_3$ in hexane as eluent. After

evaporating the solvent under reduced pressure, the products were separated by the same eluent (15% $CHCl_3$ in hexane), in which the first fraction was isolated and identified as adamantylideneadamantane **(108)** (0.15 g, 91%). Mp. 185-186 °C (lit. Mp. 183-185 °C[289], 184-187 °C[291]). ^{1}H-NMR ($CDCl_3$) δ: 1.59-1.98 (m, 24H) and 2.91 (br., 4H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 28.87, 32.21, 37.70, 39.95 and 133.48 ppm. MS (m/z, rel. int., assignment): 268, 100%, $M^{+\cdot}$. The second fraction was isolated and identified as elemental sulfur (55%).

The reaction was repeated in toluene using the above procedure. Adamantylidene-adamantane thiirane **(116)** was completely decomposed when the solution was refluxed for 2 h in toluene solution (110 °C) giving adamantylideneadamantane **(108)** (99%) along with elemental sulfur (58%).

8.2.44 Oxidation of Adamantylideneadamantane Thiirane (116) by *m*-Chloroperoxybenzoic Acid (*m*-CPBA)



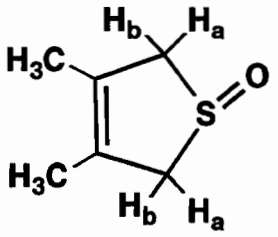
178

A solution of *m*-CPBA (0.172 g, 1.0 mmol) in 20 mL of dry methylene chloride was added dropwise to a stirred solution of adamantylideneadamantane thiirane **(116)** (0.30 g, 1.0 mmol) in 30 mL of dry methylene chloride under a nitrogen atmosphere at -78 °C . The mixture was stirred for 2 h. The solution was diluted with 5% NaOH solution and extracted three times with 20 mL portions of diethyl ether. The combined ethereal extracts were dried with $MgSO_4$, filtered and evaporated to give the crude adamantylideneadamantane thiirane 1-oxide **(178)**. Recrystallization from *n*-pentane gave 0.313 g, 99% of the corresponding thiirane 1-oxide **178**. Mp. 129-130 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.53-2.38 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ : 27.02, 27.39, 27.58, 30.02, 36.16, 37.12, 37.20, 37.56, 37.62 and 72.88 ppm. MS (m/z, rel. int., assignment): 316, 18%, $M^{+\cdot}$; 300, 10%, $M^{+\cdot}$-O; 268, 100%, $M^{+\cdot}$-SO.

8.2.45 Thermal Chemistry of Adamantylideneadamantane Thiirane 1-Oxide (178)

Adamantylideneadamantane thiirane 1-oxide **(178)** (0.25 g, 0.791 mmol) was dissolved in 25 mL of toluene and the solution was refluxed for 2.5 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% EtOAc in hexane as eluent. After evaporating the solvent under reduced pressure, the mixture was adsorbed onto silica gel and chromatographed using the same eluent (20% EtOAc in hexane) to give adamantylideneadamantane **(108)** in a yield of 97%.

8.2.46 Trapping of Sulfur Monoxide From the Decomposition of Adamantylideneadamantane Thiirane 1-Oxide (178) with 2,3-Dimethyl-1,3-butadiene (62)

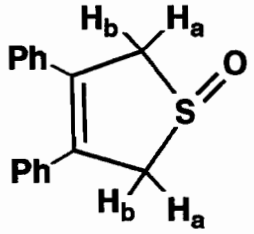


200

2,3-Dimethyl-1,3-butadiene **(62)** (0.0513 g, 0.625 mmol) was added to a mixture of adamantylideneadamantane thiirane 1-oxide **(178)** (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 thin layer chromatography 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 (15% EtOAc in hexane) and was identified as adamantylideneadamantane **(108)** (99%). By eluting with methanol, the second fraction was isolated (0.065 g, 80%) as an oily product and identified as 2,5-dihydro-3,4-dimethyl-thiophene 1-oxide **(200)**. ^{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%, $M^{+\cdot}$-$SOCH_3$.

The above reaction was repeated in a variety of solvents, varying temperature, time and concentration using the above procedure. The same products were isolated in each case but in varying yields as shown in **Table 27**.

8.2.47 Trapping of Sulfur Monoxide From the Decomposition of Adamantylideneadamantane Thiirane 1-Oxide (178) with 2,3-Diphenyl-1,3-butadiene (199)



201

2,3-Diphenyl-1,3-butadiene[293] **(199)** (0.129 g, 0.625 mmol) was added to a mixture of adamantylideneadamantane thiirane 1-oxide **(178)** (0.593 g, 1.875 mmol) in 30 mL of dry toluene. The solution was refluxed for 24 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% EtOAc in hexane as eluent. After evaporating the solvent under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (20% EtOAc in hexane) and was identified as adamantylideneadamantane **(108)** (98%). By eluting with methanol, the second fraction was isolated and identified as 2,5-dihydro-3,4-diphenylthiophene 1-oxide **(201)**. Recrystallization from *n*-hexane gave 0.111 g, 70% of pure sulfoxide **201**. Mp. 134-135 °C. ^{1}H-NMR ($CDCl_3$) δ: 4.05 (d, $2H_b$), 4.41 (d, $2H_a$) and 7.13-7.26 (m, 10H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 64.46, 127.92, 128.47, 128.60, 132.01 and 135.58 ppm. MS (m/z, rel. int., assignment): 254, 5%, $M^{+\cdot}$; 236, 100%, $M^{+\cdot}$ -H_2O; 205, 59%, $M^{+\cdot}$ -SO; 191, 12%, $M^{+\cdot}$ -$SOCH_2$.

The above reaction was further investigated by varying the reaction conditions in a variety of ways. The same products were isolated in each case but in varying yields as shown in **Table 29**.

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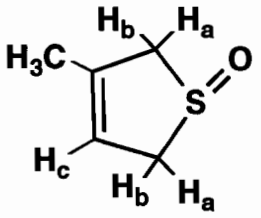
293 For the preparation of 2,3-diphenyl-1,3-butadiene **(199)** see: a) B. C. Fulcher, M. L. Hunter and M. E. Welker, *Synth. Commun.*, **23(2)**, 217 (1993); b) M. S. Newman, *J. Org. Chem.*, **26**, 582 (1961); c) K. Alder and J. Haydn, *Justus Liebigs Ann. Chem.*, **570**, 201 (1950).

8.2.48 Trapping of Sulfur Monoxide From the Decomposition of Adamantylideneadamantane Thiirane 1-Oxide (178) with Isoprene (202)

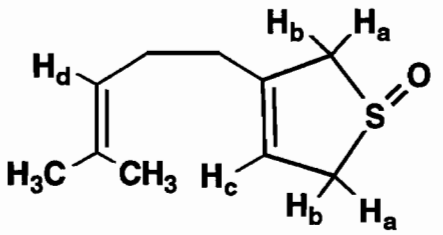


203

Isoprene **(202)** (0.014 g, 0.211 mmol) was added to a mixture of adamantylidene-adamantane thiirane 1-oxide **(178)** (0.20 g, 0.633 mmol) in 25 mL of dry toluene. The solution was refluxed for 36 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% EtOAc in hexane as eluent. After evaporating the solvent under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (20% EtOAc in hexane) and was identified as adamantylidene-adamantane **(108)** (97%). By eluting with methanol, the second fraction was isolated (0.0168 g, 69%) as an oily product and identified as 2,5-dihydro-3-methylthiolene 1-oxide **(203)**. ^{1}H-NMR ($CDCl_3$) δ: 5.58 (m, H_c), 3.69-3.90 (m, $2H_a$), 3.34-3.58 (m, $2H_b$) and 1.90 (s, 3H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 16.72, 59.99, 62.92, 119.07 and 125.01 ppm. MS (m/z, rel. int., assignment): 116, 100%, $M^{+\cdot}$; 68, 49%, $M^{+\cdot}$-SO; 67, 86%, $M^{+\cdot}$-SOH; 53, 46%, $M^{+\cdot}$-$SOCH_3$.

The above reaction was repeated in a variety of solvents, varying temperature, time and concentration using the above procedure. The same products were isolated in each case but in varying yields as shown in **Table 31**.

8.2.49 Trapping of Sulfur Monoxide From the Decomposition of Adamantylideneadamantane Thiirane 1-Oxide (178) with Myrcene (41)

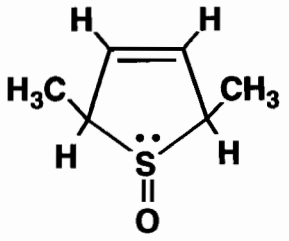


233

Myrcene **(41)** (0.069 g, 0.506 mmol) was added to a mixture of adamantylidene-adamantane thiirane 1-oxide **(178)** (0.480 g, 1.519 mmol) in 20 mL of dry toluene. The solution was refluxed for 16 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 25% EtOAc in hexane as eluent. After evaporating the solvent under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (25% EtOAc in hexane) and was identified as adamantylidene-adamantane **(108)** (98%). By eluting with methanol, the second fraction was isolated (0.048 g, 52%) as an oily product and identified as 3-(4'-methyl-3'-pentenyl)-2,5-dihydrothiophene 1-oxide **(233)**. ^{1}H-NMR ($CDCl_3$) δ: 1.60 (s, 3H), 1.68 (s, 3H), 2.12-2.31 (m, 4H), 3.35-3.59 (m, $2H_b$), 3.70-3.89 (m, $2H_a$), 5.07 (m, H_d) and 5.60 (m, H_c) ppm; ^{13}C-NMR ($CDCl_3$) δ: 17.69, 25.59, 26.25, 31.26, 59.68, 61.61, 117.93, 123.93, 132.59 and 139.87 ppm. MS (m/z, rel. int., assignment): 184, 39%, $M^{+\cdot}$; 136, 27%, $M^{+\cdot}$ -SO; 135, 55%, $M^{+\cdot}$ -SOH ; 116, 44%, $M^{+\cdot}$ -C_5H_9; 69, 100%, $M^{+\cdot}$ -C_5H_7SO.

The above reaction was further investigated by varying the reaction conditions in a variety of ways. The same products were isolated in each case but in varying yields as shown in **Table 33.**

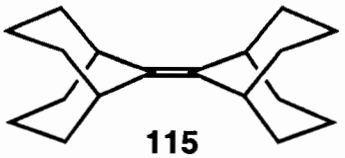
8.2.50 Trapping of Sulfur Monoxide From the Decomposition of Adamantylideneadamantane Thiirane 1-Oxide (178) with 2,4-Hexadiene



238

2,4-Hexadiene (0.0512 g, 0.625 mmol) (as a mixture of 3 isomers) was added to a mixture of adamantylideneadamantane thiirane 1-oxide **(178)** (0.593 g, 1.875 mmol) in 35 mL of dry toluene. The solution was refluxed for 15 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% EtOAc in hexane as eluent. After evaporating the solvent under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (15% EtOAc in hexane) and was identified as adamantylideneadamantane **(108)** (98%). By eluting with methanol, the second fraction was isolated (0.069 g, 85%) as an oily product and identified as *trans,trans*-2,5-dihydro-2,5-dimethylthiophene 1-oxide **(238)**. ^{1}H-NMR ($CDCl_3$) δ: 5.77 (s, 2H), 3.87 (q, 2H) and 1.41 (d, 6H) ppm; MS (m/z, rel. int., assignment): 130, 53%, $M^{+\cdot}$; 82, 97%, $M^{+\cdot}$-SO; 67, 100%, $M^{+\cdot}$-$SOCH_3$.

8.2.51 Preparation of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (115)

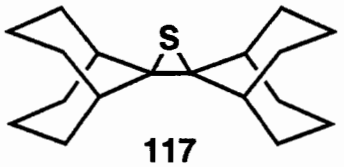


115

Potassium metal (5.76 g, 147 mmol) was added to a stirred slurry of titanium trichloride ($TiCl_3$) (6.45 g, 42 mmol) in 250 mL of dry tetrahydrofuran (THF) under a nitrogen atmosphere at room temperature. After refluxing for 1.5 h, the black mixture was cooled and a solution of bicyclo[3.3.1]nonan-9-one (1.45 g, 10.50 mmol) in 15 mL of THF was added. After the mixture was further refluxed for 24 h, the mixture was cooled to room temperature and filtered under an inert atmosphere. Removal of the solvent under

reduced pressure and chromatography of the residue on silica gel with hexane, afforded a solid product which upon crystallization from *n*-hexane gave 2.17 g, 85% of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane **(115)**. Mp. 144-145 °C (lit. Mp. 143-144 °C[294], 144-145 °C[295]). ^{1}H-NMR ($CDCl_3$) δ: 1.40-2.12 (m, 24H) and 2.85 (br., 4H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 23.02, 32.53, 34.51 and 131.61 ppm. MS (m/z, rel. int., assignment): 244, 72%, $M^{+\cdot}$; 121, 100%, $M^{+\cdot}$ -C_9H_{14}.

8.2.52 Reaction of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (115) with Triphenylmethanesulfenyl Chloride (65)



117

A solution of triphenylmethanesulfenyl chloride **(65)** (0.152 g, 0.492 mmol) in 30 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo[3.3.1]-nonylidenebicyclo[3.3.1]nonane **(115)** (0.12 g, 0.492 mmol) in 25 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 5 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 15% chloroform in hexane, afforded a solid product which upon crystallization from *n*-hexane gave 0.107 g, 86% of bicyclo[3.3.1]nonylidenebicyclo-[3.3.1]nonane thiirane **(117)**. Mp. 166-167 °C (lit.[54] Mp. 166.5-167 °C). ^{1}H-NMR ($CDCl_3$) δ: 1.52-2.03 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 20.75, 21.26, 31.92, 33.65, 34.76 and 70.43 ppm. In addition, chlorotriphenylmethane was isolated in a yield of 55%.

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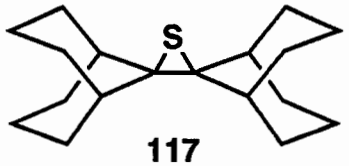
294 H. Keul, *Chem. Ber.*, **108,** 1207 (1975).

295 R. S. Brown, R. W. Nagorski, A. J. Bennet, R. E. D. McClung, G. H. M. Arts, M. Klobukowski, R. McDonald and B. D. Santarsiero, *J. Am. Chem. Soc.*, **116,** 2448 (1994).

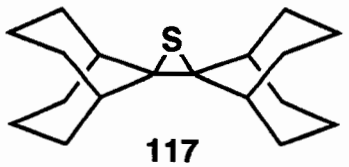
8.2.53 Reaction of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (115) with Triphenylmethanethiosulfenyl Chloride (61)



117

A solution of triphenylmethanethiosulfenyl chloride **(61)** (0.210 g, 0.615 mmol) in 25 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane **(115)** (0.15 g, 0.615 mmol) in 20 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 4 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 15% chloroform in hexane afforded a solid product which upon crystallization from *n*-hexane gave 0.155 g, 91% of bicyclo[3.3.1]nonylidenebicyclo-[3.3.1]nonane thiirane **(117)**. Mp. 166-167 °C (lit.[54] Mp. 166.5-167 °C). ^{1}H-NMR ($CDCl_3$) δ: 1.53-2.02 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 20.74, 21.26, 31.92, 33.66, 34.77 and 70.43 ppm. MS (m/z, rel. int., assignment): 276, 18%, $M^{+\cdot}$; 244, 100%, $M^{+\cdot}$ -S; 121, 19%, $M^{+\cdot}$ -$C_9H_{14}S$. In addition, elemental sulfur was isolated in a yield of 50% along with chlorotriphenylmethane (43%).

8.2.54 Reaction of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (115) with Triphenylmethanedithiosulfenyl Chloride (70)



117

A solution of triphenylmethanedithiosulfenyl chloride **(70)** (0.199 g, 0.533 mmol) in 30 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane **(115)** (0.13 g, 0.533 mmol) in 25 mL of dry methylene chloride under a nitrogen atmosphere at room temperature. The mixture was stirred for 3.5 h.

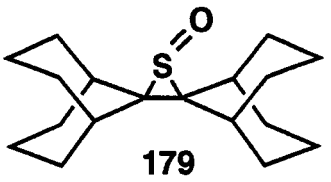
Removal of the solvent under reduced pressure and chromatography of the residue on silica gel with 25% chloroform in hexane, afforded a solid product which upon crystallization from *n*-hexane gave 0.132 g, 90% of bicyclo[3.3.1]nonylidene- bicyclo[3.3.1]nonane thiirane **(117)**. Mp. 166-167 °C (lit.[54] Mp. 166.5-167 °C). ^{1}H-NMR ($CDCl_3$) δ: 1.52-2.03 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 20.75, 21.24, 31.93, 33.65, 34.77 and 70.43 ppm. In addition, elemental sulfur was isolated in a yield of 54% along with chlorotriphenylmethane (65%).

8.2.55 Thermal Chemistry of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]-nonane Thiirane (117) in the Presence of 2,3-Dimethyl-1,3-butadiene (62)

2,3-Dimethyl-1,3-butadiene **(62)** (0.036 g, 0.435 mmol) was added to a mixture of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane **(117)** (0.12 g, 0.435 mmol) in 20 mL of dry ethyl acetate. The solution was refluxed for 8 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% $CHCl_3$ in hexane as eluent. After evaporating the solvent 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 and identified as bicyclo[3.3.1]nonylidenebicyclo[3.3.1] nonane **(115)** (0.10 g, 95%). Mp. 144-146 °C (lit. Mp. 143-144 °C[294], 144-145 °C[295]). ^{1}H-NMR ($CDCl_3$) δ: 1.40-2.11 (m, 24H) and 2.86 (br., 4H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 23.01, 32.53, 34.52 and 131.61 ppm. The second fraction was isolated and identified as elemental sulfur in a yield of 50%.

The reaction was repeated in toluene using the above procedure. Bicyclo[3.3.1]-nonylidenebicyclo[3.3.1] nonane thiirane was completely decomposed after the solution was refluxed for 2.5 h in toluene (110 °C) under a nitrogen atmosphere giving bicyclo-[3.3.1]nonylidenebicyclo[3.3.1]nonane **(115)** in a yield of 98%. In addition, elemental sulfur was isolated (58%).

8.2.56 Oxidation of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane Thiirane (117) by *m*-Chloroperoxybenzoic Acid (*m*-CPBA)



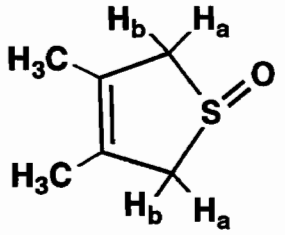
179

A solution of *m*-CPBA (0.0624 g, 0.362 mmol) in 20 mL of dry methylene chloride was added dropwise to a stirred solution of bicyclo[3.3.1]nonylidene-bicyclo[3.3.1]nonane thiirane (**117**) (0.10 g, 0.362 mmol) in 25 mL of dry methylene chloride under a nitrogen atmosphere at -78 °C . The mixture was stirred for 2.5 h. The solution was diluted with 5% NaOH solution and extracted three times with 20 mL portions of diethyl ether. The combined ethereal extracts were dried with $MgSO_4$, filtered and evaporated to give the crude bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide (**179**). Recrystallization from *n*-hexane gave 0.104 g, 98% of the corresponding thiirane 1-oxide **179**. Mp. 150-151 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.45-2.34 (m, 28H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 21.28, 27.45, 30.07, 30.34, 30.78, 31.31, 32.35 and 71.52 ppm. MS (m/z, rel. int., assignment): 292, 17%, $M^{+\cdot}$; 276, 7%, $M^{+\cdot}$ -O; 244, 100%, $M^{+\cdot}$ -SO; 121, 81%, $M^{+\cdot}$ -$C_9H_{14}SO$.

8.2.57 Thermal Chemistry of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]-nonane Thiirane 1-Oxide (179)

A sample of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide (**179**) (0.20 g, 0.685 mmol) was dissolved in toluene and the solution was refluxed for 4 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 30% EtOAc in hexane as eluent. After evaporating the solvent under reduced pressure, the mixture was adsorbed onto silica gel and chromatographed using the same eluent (30% EtOAc in hexane) to give bicyclo[3.3.1]nonylidenebicyclo[3.3.1] nonane (**115**) in a yield of 98%.

8.2.58 Trapping of Sulfur Monoxide From the Decomposition of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane Thiirane 1-Oxide (179) with 2,3-Dimethyl-1,3-butadiene (62)

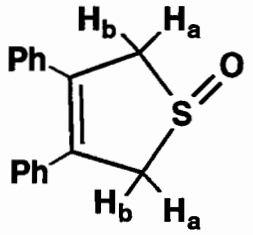


200

2,3-Dimethyl-1,3-butadiene **(62)** (0.0234 g, 0.285 mmol) was added to a mixture of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide **(179)** (0.250 g, 0.856 mmol) in 20 mL of dry toluene. The solution was refluxed for 8 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 20% EtOAc in hexane as eluent. After evaporating the solvent under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (20% EtOAc in hexane) and was identified as bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane **(115)** (98%). By eluting with methanol, the second fraction was isolated (0.030 g, 82%) as an oily product and identified as 2,5-dihydro-3,4-dimethylthiophene 1-oxide **(200)**. ^{1}H-NMR ($CDCl_3$) δ: 3.84 (d, $2H_a$), 3.48 (d, $2H_b$) and 1.77 (s, 6H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 14.46, 64.31 and 126.08 ppm.

The above reaction was repeated in a variety of solvents, varying temperature, time and concentration using the above procedure. The same products were isolated in each case but in varying yields as shown in **Table 28**.

8.2.59 Trapping of Sulfur Monoxide From the Decomposition of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane Thiirane 1-Oxide (179) with 2,3-Diphenyl-1,3-butadiene (199)

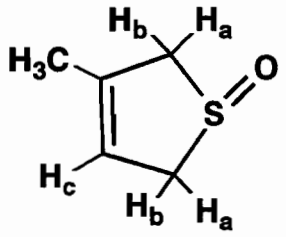


201

2,3-Diphenyl-1,3-butadiene (**199**) (0.035 g, 0.171 mmol) was added to a mixture of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide (**179**) (0.150 g, 0.514 mmol) in 25 mL of dry toluene. The solution was refluxed for 12 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 30% EtOAc in hexane as eluent. After evaporating the solvent under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (30% EtOAc in hexane) and was identified as bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**115**) (97%). By eluting with methanol, the second fraction was isolated and identified as 2,5-dihydro-3,4-diphenylthiophene 1-oxide (**201**). Recrystallization from *n*-hexane gave 0.032 g, 73% of pure sulfoxide **201**. Mp. 134-135 °C. ^{1}H-NMR ($CDCl_3$) δ: 4.06 (d, $2H_b$), 4.41 (d, $2H_a$) and 7.13-7.25 (m, 10H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 64.46, 127.91, 128.47, 128.61, 132.01 and 135.58 ppm.

The above reaction was repeated in a variety of solvents, varying temperature, time and concentration using the above procedure. The same products were isolated in each case but in varying yields as shown in **Table 30**.

8.2.60 Trapping of Sulfur Monoxide From the Decomposition of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane Thiirane 1-Oxide (179) with Isoprene (202)

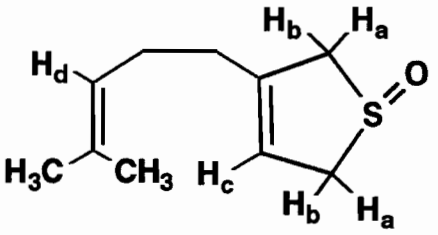


203

Isoprene **(202)** (0.0139 g, 0.255 mmol) was added to a mixture of bicyclo[3.3.1]-nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide **(179)** (0.18 g, 0.616 mmol) in 20 mL of dry toluene. The solution was refluxed for 20 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 30% EtOAc in hexane as eluent. After evaporating the solvent under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (30% EtOAc in hexane) and was identified as bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane **(115)** (99%). By eluting with methanol, the second fraction was isolated (0.0122 g, 72%) as an oily product and identified as 2,5-dihydro-3-methylthiolene 1-oxide **(203)**. ^{1}H-NMR ($CDCl_3$) δ: 5.58 (m, H_c), 3.68-3.90 (m, $2H_a$), 3.34-3.58 (m, $2H_b$) and 1.90 (s, 3H) ppm; ^{13}C-NMR ($CDCl_3$) δ: 16.72, 59.98, 62.92, 119.07 and 125.02 ppm.

The above reaction was further investigated by varying the reaction conditions in a variety of ways. The same products were isolated in each case but in varying yields as shown in **Table 32.**

8.2.61 Trapping of Sulfur Monoxide From the Decomposition of Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane Thiirane 1-Oxide (179) with Myrcene (41)



233

Myrcene **(41)** (0.0388 g, 0.285 mmol) was added to a mixture of bicyclo[3.3.1]-nonylidenebicyclo[3.3.1]nonane thiirane 1-oxide **(179)** (0.250 g, 0.856 mmol) in 25 mL of dry toluene. The solution was refluxed for 14 h under a nitrogen atmosphere. The reaction was followed by thin layer chromatography using 30% EtOAc in hexane as eluent. After evaporating the solvent under reduced pressure, the first fraction was isolated by column chromatography using the same eluent (30% EtOAc in hexane) and was identified as bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane **(115)** (98%). By eluting with methanol, the second fraction was isolated (0.029 g, 55%) as an oily product and identified as 3-(4'-methyl-3'-pentenyl)-2,5-dihydrothiophene 1-oxide **(233)**. ^{1}H-NMR ($CDCl_3$) δ: 1.60 (s, 3H), 1.68 (s, 3H), 2.11-2.32 (m, 4H), 3.35-3.60 (m, $2H_b$), 3.71-3.88 (m, $2H_a$), 5.07 (m, H_d) and 5.60 (m, H_c) ppm; ^{13}C-NMR ($CDCl_3$) δ: 17.69, 25.59, 26.26, 31.25, 59.68, 61.62, 117.94, 123.93, 132.59 and 139.87 ppm.

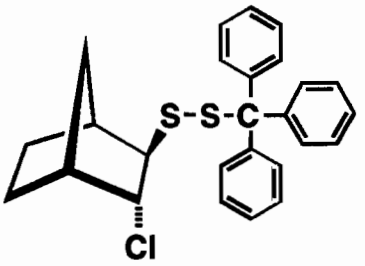
The above reaction was repeated in a variety of solvents, varying temperature, time and concentration using the above procedure. The same products were isolated in each case but in varying yields as shown in **Table 34**.

APPENDIX

X-RAY STRUCTURE DETERMINATIONS

APPENDIX I

X-RAY STRUCTURE DETERMINATION OF *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane (68)



- Crystal Data for the Structure Determination of 68 (Table XR-1)
- Atomic Coordinates and Temperature Factors for 68 (Table XR-2)
- Bond Distances and Bond Angles for 68 (Table XR-3)

Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer controlled by TEXRAY software using the θ/2θ scan mode.

Table XR-1. Crystal data for the structure determination of **68**

Chemical Formula	$C_{26}H_{25}ClS_2$
Formula Weight	437.05
X-ray crystal dimension (mm)[a]	0.35 x 0.15 x 0.15
Radiation	MoK_α
Crystal system	monoclinic
Space group	P $2_1/c$
Lattice constants	
a (Å)	10.1400(20)
b (Å)	12.860(3)
c (Å)	17.407(14)
V (Å^3)	2239.6(19)
Z	4
F (000)	921.62
Density (calc'd) (g cm^{-3})	1.296
μ (mm^{-1})	0.36
λ (Å)	0.70930
2θ max (°)	44.90
No. of reflections measured	3114
No. of unique reflections	2921
No. of reflections with $I_{net} > 2.5\sigma(I_{net})$	1600
For significant reflections	RF = 0.057[b], R_w = 0.058[c], G_oF = 1.80[d]
Maximum shift / σ ratio	0.035
Deepest hole in D-map (e / Å^3)	-0.330
Highest peak in D-map (e / Å^3)	0.600
Method of structure determination	solved by direct methods
Method of structure refinement	NRCVAX system programs

[a]cell dimensions were obtained from 25 reflections with 2θ angles in the range 30.00-35.00°.

[b]$RF = \Sigma(F_o-F_c) / \Sigma(F_o)$

[c]$R_w = (\Sigma[wF_o-F_c)^2 / \Sigma (wF_o^2)])^{1/2}$

[d]$G_oF = (\Sigma[wF_o-F_c)^2 / (\#\text{ reflections} - \#\text{ parameters})])^{1/2}$

Table XR-2. Atomic coordinates (x, y, z) and temperature factors (B_{eq}) for compound **68**. Estimated σs refer to the last digit.

Atomic Parameters x, y, z and B_{eq}
E. S. DS. refer to the last digit printed

atom	x	y	z	Beq
S 1	0.69273(20)	0.27449(16)	0.23200(11)	3.80(10)
S 2	0.81089(19)	0.33765(15)	0.16097(11)	3.62(9)
Cl	0.3075 (3)	0.22215(21)	0.22743(20)	8.75(19)
C 1	0.5345 (8)	0.4563 (6)	0.2139 (5)	4.2 (4)
C 2	0.5287 (7)	0.3377 (6)	0.2051 (4)	3.5 (4)
C 3	0.4419 (8)	0.3067 (6)	0.2672 (5)	4.4 (4)
C 4	0.3957 (10)	0.4104 (7)	0.2952 (5)	5.6 (5)
C 5	0.3044 (9)	0.4647 (7)	0.2299 (6)	6.1 (6)
C 6	0.4055 (10)	0.5001 (6)	0.1696 (6)	7.4 (6)
C 7	0.5216 (10)	0.4702 (7)	0.2987 (6)	6.4 (5)
C 8	0.8041 (7)	0.2448 (5)	0.0762 (4)	3.0 (3)
C11	0.8689 (7)	0.1397 (5)	0.1026 (4)	3.0 (3)
C12	0.8523 (8)	0.0567 (6)	0.0492 (5)	4.2 (4)
C13	0.9137 (9)	-0.0386 (6)	0.0698 (6)	5.3 (5)
C14	0.9946 (10)	-0.0512 (7)	0.1402 (7)	5.9 (6)
C15	1.0163 (10)	0.0312 (8)	0.1917 (6)	6.4 (6)
C16	0.9527 (8)	0.1261 (6)	0.1717 (5)	4.6 (4)
C21	0.6560 (7)	0.2387 (6)	0.0417 (4)	2.9 (3)
C22	0.5780 (7)	0.1522 (6)	0.0523 (4)	3.8 (4)
C23	0.4415 (8)	0.1520 (7)	0.0231 (5)	5.0 (5)
C24	0.3831 (8)	0.2356 (8)	-0.0174 (5)	5.6 (5)
C25	0.4569 (9)	0.3233 (7)	-0.0269 (5)	5.1 (5)
C26	0.5921 (8)	0.3239 (6)	0.0019 (4)	3.8 (4)
C31	0.8913 (7)	0.2975 (5)	0.0233 (4)	3.0 (3)
C32	1.0143 (7)	0.3383 (7)	0.0552 (4)	4.4 (4)
C33	1.0977 (8)	0.3833 (7)	0.0078 (6)	5.4 (5)
C34	1.0602 (8)	0.3839 (7)	-0.0714 (6)	4.9 (5)

C35	0.9405 (9)	0.3407 (7)	-0.1034 (4)	4.7 (4)
C36	0.8574 (7)	0.2971 (6)	-0.0567 (4)	3.8 (4)

$\mathbf{B_{eq}}$ is the mean of the principal axes of the thermal ellipsoid.

Table XR-3. Bond distances (Å) and bond angles (degrees) for compound **68.** Estimated σs refer to the last digit.

Bond Distances (Å)

S(1)-S(2)	2.026(3)	C(12)-C(13)	1.395(12)
S(1)-C(2)	1.842(7)	C(13)-C(14)	1.369(16)
S(2)-C(8)	1.891(7)	C(14)-C(15)	1.382(16)
Cl-C(3)	1.792(8)	C(15)-C(16)	1.397(12)
C(1)-C(2)	1.532(11)	C(21)-C(22)	1.395(11)
C(1)-C(6)	1.514(12)	C(21)-C(26)	1.398(10)
C(1)-C(7)	1.514(12)	C(22)-C(23)	1.395(11)
C(2)-C(3)	1.554(11)	C(23)-C(24)	1.366(14)
C(3)-C(4)	1.520(12)	C(24)-C(25)	1.378(14)
C(4)-C(5)	1.515(14)	C(25)-C(26)	1.381(11)
C(4)-C(7)	1.484(14)	C(31)-C(32)	1.383(10)
C(5)-C(6)	1.646(16)	C(31)-C(36)	1.381(11)
C(8)-C(11)	1.540(10)	C(32)-C(33)	1.399(12)
C(8)-C(21)	1.526(10)	C(33)-C(34)	1.368(14)
C(8)-C(31)	1.534(10)	C(34)-C(35)	1.368(13)
C(11)-C(12)	1.406(11)	C(35)-C(36)	1.381(12)
C(11)-C(16)	1.366(11)		

Bond Angles (Degrees)

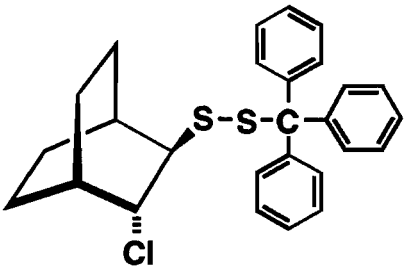
S(2)-S(1)-C(2)	105.5(3)	C(8)-C(11)-C(16)	123.3(6)
S(1)-S(2)-C(8)	105.84(24)	C(12)-C(11)-C(16)	118.3(7)
C(2)-C(1)-C(6)	107.7(6)	C(11)-C(12)-C(13)	119.7(8)
C(2)-C(1)-C(7)	101.9(6)	C(12)-C(13)-C(14)	120.8(8)
C(6)-C(1)-C(7)	104.3(7)	C(13)-C(14)-C(15)	119.9(8)
S(1)-C(2)-C(1)	113.3(5)	C(14)-C(15)-C(16)	119.3(9)
S(1)-C(2)-C(3)	107.5(5)	C(11)-C(16)-C(15)	121.8(8)
C(1)-C(2)-C(3)	101.7(6)	C(8)-C(21)-C(22)	122.1(6)

Table XR-3. continued

Cl-C(3)-C(2)	111.6(6)	C(8)-C(21)-C(26)	120.1(6)
Cl-C(3)-C(4)	113.7(6)	C(22)-C(21)-C(26)	117.6(6)
C(2)-C(3)-C(4)	103.7(6)	C(21)-C(22)-C(23)	120.3(7)
C(3)-C(4)-C(5)	110.3(7)	C(22)-C(23)-C(24)	120.5(8)
C(3)-C(4)-C(7)	99.2(7)	C(23)-C(24)-C(25)	120.6(7)
C(5)-C(4)-C(7)	102.0(8)	C(24)-C(25)-C(26)	119.1(8)
C(4)-C(5)-C(6)	103.8(7)	C(21)-C(26)-C(25)	121.9(7)
C(1)-C(6)-C(5)	98.6(7)	C(8)-C(31)-C(32)	119.9(6)
C(1)-C(7)-C(4)	96.3(7)	C(8)-C(31)-C(36)	122.1(6)
S(2)-C(8)-C(11)	111.2(5)	C(32)-C(31)-C(36)	117.7(7)
S(2)-C(8)-C(21)	104.4(4)	C(31)-C(32)-C(33)	120.9(7)
S(2)-C(8)-C(31)	103.8(5)	C(32)-C(33)-C(34)	120.0(7)
C(11)-C(8)-C(21)	114.7(6)	C(33)-C(34)-C(35)	119.4(7)
C(11)-C(8)-C(31)	107.9(5)	C(34)-C(35)-C(36)	120.7(7)
C(21)-C(8)-C(31)	114.4(6)	C(31)-C(36)-C(35)	121.2(7)
C(8)-C(11)-C(12)	118.0(6)		

APPENDIX II

X-RAY STRUCTURE DETERMINATION OF *endo*-2-Chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane (69)



- Crystal Data for the Structure Determination of 69 (Table XR-4)
- Atomic Coordinates and Temperature Factors for 69 (Table XR-5)
- Bond Distances and Bond Angles for 69 (Table XR-6)

Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer controlled by TEXRAY software using the θ/2θ scan mode.

Table XR-4. Crystal data for the structure determination of **69**

Chemical Formula	$C_{27}H_{27}ClS_2$
Formula Weight	451.08
X-ray crystal dimension (mm)[a]	0.20 x 0.20 x 0.35
Radiation	MoK_α
Crystal system	triclinic
Space group	P_1(# 2)
Lattice constants	
a (Å)	9.1129(14)
b (Å)	11.626(21)
c (Å)	22.2218(23)
V (Å^3)	2308.6(6)
Z	4
F (000)	95.91
Density (calc'd) (g cm^{-3})	1.298
μ (mm^{-1})	0.35
λ (Å)	0.70930
2θ max (°)	47.00
No. of reflections measured	7304
No. of unique reflections	6807
No. of reflections with $I_{net} > 2.5\sigma(I_{net})$	4439
For significant reflections	RF = 0.109[b], R_w = 0.129[c], G_oF = 5.39[d]
Maximum shift / σ ratio	0.565
Deepest hole in D-map (e / Å^3)	-0.640
Highest peak in D-map (e / Å^3)	0.880
Method of structure determination	solved by direct methods
Method of structure refinement	NRCVAX system programs

[a]cell dimensions were obtained from 25 reflections with 2θ angles in the range 40.00-45.00°.

[b]$RF = \Sigma(F_o-F_c) / \Sigma(F_o)$

[c]$R_w = (\Sigma[wF_o-F_c)^2 / \Sigma (wF_o^2)])^{1/2}$

[d]$G_oF = (\Sigma[wF_o-F_c)^2 / (\#\text{ reflections} - \#\text{ parameters})])^{1/2}$

Table XR-5. Atomic coordinates (x, y, z) and temperature factors (B_{eq}) for compound **69**. Estimated σs refer to the last digit.

Atomic Parameters x, y, z and B_{eq}
E. S. DS. refer to the last digit printed

atom	x	y	z	Beq
S 1	0.2585(3)	0.3266(3)	0.43658(13)	2.70(15)
S 2	0.4057(4)	0.1695(3)	0.43952(14)	2.72(14)
Cl 1	0.7836(5)	0.0152(3)	0.40304(17)	5.35(20)
C 1	0.5928(10)	0.2051(8)	0.4521 (4)	3.7 (5)
C 2	0.6856(12)	0.0844(8)	0.4687 (4)	4.0 (5)
C 3	0.8035(12)	0.0990(9)	0.5151 (4)	4.3 (5)
C 4	0.7267(12)	0.1259(9)	0.5747 (4)	4.6 (5)
C 5	0.5928(14)	0.2259(10)	0.5648 (5)	5.6 (6)
C 6	0.6039(12)	0.2888(9)	0.5031 (5)	4.7 (6)
C 7	0.7613(14)	0.3163(9)	0.4968 (5)	5.4 (6)
C 8	0.8803(12)	0.2000(11)	0.4957 (5)	5.6 (7)
C 9	0.2430(11)	0.3722(8)	0.3548 (4)	3.6 (5)
C10	0.4038(10)	0.3786(8)	0.3356 (4)	3.3 (4)
C11	0.4867(10)	0.2917(9)	0.3009 (4)	4.2 (5)
C12	0.6375(11)	0.2923(10)	0.2871 (5)	4.8 (6)
C13	0.7036(11)	0.3815(10)	0.3090 (5)	5.3 (6)
C14	0.6221(11)	0.4692(9)	0.3427 (5)	4.7 (5)
C15	0.4742(11)	0.4658(8)	0.3574 (5)	4.2 (5)
C16	0.1696(10)	0.2950(8)	0.3146 (4)	3.5 (5)
C17	0.1041(11)	0.2047(8)	0.3380 (5)	4.0 (5)
C18	0.0339(12)	0.1414(9)	0.2982 (5)	4.6 (6)
C19	0.0251(11)	0.1680(9)	0.2357 (5)	4.7 (6)
C20	0.0909(11)	0.2595(9)	0.2133 (5)	4.7 (6)
C21	0.1618(11)	0.3217(9)	0.2528 (4)	3.9 (5)
C22	0.1373(10)	0.4936(9)	0.3562 (5)	4.3 (5)

Table XR-5. continued

atom	x	y	z	Beq
C23	0.0171(11)	0.5115(11)	0.3953 (6)	6.0 (7)
C24	-0.0790(12)	0.6233(11)	0.3958 (6)	6.8 (7)
C25	-0.0555(14)	0.7116(11)	0.3575 (6)	7.8 (8)
C26	0.0629(13)	0.6949(10)	0.3180 (6)	6.6 (7)
C27	0.1599(12)	0.5873(9)	0.3183 (5)	5.1 (6)
S 1'	0.2907(23)	0.2312(24)	0.4217 (9)	14.3 (17)
S 2'	0.389 (3)	0.292 (3)	0.4741 (8)	18.5 (24)
Cl 1'	0.7172(16)	0.0287(11)	0.3996 (6)	6.5 (7)
S 3	0.5531(4)	0.8264(3)	0.02874(14)	3.60(17)
S 4	0.6038(5)	0.9316(3)	0.09284(15)	4.28(18)
Cl 2	0.8110(6)	0.9336(4)	0.22855(22)	8.1 (3)
C28	0.5853(13)	0.8505(9)	0.1631 (4)	5.0 (6)
C29	0.6238(17)	0.9450(16)	0.2144 (7)	10.9 (12)
C30	0.5259(20)	0.9154(13)	0.2707 (6)	10.1 (11)
C31	0.3747(19)	0.9621(17)	0.2507 (7)	12.6 (12)
C32	0.3204(19)	0.9204(13)	0.1959 (8)	10.9 (11)
C33	0.4453(17)	0.8171(13)	0.1789 (6)	8.4 (9)
C34	0.4668(19)	0.7205(11)	0.2383 (6)	8.7 (10)
C35	0.5562(20)	0.7880(12)	0.2805 (6)	9.7 (11)
C36	0.7434(13)	0.7308(10)	0.0083 (4)	5.4 (6)
C37	0.8036(11)	0.6665(9)	0.0663 (4)	3.9 (5)
C38	0.9159(11)	0.6998(10)	0.0979 (5)	4.9 (6)
C39	0.9589(12)	0.6495(11)	0.1549 (5)	5.7 (7)
C40	0.8892(12)	0.5624(9)	0.1785 (5)	4.5 (5)
C41	0.7787(12)	0.5281(9)	0.1465 (5)	4.8 (6)
C42	0.7297(12)	0.5815(9)	0.0917 (5)	4.4 (5)
C43	0.8609(16)	0.7903(10)	-0.0227 (5)	6.6 (8)
C44	0.9916(17)	0.7249(14)	-0.0380 (6)	9.9 (10)
C45	1.1045(19)	0.7780(17)	-0.0659 (7)	12.1 (12)
C46	1.0733(21)	0.8989(15)	-0.0810 (5)	11.9 (12)
C47	0.9359(23)	0.9571(17)	-0.0633 (6)	13.5 (15)

Table XR-5. continued

atom	x	y	z	Beq
C48	0.8214(18)	0.9128(13)	-0.0385 (5)	9.3 (9)
C49	0.6856(12)	0.6625(11)	-0.0409 (4)	5.7 (7)
C50	0.7328(16)	0.5406(14)	-0.0420 (6)	9.7 (9)
C51	0.6871(18)	0.4802(15)	-0.0930 (7)	10.7 (11)
C52	0.5952(13)	0.5412(14)	-0.1352 (5)	8.3 (9)
C53	0.5454(15)	0.6556(14)	-0.1326 (6)	9.0 (10)
C54	0.5911(13)	0.7190(12)	-0.0855 (6)	6.9 (8)
S 3'	0.6640(13)	0.8945(9)	0.0314 (5)	4.5 (6)
S 4'	0.4970(13)	0.8468(10)	0.0782 (6)	5.5 (7)
Cl 2'	0.337 (3)	0.7414(23)	0.1773 (13)	17.4 (20)

Beq is the mean of the principal axes of the thermal ellipsoid.

Atoms labelled **X'** are the minor positions of the atoms **X**, refined assuming occupancy of 0.25.

Table XR-6. Bond distances (Å) and bond angles (degrees) for compound **69**. Estimated σs refer to the last digit.

Bond Distances (Å)

S(1)-S(2)	2.046(5)	S(1)-C(9)	1.871(9)
S(2)-C(1)	1.854(9)	Cl(1)-C(2)	1.840(10)
C(1)-C(2)	1.525(14)	C(1)-C(6)	1.536(14)
C(1)-S(2')	2.00(3)	C(2)-C(3)	1.527(14)
C(2)-Cl(1')	1.692(15)	C(3)-C(4)	1.513(15)
C(3)-C(8)	1.527(15)	C(4)-C(5)	1.525(16)
C(5)-C(6)	1.542(15)	C(6)-C(7)	1.533(16)
C(7)-C(8)	1.563(17)	C(9)-C(10)	1.541(13)
C(9)-C(16)	1.531(13)	C(9)-C(22)	1.549(14)
C(9)-S(1')	2.151(22)	C(10)-C(11)	1.396(14)
C(10)-C(15)	1.401(14)	C(11)-C(12)	1.409(14)
C(12)-C(13)	1.399(17)	C(13)-C(14)	1.384(16)
C(14)-C(15)	1.394(14)	C(16)-C(17)	1.389(13)
C(16)-C(21)	1.397(14)	C(17)-C(18)	1.402(14)
C(18)-C(19)	1.410(16)	C(19)-C(20)	1.395(15)
C(20)-C(21)	1.392(14)	C(22)-C(23)	1.388(15)
C(22)-C(27)	1.398(16)	C(23)-C(24)	1.421(16)
C(24)-C(25)	1.357(22)	C(25)-C(26)	1.380(20)
C(26)-C(27)	1.386(15)	S(1')-S(2')	1.73(3)
S(3)-S(4)	2.022(5)	S(3)-C(36)	1.935(12)
S(4)-C(28)	1.818(10)	Cl(2)-C(29)	1.714(15)
C(28)-C(29)	1.696(20)	C(28)-C(33)	1.442(18)
C(28)-S(4')	2.056(17)	C(29)-C(30)	1.601(22)
C(30)-C(31)	1.444(23)	C(30)-C(35)	1.462(20)
C(31)-C(32)	1.450(23)	C(32)-C(33)	1.546(21)
C(33)-C(34)	1.687(19)	C(33)-Cl(2')	1.442(23)
C(34)-C(35)	1.568(22)	C(36)-C(37)	1.514(14)
C(36)-C(43)	1.533(17)	C(36)-C(49)	1.528(15)
C(36)-S(3')	1.987(15)	C(37)-C(38)	1.366(14)
C(37)-C(42)	1.400(15)	C(38)-C(39)	1.397(15)
C(39)-C(40)	1.381(16)	C(40)-C(41)	1.363(15)

Table XR-6. continued

C(41)-C(42)	1.380(15)	C(43)-C(44)	1.334(20)
C(43)-C(48)	1.431(19)	C(44)-C(45)	1.427(19)
C(45)-C(46)	1.41(3)	C(46)-C(47)	1.37(3)
C(47)-C(48)	1.358(21)	C(49)-C(50)	1.401(20)
C(49)-C(54)	1.374(16)	C(50)-C(51)	1.457(19)
C(51)-C(52)	1.343(22)	C(52)-C(53)	1.323(23)
C(53)-C(54)	1.411(19)	S(3')-S(4')	1.997(18)

Bond Angles (Degrees)

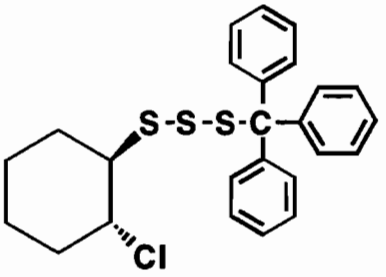
S(2)-S(1)-C(9)	104.6(3)	S(1)-S(2)-C(1)	105.9(3)
S(2)-C(1)-C(2)	101.5(6)	S(2)-C(1)-C(6)	116.0(7)
C(2)-C(1)-C(6)	109.4(8)	C(2)-C(1)-S(2')	134.9(11)
C(6)-C(1)-S(2')	69.4(9)	Cl(1)-C(2)-C(1)	111.8(7)
Cl(1)-C(2)-C(3)	107.8(7)	C(1)-C(2)-C(3)	108.5(8)
C(1)-C(2)-Cl(1')	100.6(8)	C(3)-C(2)-Cl(1')	126.7(9)
C(2)-C(3)-C(4)	108.4(9)	C(2)-C(3)-C(8)	110.4(8)
C(4)-C(3)-C(8)	109.1(8)	C(3)-C(4)-C(5)	109.0(8)
C(4)-C(5)-C(6)	110.3(9)	C(1)-C(6)-C(5)	110.2(8)
C(1)-C(6)-C(7)	104.3(8)	C(5)-C(6)-C(7)	108.6(9)
C(6)-C(7)-C(8)	110.2(8)	C(3)-C(8)-C(7)	107.9(8)
S(1)-C(9)-C(10)	104.9(6)	S(1)-C(9)-C(16)	115.7(6)
S(1)-C(9)-C(22)	101.9(6)	C(10)-C(9)-C(16)	112.8(7)
C(10)-C(9)-C(22)	113.7(8)	C(10)-C(9)-S(1')	99.4(8)
C(16)-C(9)-C(22)	107.5(7)	C(16)-C(9)-S(1')	90.1(9)
C(22)-C(9)-S(1')	131.1(9)	C(9)-C(10)-C(11)	120.8(8)
C(9)-C(10)-C(15)	120.2(8)	C(11)-C(10)-C(15)	118.7(8)
C(10)-C(11)-C(12)	121.0(9)	C(11)-C(12)-C(13)	118.7(10)
C(12)-C(13)-C(14)	120.8(9)	C(13)-C(14)-C(15)	119.8(9)
C(10)-C(15)-C(14)	120.8(9)	C(9)-C(16)-C(17)	122.2(9)
C(9)-C(16)-C(21)	118.1(8)	C(17)-C(16)-C(21)	119.6(9)
C(16)-C(17)-C(18)	118.5(9)	C(17)-C(18)-C(19)	122.3(9)
C(18)-C(19)-C(20)	118.2(9)	C(19)-C(20)-C(21)	119.5(10)
C(16)-C(21)-C(20)	121.9(9)	C(9)-C(22)-C(23)	120.3(10)

Table XR-6. continued

C(9)-C(22)-C(27)	121.3(9)	C(23)-C(22)-C(27)	118.4(10)
C(22)-C(23)-C(24)	119.5(12)	C(23)-C(24)-C(25)	120.4(11)
C(24)-C(25)-C(26)	120.7(11)	C(25)-C(26)-C(27)	119.5(12)
C(22)-C(27)-C(26)	121.4(11)	C(9)-S(1')-S(2')	100.9(15)
C(1)-S(2')-S(1')	96.7(15)		
S(4)-S(3)-C(36)	104.4(4)	S(3)-S(4)-C(28)	104.0(4)
S(4)-C(28)-C(29)	101.4(8)	S(4)-C(28)-C(33)	120.6(9)
C(29)-C(28)-C(33)	108.5(9)	C(29)-C(28)-S(4')	141.6(9)
C(33)-C(28)-S(4')	80.7(8)	Cl(2)-C(29)-C(28)	113.8(11)
Cl(2)-C(29)-C(30)	115.5(11)	C(28)-C(29)-C(30)	101.9(10)
C(29)-C(30)-C(31)	102.9(13)	C(29)-C(30)-C(35)	107.4(12)
C(31)-C(30)-C(35)	113.2(16)	C(30)-C(31)-C(32)	119.2(13)
C(31)-C(32)-C(33)	104.2(13)	C(28)-C(33)-C(32)	114.3(12)
C(28)-C(33)-C(34)	111.0(12)	C(28)-C(33)-Cl(2')	153.6(15)
C(32)-C(33)-C(34)	106.5(11)	C(32)-C(33)-Cl(2')	90.0(15)
C(34)-C(33)-Cl(2')	68.6(15)	C(33)-C(34)-C(35)	98.1(10)
C(30)-C(35)-C(34)	115.0(13)	S(3)-C(36)-C(37)	105.7(7)
S(3)-C(36)-C(43)	118.6(8)	S(3)-C(36)-C(49)	97.2(7)
C(37)-C(36)-C(43)	111.4(9)	C(37)-C(36)-C(49)	119.0(10)
C(37)-C(36)-S(3')	105.0(7)	C(43)-C(36)-C(49)	104.9(8)
C(43)-C(36)-S(3')	81.6(8)	C(49)-C(36)-S(3')	127.9(8)
C(36)-C(37)-C(38)	121.2(9)	C(36)-C(37)-C(42)	118.9(9)
C(38)-C(37)-C(42)	119.4(9)	C(37)-C(38)-C(39)	120.9(10)
C(38)-C(39)-C(40)	119.2(10)	C(39)-C(40)-C(41)	119.8(9)
C(40)-C(41)-C(42)	121.6(10)	C(37)-C(42)-C(41)	118.9(9)
C(36)-C(43)-C(44)	119.2(11)	C(36)-C(43)-C(48)	118.3(12)
C(44)-C(43)-C(48)	122.4(12)	C(43)-C(44)-C(45)	120.5(15)
C(44)-C(45)-C(46)	119.4(16)	C(45)-C(46)-C(47)	114.9(12)
C(46)-C(47)-C(48)	129.0(17)	C(43)-C(48)-C(47)	113.2(16)
C(36)-C(49)-C(50)	119.7(10)	C(36)-C(49)-C(54)	121.1(11)
C(50)-C(49)-C(54)	119.1(11)	C(49)-C(50)-C(51)	118.0(13)
C(50)-C(51)-C(52)	119.5(14)	C(51)-C(52)-C(53)	122.3(12)
C(52)-C(53)-C(54)	120.4(13)	C(49)-C(54)-C(53)	120.5(13)
C(36)-S(3')-S(4')	92.3(7)	C(28)-S(4')-S(3')	98.1(7)

APPENDIX III

X-RAY STRUCTURE DETERMINATION OF *trans*-2-Chloro-1-(triphenylmethyltrithio)cyclohexane (76)



- **Crystal Data for the Structure Determination of 76** **(Table XR-7)**
- **Atomic Coordinates and Temperature Factors for 76** **(Table XR-8)**
- **Bond Distances and Bond Angles for 76** **(Table XR-9)**

Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer controlled by TEXRAY software using the θ/2θ scan mode.

Table XR-7. Crystal data for the structure determination of **76**

Chemical Formula	$C_{25}H_{25}ClS_3$
Formula Weight	457.11
X-ray crystal dimension (mm)[a]	0.30 x 0.12 x 0.10
Radiation	CuK_α
Crystal system	monoclinic
Space group	P $2_1/c$ (#14)
Lattice constants	
a (Å)	13.934(2)
b (Å)	18.171(1)
c (Å)	9.5180(1)
V (Å^3)	2309.4(9)
Z	4
F (000)	960
Density (calc'd) (g cm^{-3})	1.315
μ (mm^{-1})	4.040
λ (Å)	1.54178
2θ max (°)	144.2
No. of reflections measured	9181
No. of unique reflections	5114
No. of reflections with $I_{net} > 3.0\sigma(I_{net})$	3636
For significant reflections	RF = 0.064[b], R_w = 0.075[c], G_oF = 2.75[d]
Maximum shift / σ ratio	1.83
Deepest hole in D-map (e / Å^3)	-0.40
Highest peak in D-map (e / Å^3)	0.570
Method of structure determination	solved by direct methods
Method of structure refinement	NRCVAX system programs

[a]cell dimensions were obtained from 24 reflections with 2θ angles in the range 30.00-33.00°.

[b]$RF = \Sigma(F_o-F_c) / \Sigma(F_o)$

[c]$R_w = (\Sigma[wF_o-F_c)^2 / \Sigma (wF_o^2)])^{1/2}$

[d]$G_oF = (\Sigma[wF_o-F_c)^2 / (\#\text{ reflections} - \#\text{ parameters})])^{1/2}$

Table XR-8. Atomic coordinates (x, y, z) and temperature factors (B_{eq}) for compound **76**. Estimated σs refer to the last digit.

Atomic Parameters x, y, z and B_{eq}
E. S. DS. refer to the last digit printed

atom	x	y	z	B_{eq}
Cl	0.34645(08)	0.24152(09)	0.08578(17)	7.30(6)
S(1)	0.58999(08)	0.21607(07)	0.20088(14)	5.96(5)
S(2)	0.60210(07)	0.14720(07)	0.37252(15)	5.44(5)
S(3)	0.73245(07)	0.17077(05)	0.53051(12)	4.57(4)
C(1)	0.5256(03)	0.2962(03)	0.2415(08)	9.3(3)
C(2)	0.5942(03)	0.3528(03)	0.3349(05)	5.7(2)
C(3)	0.5422(05)	0.4221(03)	0.3572(09)	9.5(3)
C(4)	0.4470(07)	0.4130(06)	0.3658(14)	6.5(5)
C(4')	0.4507(10)	0.4438(06)	0.2585(16)	7.0(6)
C(5)	0.3784(03)	0.3729(04)	0.2234(08)	8.4(3)
C(6)	0.4304(06)	0.2918(05)	0.2403(10)	4.8(3)
C(6')	0.4323(06)	0.3155(05)	0.1515(10)	4.4(3)
C(7)	0.8264(03)	0.0969(02)	0.5249(04)	3.9(1)
C(8)	0.8090(03)	0.0269(02)	0.6058(04)	4.2(1)
C(9)	0.8905(03)	-0.0172(03)	0.6716(06)	5.4(2)
C(10)	0.8794(04)	-0.0814(03)	0.7430(06)	6.7(2)
C(11)	0.7872(05)	-0.1022(03)	0.7501(07)	6.8(3)
C(12)	0.7050(05)	-0.0602(03)	0.6834(07)	6.7(3)
C(13)	0.7165(03)	0.0047(03)	0.6127(06)	5.4(2)
C(14)	0.8252(02)	0.0825(02)	0.3669(04)	3.6(1)
C(15)	0.8300(03)	0.1412(02)	0.2745(05)	4.3(2)
C(16)	0.8322(03)	0.1286(03)	0.1313(05)	5.0(2)
C(17)	0.8278(04)	0.0580(03)	0.0793(06)	5.4(2)
C(18)	0.8226(04)	-0.0000(03)	0.1682(06)	5.4(2)
C(19)	0.8209(03)	0.0127(02)	0.3102(05)	4.5(2)
C(20)	0.9224(03)	0.1348(02)	0.6176(04)	4.1(1)

Table XR-8. continued

atom	x	y	z	B_{eq}
C(21)	0.9287(04)	0.1545(02)	0.7610(05)	5.4(2)
C(22)	1.0128(04)	0.1887(03)	0.8503(07)	6.6(2)
C(23)	1.0918(04)	0.2032(03)	0.7966(07)	6.8(2)
C(24)	1.0889(03)	0.1835(03)	0.6572(07)	5.9(2)
C(25)	1.0038(03)	0.1489(02)	0.5670(06)	4.7(2)

$\mathbf{B_{eq}}$ is the mean of the principal axes of the thermal ellipsoid.

Table XR-9. Bond distances (Å) and bond angles (degrees) for compound **76.** Estimated σs refer to the last digit.

Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Cl	C(6)	1.839(9)	C(7)	C(20)	1.539(5)
Cl	C(6')	1.790(9)	C(8)	C(9)	1.385(6)
S(1)	S(2)	2.027(2)	C(8)	C(13)	1.370(6)
S(1)	C(1)	1.811(5)	C(9)	C(10)	1.381(7)
S(2)	S(3)	2.046(1)	C(10)	C(11)	1.360(8)
S(3)	C(7)	1.887(4)	C(11)	C(12)	1.373(8)
C(1)	C(2)	1.510(7)	C(12)	C(13)	1.391(7)
C(1)	C(6)	1.327(9)	C(14)	C(15)	1.396(5)
C(1)	C(6')	1.382(9)	C(14)	C(19)	1.375(5)
C(2)	C(3)	1.498(7)	C(15)	C(16)	1.392(6)
C(3)	C(4)	1.36(1)	C(16)	C(17)	1.369(7)
C(3)	C(4')	1.41(1)	C(17)	C(18)	1.368(7)
C(4)	C(4')	1.18(1)	C(18)	C(19)	1.379(6)
C(4)	C(5)	1.59(1)	C(20)	C(21)	1.391(6)
C(4')	C(5)	1.61(1)	C(20)	C(25)	1.377(6)
C(5)	C(6)	1.63(1)	C(21)	C(22)	1.384(6)
C(5)	C(6')	1.56(1)	C(22)	C(23)	1.367(8)
C(6)	C(6')	0.96(1)	C(23)	C(24)	1.364(8)
C(7)	C(8)	1.543(5)	C(24)	C(25)	1.399(6)
C(7)	C(14)	1.523(5)			

Bond Angles (Degrees)

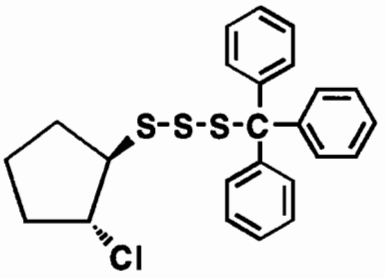
atom	atom	atom	angle	atom	atom	atom	angle
C(6)	Cl	C(6')	30.5(3)	Cl	C(6)	C(1)	116.3(6)
S(2)	S(1)	C(1)	104.9(3)	Cl	C(6)	C(5)	102.0(5)

Table XR-9. continued

atom	atom	atom	angle	atom	atom	atom	angle
S(1)	S(2)	S(3)	108.38(7)	Cl	C(6)	C(6')	71.9(8)
S(2)	S(3)	C(7)	107.9(1)	C(1)	C(6)	C(5)	111.2(7)
S(1)	C(1)	C(2)	113.9(3)	C(1)	C(6)	C(6')	72.5(8)
S(1)	C(1)	C(6)	120.3(6)	C(5)	C(6)	C(6')	68.3(8)
S(1)	C(1)	C(6')	120.5(5)	Cl	C(6')	C(1)	116.3(6)
C(2)	C(1)	C(6)	120.7(6)	Cl	C(6')	C(5)	107.4(5)
C(2)	C(1)	C(6')	121.2(6)	Cl	C(6')	C(6)	77.6(8)
C(6)	C(1)	C(6')	41.3(5)	C(1)	C(6')	C(5)	112.6(7)
C(1)	C(2)	C(3)	113.9(4)	C(1)	C(6')	C(6)	66.3(8)
C(2)	C(3)	C(4)	115.2(6)	C(5)	C(6')	C(6)	76.9(9)
C(2)	C(3)	C(4')	121.6(7)	S(3)	C(7)	C(8)	111.3(3)
C(4)	C(3)	C(4')	50.3(7)	S(3)	C(7)	C(14)	109.8(3)
C(3)	C(4)	C(4')	66.8(9)	S(3)	C(7)	C(20)	99.4(2)
C(3)	C(4)	C(5)	111.2(8)	C(8)	C(7)	C(14)	113.1(3)
C(4')	C(4)	C(5)	69.2(9)	C(8)	C(7)	C(20)	108.6(3)
C(3)	C(4')	C(4)	62.9(8)	C(14)	C(7)	C(20)	113.9(3)
C(3)	C(4')	C(5)	108.0(8)	C(7)	C(8)	C(9)	118.5(3)
C(4)	C(4')	C(5)	67.7(8)	C(7)	C(8)	C(13)	123.4(4)
C(4)	C(5)	C(4')	43.1(6)	C(9)	C(8)	C(13)	118.0(4)
C(4)	C(5)	C(6)	100.8(6)	C(8)	C(9)	C(10)	121.2(5)
C(4)	C(5)	C(6')	115.7(5)	C(9)	C(10)	C(11)	120.0(5)
C(4')	C(5)	C(6)	117.9(5)	C(10)	C(11)	C(12)	119.9(5)
C(4')	C(5)	C(6')	106.0(6)	C(11)	C(12)	C(13)	119.9(5)
C(6)	C(5)	C(6')	34.8(4)	C(8)	C(13)	C(12)	120.9(5)
C(7)	C(14)	C(15)	120.2(3)	C(7)	C(14)	C(19)	122.3(4)
C(15)	C(14)	C(19)	117.5(4)	C(14)	C(15)	C(16)	120.7(4)
C(15)	C(16)	C(17)	119.8(4)	C(16)	C(17)	C(18)	120.2(5)
C(17)	C(18)	C(19)	119.8(5)	C(14)	C(19)	C(18)	122.0(4)
C(7)	C(20)	C(21)	118.5(4)	C(7)	C(20)	C(25)	123.5(4)
C(21)	C(20)	C(25)	118.0(4)	C(20)	C(21)	C(22)	121.5(5)
C(21)	C(22)	C(23)	119.3(6)	C(22)	C(23)	C(24)	120.7(5)
C(23)	C(24)	C(25)	120.0(5)	C(20)	C(25)	C(24)	120.5(5)

APPENDIX IV

X-RAY STRUCTURE DETERMINATION OF
trans-2-Chloro-1-(triphenylmethyltrithio)cyclopentane (75)



- **Crystal Data for the Structure Determination of 75** **(Table XR-10)**
- **Atomic Coordinates and Temperature Factors for 75** **(Table XR-11)**
- **Bond Distances and Bond Angles for 75** **(Table XR-12)**

Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer controlled by TEXRAY software using the θ/2θ scan mode.

Table XR-10. Crystal data for the structure determination of **75**

Chemical Formula	$C_{24}H_{23}ClS_3$
Formula Weight	443.07
X-ray crystal dimension (mm)[a]	0.39 x 0.24 x 0.07
Radiation	CuK_α
Crystal system	triclinic
Space group	P -1
Lattice constants	
a (Å)	9.7949(13)
b (Å)	13.7746(15)
c (Å)	17.4663(22)
V (Å^3)	2204.6(4)
Z	4
F (000)	935.02
Density (calc'd) (g cm^{-3})	1.335
μ (mm^{-1})	4.22
λ (Å)	1.54178
2θ max (°)	139.6
No. of reflections measured	16408
No. of unique reflections	8336
No. of reflections with $I_{net} > 3.0\sigma(I_{net})$	6075
For significant reflections	RF = 0.057[b], R_w = 0.070[c], G_oF = 1.98[d]
Maximum shift / σ ratio	0.203
Deepest hole in D-map (e / Å^3)	-0.540
Highest peak in D-map (e / Å^3)	0.780
Method of structure determination	solved by direct methods
Method of structure refinement	NRCVAX system programs

[a]cell dimensions were obtained from 25 reflections with 2θ angles in the range 40.00-42.00°.

[b]$RF = \Sigma(F_o-F_c) / \Sigma(F_o)$

[c]$R_w = (\Sigma[wF_o-F_c)^2 / \Sigma (wF_o^2)])^{1/2}$

[d]$G_oF = (\Sigma[wF_o-F_c)^2 / (\#\text{ reflections} - \#\text{ parameters})])^{1/2}$

Table XR-11. Atomic coordinates (x, y, z) and temperature factors (B_{eq}) for compound **75**. Estimated σs refer to the last digit.

Atomic Parameters x, y, z and B_{eq}
E. S. DS. refer to the last digit printed

atom	x	y	z	Beq
CL1	0.92958(13)	0.87833(9)	0.64554(8)	5.51(6)
S1	0.77833(12)	0.56468(8)	0.50278(8)	4.90(5)
S2	0.73503(11)	0.60152(9)	0.40181(7)	4.38(5)
S3	0.52963(10)	0.60139(8)	0.38487(6)	3.87(4)
C1	0.8117(4)	0.6878(3)	0.5878(3)	4.04(20)
C2	0.8695(5)	0.6569(4)	0.6582(3)	5.15(25)
C3	1.0232(5)	0.6558(5)	0.6478(3)	5.98(29)
C4	1.0552(4)	0.6931(4)	0.5783(3)	4.44(23)
C5	0.9296(4)	0.7480(3)	0.5684(2)	3.83(19)
C6	0.4734(4)	0.7381(3)	0.4404(2)	3.16(17)
C7	0.5850(4)	0.8092(3)	0.4273(2)	3.15(15)
C8	0.6694(4)	0.8720(3)	0.4895(2)	3.53(18)
C9	0.7779(4)	0.9295(3)	0.4738(3)	4.41(21)
C10	0.8034(5)	0.9245(4)	0.3948(3)	5.01(24)
C11	0.7209(5)	0.8619(4)	0.3319(3)	5.07(24)
C12	0.6130(5)	0.8042(3)	0.3467(3)	4.32(20)
C13	0.3360(4)	0.7399(3)	0.3977(2)	3.45(17)
C14	0.3031(5)	0.8186(4)	0.3692(3)	4.93(23)
C15	0.1744(6)	0.8175(4)	0.3348(3)	6.21(28)
C16	0.0791(5)	0.7402(5)	0.3291(3)	6.13(28)
C17	0.1110(5)	0.6636(4)	0.3577(3)	5.32(26)
C18	0.2372(4)	0.6633(4)	0.3924(3)	4.24(22)
C19	0.4436(4)	0.7576(3)	0.5310(2)	2.95(15)
C20	0.3998(4)	0.8555(3)	0.5788(2)	3.63(18)
C21	0.3660(5)	0.8765(3)	0.6600(3)	4.37(21)
C22	0.3757(5)	0.8013(4)	0.6946(3)	4.57(23)
C23	0.4162(4)	0.7035(4)	0.6475(3)	4.34(22)

Table XR-11. continued

atom	x	y	z	Beq
C24	0.4507(4)	0.6823(3)	0.5660(2)	3.54(18)
CL2	0.91296(16)	0.21715(11)	1.12578(8)	6.46(7)
S4	0.80104(12)	0.43579(9)	1.00721(7)	4.54(5)
S5	0.74408(10)	0.31967(9)	0.90076(6)	3.88(4)
S6	0.53750(10)	0.31307(8)	0.88556(6)	3.44(4)
C25	0.8180(4)	0.3752(3)	1.0853(3)	4.21(21)
C26	0.8708(6)	0.4616(4)	1.1644(3)	6.22(28)
C27	1.0267(6)	0.4544(4)	1.1638(3)	6.22(27)
C28	1.0624(5)	0.3646(4)	1.0891(3)	5.25(26)
C29	0.9328(5)	0.2990(3)	1.0639(3)	4.26(21)
C30	0.4708(4)	0.2212(3)	0.9364(2)	2.95(15)
C31	0.4543(4)	0.2774(3)	1.0293(2)	2.95(16)
C32	0.4181(4)	0.2193(3)	1.0773(2)	3.64(18)
C33	0.3975 5)	0.2666(3)	1.1607(2)	4.12(19)
C34	0.4086(4)	0.3735(3)	1.1970(2)	4.01(20)
C35	0.4396(5)	0.4318(3)	1.1494(3)	4.16(19)
C36	0.4625(4)	0.3849(3)	1.0661(2)	3.52(17)
C37	0.3248(4)	0.1908(3)	0.9006(2)	3.22(16)
C38	0.2391(4)	0.2650(3)	0.8945(3)	3.76(18)
C39	0.1056(4)	0.2400(4)	0.8658(3)	4.41(22)
C40	0.0551(4)	0.1406(4)	0.8446(3)	4.56(23)
C41	0.1385(4)	0.0652(4)	0.8522(3)	4.75(23)
C42	0.2731(4)	0.0892(3)	0.8797(3)	3.94(19)
C43	0.5682(4)	0.1309(3)	0.9117(2)	3.34(16)
C44	0.5766(4)	0.0700(3)	0.8290(3)	4.13(19)
C45	0.6699(5)	-0.0076(4)	0.8021(3)	5.05(22)
C46	0.7594(4)	-0.0245(3)	0.8574(3)	5.09(24)
C47	0.7525(4)	0.0344(4)	0.9389(3)	4.83(25)
C48	0.6573(4)	0.1128(3)	0.9663(3)	3.82(20)

$\mathbf{B_{eq}}$ is the mean of the principal axes of the thermal ellipsoid.

Table XR-12. Bond distances (Å) and bond angles (degrees) for compound **75**. Estimated σs refer to the last digit.

Bond Distances (Å)

Cl(1)-C(5)	1.826(4)	Cl(2)-C(29)	1.824(5)
S(1)-S(2)	2.0452(18)	S(4)-S(5)	2.0435(16)
S(1)-C(1)	1.838(4)	S(4)-C(25)	1.842(5)
S(2)-S(3)	2.0322(14)	S(5)-S(6)	2.0351(14)
S(3)-C(6)	1.887(4)	S(6)-C(30)	1.889(4)
C(1)-C(2)	1.545(7)	C(25)-C(26)	1.547(7)
C(1)-C(5)	1.512(6)	C(25)-C(29)	1.515(6)
C(2)-C(3)	1.517(7)	C(26)-C(27)	1.533(8)
C(3)-C(4)	1.508(7)	C(27)-C(28)	1.498(8)
C(4)-C(5)	1.502(6)	C(28)-C(29)	1.509(6)
C(6)-C(7)	1.520(5)	C(30)-C(31)	1.543(5)
C(6)-C(13)	1.542(5)	C(30)-C(37)	1.546(5)
C(6)-C(19)	1.538(5)	C(30)-C(43)	1.526(5)
C(7)-C(8)	1.381(5)	C(31)-C(32)	1.389(5)
C(7)-C(12)	1.413(6)	C(31)-C(36)	1.391(5)
C(8)-C(9)	1.394(6)	C(32)-C(33)	1.388(6)
C(9)-C(10)	1.381(7)	C(33)-C(34)	1.384(6)
C(10)-C(11)	1.375(8)	C(34)-C(35)	1.374(6)
C(11)-C(12)	1.386(7)	C(35)-C(36)	1.391(6)
C(13)-C(14)	1.386(6)	C(37)-C(38)	1.372(6)
C(13)-C(18)	1.390(6)	C(37)-C(42)	1.396(6)
C(14)-C(15)	1.392(7)	C(38)-C(39)	1.389(6)
C(15)-C(16)	1.373(9)	C(39)-C(40)	1.364(7)
C(16)-C(17)	1.360(8)	C(40)-C(41)	1.380(7)
C(17)-C(18)	1.376(6)	C(41)-C(42)	1.392(6)
C(19)-C(20)	1.393(5)	C(43)-C(44)	1.397(6)
C(19)-C(24)	1.381(5)	C(43)-C(48)	1.381(6)
C(20)-C(21)	1.388(6)	C(44)-C(45)	1.378(6)
C(21)-C(22)	1.375(7)	C(45)-C(46)	1.385(7)
C(22)-C(23)	1.379(7)	C(46)-C(47)	1.372(7)
C(23)-C(24)	1.393(6)	C(47)-C(48)	1.399(6)

Table XR-12. continued

Bond Angles (Degrees)

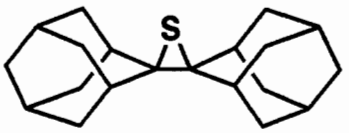
S(2)-S(1)-C(1)	106.85(15)	S(5)-S(4)-C(25)	106.57(15)
S(1)-S(2)-S(3)	110.24(7)	S(4)-S(5)-S(6)	110.48(7)
S(2)-S(3)-C(6)	107.01(12)	S(5)-S(6)-C(30)	105.81(12)
S(1)-C(1)-C(2)	105.3(3)	S(4)-C(25)-C(26)	106.6(3)
S(1)-C(1)-C(5)	110.7(3)	S(4)-C(25)-C(29)	110.3(3)
C(2)-C(1)-C(5)	103.2(3)	C(26)-C(25)-C(29)	103.4(4)
C(1)-C(2)-C(3)	105.5(4)	C(25)-C(26)-C(27)	106.0(4)
C(2)-C(3)-C(4)	107.7(4)	C(26)-C(27)-C(28)	107.2(4)
C(3)-C(4)-C(5)	104.7(4)	C(27)-C(28)-C(29)	105.5(4)
Cl(1)-C(5)-C(1)	106.6(3)	Cl(2)-C(29)-C(25)	107.6(3)
Cl(1)-C(5)-C(4)	110.0(3)	Cl(2)-C(29)-C(28)	109.5(3)
C(1)-C(5)-C(4)	105.1(4)	C(25)-C(29)-C(28)	105.3(4)
S(3)-C(6)-C(7)	106.00(25)	S(6)-C(30)-C(31)	111.37(24)
S(3)-C(6)-C(13)	102.35(24)	S(6)-C(30)-C(37)	104.07(24)
S(3)-C(6)-C(19)	111.9(3)	S(6)-C(30)-C(43)	105.51(24)
C(7)-C(6)-C(13)	114.7(3)	C(31)-C(30)-C(37)	106.1(3)
C(7)-C(6)-C(19)	114.0(3)	C(31)-C(30)-C(43)	115.7(3)
C(13)-C(6)-C(19)	107.3(3)	C(37)-C(30)-C(43)	113.7(3)
C(6)-C(7)-C(8)	123.1(3)	C(30)-C(31)-C(32)	118.9(3)
C(6)-C(7)-C(12)	118.9(3)	C(30)-C(31)-C(36)	122.6(3)
C(8)-C(7)-C(12)	117.8(4)	C(32)-C(31)-C(36)	118.2(3)
C(7)-C(8)-C(9)	121.3(4)	C(31)-C(32)-C(33)	121.0(4)
C(8)-C(9)-C(10)	120.3(4)	C(32)-C(33)-C(34)	120.2(4)
C(9)-C(10)-C(11)	119.3(4)	C(33)-C(34)-C(35)	119.2(4)
C(10)-C(11)-C(12)	121.0(4)	C(34)-C(35)-C(36)	121.0(4)
C(7)-C(12)-C(11)	120.4(4)	C(31)-C(36)-C(35)	120.3(4)
C(6)-C(13)-C(14)	122.8(4)	C(30)-C(37)-C(38)	120.5(3)
C(6)-C(13)-C(18)	118.6(4)	C(30)-C(37)-C(42)	121.1(3)
C(14)-C(13)-C(18)	118.4(4)	C(38)-C(37)-C(42)	118.3(3)
C(13)-C(14)-C(15)	119.5(5)	C(37)-C(38)-C(39)	121.4(4)
C(14)-C(15)-C(16)	121.1(5)	C(38)-C(39)-C(40)	120.5(4)
C(15)-C(16)-C(17)	119.4(4)	C(39)-C(40)-C(41)	119.1(4)

Table XR-12. continued

C(16)-C(17)-C(18)	120.5(5)	C(40)-C(41)-C(42)	120.8(4)
C(13)-C(18)-C(17)	121.0(4)	C(37)-C(42)-C(41)	119.9(4)
C(6)-C(19)-C(20)	117.7(3)	C(30)-C(43)-C(44)	118.4(3)
C(6)-C(19)-C(24)	123.7(3)	C(30)-C(43)-C(48)	122.9(3)
C(20)-C(19)-C(24)	118.5(3)	C(44)-C(43)-C(48)	118.4(4)
C(19)-C(20)-C(21)	120.3(4)	C(43)-C(44)-C(45)	121.2(4)
C(20)-C(21)-C(22)	120.7(4)	C(44)-C(45)-C(46)	119.9(4)
C(21)-C(22)-C(23)	119.5(4)	C(45)-C(46)-C(47)	119.8(4)
C(22)-C(23)-C(24)	120.0(4)	C(46)-C(47)-C(48)	120.4(4)
C(19)-C(24)-C(23)	121.0(4)	C(43)-C(48)-C(47)	120.4(4)

APPENDIX V

X-RAY STRUCTURE DETERMINATION OF
Adamantylideneadamantane Thiirane (116)



- **Crystal Data for the Structure Determination of 116** **(Table XR-13)**
- **Atomic Coordinates and Temperature Factors for 116** **(Table XR-14)**
- **Bond Distances and Bond Angles for 116** **(Table XR-15)**

Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer controlled by TEXRAY software using the θ/2θ scan mode.

Table XR-13. Crystal data for the structure determination of **116**

Chemical Formula	$C_{20}H_{28}S$
Formula Weight	300.50
X-ray crystal dimension (mm)[a]	0.40 x 0.30 x 0.30
Radiation	CuK_α
Crystal system	monoclinic
Space group	$P\ 2_1/a$
Lattice constants	
a (Å)	12.7522(19)
b (Å)	10.5600(13)
c (Å)	13.441(3)
V (Å^3)	1604.0(4)
Z	4
F (000)	658.67
Density (calc'd) (g cm^{-3})	1.244
μ (mm^{-1})	1.65
λ (Å)	1.54178
2θ max (°)	110
No. of reflections measured	2129
No. of unique reflections	2018
No. of reflections with $I_{net} > 2.5\sigma(I_{net})$	1787
For significant reflections	RF = 0.031[b], R_w = 0.035[c], G_oF = 2.06[d]
Maximum shift / σ ratio	0.018
Deepest hole in D-map (e / Å^3)	-0.100
Highest peak in D-map (e / Å^3)	0.150
Method of structure determination	solved by direct methods
Method of structure refinement	NRCVAX system programs

[a]cell dimensions were obtained from 25 reflections with 2θ angles in the range 80.00-100.00°.

[b]$RF = \Sigma(F_o-F_c) / \Sigma(F_o)$

[c]$R_w = (\Sigma[wF_o-F_c)^2 / \Sigma (wF_o^2)])^{1/2}$

[d]$G_oF = (\Sigma[wF_o-F_c)^2 / (\#\text{ reflections} - \#\text{ parameters})])^{1/2}$

Table XR-14. Atomic coordinates (x, y, z) and temperature factors (B_{eq}) for compound **116**. Estimated σs refer to the last digit.

Atomic Parameters x, y, z and B_{eq}
E. S. DS. refer to the last digit printed

atom	x	y	z	Beq
S	0.15883(5)	0.49868(5)	0.26393(5)	3.91(3)
C 1	0.05843(16)	0.38780(18)	0.28413(16)	2.82(10)
C 2	0.09383(17)	0.35680(20)	0.40644(16)	3.19(10)
C 3	-0.00587(20)	0.28262(22)	0.41386(18)	3.58(12)
C 4	-0.02930(19)	0.15938(21)	0.34798(19)	3.82(11)
C 5	-0.06587(20)	0.19138(22)	0.22600(19)	3.80(11)
C 6	0.03281(18)	0.26525(19)	0.21705(17)	3.19(10)
C 7	0.08365(21)	0.07897(23)	0.39653(22)	4.35(14)
C 8	0.18233(20)	0.15231(21)	0.38805(19)	3.92(12)
C 9	0.14512(21)	0.18319(23)	0.26527(20)	4.05(13)
C10	0.20607(19)	0.27482(21)	0.45482(19)	3.67(12)
C 1'	0.00209(16)	0.51163(18)	0.23126(16)	2.91(10)
C 2'	-0.02504(19)	0.61348(19)	0.29606(18)	3.50(11)
C 3'	-0.15339(20)	0.59972(25)	0.27655(19)	3.96(12)
C 4'	-0.23871(20)	0.61489(20)	0.15116(19)	3.77(12)
C 5'	-0.21182(20)	0.51158(22)	0.08770(19)	3.73(12)
C 6'	-0.08383(18)	0.52444(20)	0.10642(17)	3.35(11)
C 7'	-0.22249(22)	0.74459(23)	0.11096(21)	4.34(13)
C 8'	-0.09557(21)	0.75837(23)	0.13033(21)	4.48(14)
C 9'	-0.06910(24)	0.65544(23)	0.06561(22)	4.43(14)
C10'	-0.01062(23)	0.74451(22)	0.25529(21)	4.64(14)

B_{eq} is the mean of the principal axes of the thermal ellipsoid for atoms refined anisotropically.

Table XR-15. Bond distances (Å) and bond angles (degrees) for compound **116**. Estimated σs refer to the last digit.

Bond Distances (Å)

S-C(1)	1.8455(19)	S-C(1')	1.8421(20)
C(1')-C(2')	1.521(3)	C(1)-C(2)	1.525(3)
C(1')-C(6')	1.527(3)	C(1)-C(6)	1.524(3)
C(2')-C(3')	1.540(3)	C(1)-C(1')	1.503(3)
C(2')-C(10')	1.530(3)	C(2)-C(3)	1.535(3)
C(2)-C(10)	1.536(3)	C(3')-C(4')	1.533(3)
C(3)-C(4)	1.524(3)	C(4')-C(5')	1.519(3)
C(4')-C(7')	1.521(3)	C(4)-C(5)	1.520(3)
C(4)-C(7)	1.533(3)	C(5')-C(6')	1.538(3)
C(5)-C(6)	1.532(3)	C(6')-C(9')	1.531(3)
C(6)-C(9)	1.537(3)	C(7')-C(8')	1.523(4)
C(7)-C(8)	1.526(3)	C(8')-C(9')	1.525(4)
C(8')-C(10')	1.526(3)	C(8)-C(9)	1.526(3)
C(8)-C(10)	1.523(3)		

Bond Angles (Degrees)

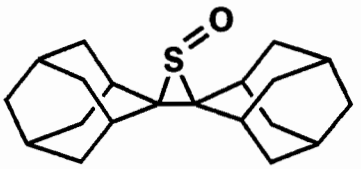
C(1)-S-C(1')	48.09(8)	S-C(1')-C(1)	66.07(10)
S-C(1)-C(2)	114.57(13)	S-C(1')-C(2')	115.18(14)
S-C(1)-C(6)	115.15(13)	S-C(1')-C(6')	114.54(14)
S-C(1)-C(1')	65.83(10)	C(1)-C(1')-C(2')	122.02(17)
C(2)-C(1)-C(6)	109.32(16)	C(1)-C(1')-C(6')	122.64(16)
C(2)-C(1)-C(1')	122.30(16)	C(2')-C(1')-C(6')	109.20(16)
C(6)-C(1)-C(1')	122.33(16)	C(1')-C(2')-C(3')	109.97(17)
C(1)-C(2)-C(3)	109.83(16)	C(1')-C(2')-C(10')	109.71(19)
C(1)-C(2)-C(10)	109.25(17)	C(3')-C(2')-C(10')	108.60(19)
C(3)-C(2)-C(10)	108.80(18)	C(2')-C(3')-C(4')	109.52(18)
C(2)-C(3)-C(4)	110.08(18)	C(3')-C(4')-C(5')	108.21(18)

Table XR-15. continued

C(3)-C(4)-C(5)	108.44(18)	C(3')-C(4')-C(7')	109.91(19)
C(3)-C(4)-C(7)	109.46(19)	C(5')-C(4')-C(7')	110.12(20)
C(5)-C(4)-C(7)	109.90(20)	C(4')-C(5')-C(6')	110.09(18)
C(4)-C(5)-C(6)	110.20(17)	C(1')-C(6')-C(5')	109.79(17)
C(1)-C(6)-C(5)	110.16(17)	C(1')-C(6')-C(9')	109.21(18)
C(1)-C(6)-C(9)	109.08(17)	C(5')-C(6')-C(9')	108.55(18)
C(5)-C(6)-C(9)	108.58(18)	C(4')-C(7')-C(8')	109.51(19)
C(4)-C(7)-C(8)	109.38(19)	C(7')-C(8')-C(9')	109.46(21)
C(7)-C(8)-C(9)	109.58(20)	C(7')-C(8')-C(10')	109.58(21)
C(7)-C(8)-C(10)	109.43(20)	C(9')-C(8')-C(10')	109.13(20)
C(9)-C(8)-C(10)	109.45(19)	C(6')-C(9')-C(8')	110.08(19)
C(6)-C(9)-C(8)	109.79(18)	C(2')-C(10')-C(8')	109.82(19)
C(2)-C(10)-C(8)	109.73(17)		

APPENDIX VI

X-RAY STRUCTURE DETERMINATION OF
Adamantylideneadamantane Thiirane 1-Oxide (178)



- **Crystal Data for the Structure Determination of 178** **(Table XR-16)**
- **Atomic Coordinates and Temperature Factors for 178** **(Table XR-17)**
- **Bond Distances and Bond Angles for 178** **(Table XR-18)**

Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer controlled by TEXRAY software using the θ/2θ scan mode.

Table XR-16. Crystal data for the structure determination of **178**

Chemical Formula	$C_{20}H_{28}OS$
Formula Weight	316.50
X-ray crystal dimension (mm)[a]	0.275 x 0.450 x 0.275
Radiation	CuK_α
Crystal system	monoclinic
Space group	P $2_1/n$ (#14)
Lattice constants	
a (Å)	10.851(2)
b (Å)	13.680(2)
c (Å)	11.313(2)
V (Å^3)	1617.0(8)
Z	4
F (000)	688
Density (calc'd) (g cm^{-3})	1.30
μ (mm^{-1})	1.712
λ (Å)	1.54178
2θ max (°)	140
No. of reflections measured	3151
No. of unique reflections	2978
No. of reflections with $I_{net} > 3.0\sigma(I_{net})$	2033
For significant reflections	RF = 0.041[b], R_w = 0.047[c], G_oF = 1.62[d]
Maximum shift / σ ratio	0.21
Deepest hole in D-map (e / Å^3)	-0.230
Highest peak in D-map (e / Å^3)	0.200
Method of structure determination	solved by direct methods
Method of structure refinement	NRCVAX system programs

[a]cell dimensions were obtained from 25 reflections with 2θ angles in the range 50.00-60.00°.

[b]$RF = \Sigma(F_o-F_c) / \Sigma(F_o)$

[c]$R_w = (\Sigma[wF_o-F_c)^2 / \Sigma (wF_o^2)])^{1/2}$

[d]$G_oF = (\Sigma[wF_o-F_c)^2 / (\#\text{ reflections} - \#\text{ parameters})])^{1/2}$

Table XR-17. Atomic coordinates (x, y, z) and temperature factors (B_{eq}) for compound **178**. Estimated σs refer to the last digit.

Atomic Parameters x, y, z and B_{eq}
E. S. DS. refer to the last digit printed

atom	x	y	z	B_{eq}
S(1)	0.04312(07)	0.27436(05)	0.60393(06)	2.98(3)
O(1)	-0.0229(02)	0.3225(02)	0.4856(02)	4.3(1)
C(1)	-0.0015(02)	0.3329(02)	0.7354(02)	2.4(1)
C(2)	-0.1203(03)	0.3961(02)	0.6973(03)	3.2(1)
C(3)	-0.1338(04)	0.4537(03)	0.8099(04)	4.4(2)
C(4)	-0.1464(03)	0.3834(03)	0.9106(03)	4.3(2)
C(5)	-0.0255(03)	0.3197(03)	0.9470(03)	3.9(1)
C(6)	-0.0126(03)	0.2616(02)	0.8361(02)	2.9(1)
C(7)	-0.1313(03)	0.1971(02)	0.7892(03)	3.8(1)
C(8)	-0.2513(03)	0.2614(03)	0.7528(03)	4.0(1)
C(9)	-0.2389(03)	0.3314(03)	0.6518(03)	4.2(1)
C(10)	-0.2628(03)	0.3190(03)	0.8641(04)	4.7(2)
C(11)	0.1257(02)	0.3657(02)	0.7202(02)	2.2(1)
C(12)	0.2531(02)	0.3309(02)	0.8060(02)	2.4(1)
C(13)	0.2979(03)	0.4070(02)	0.9088(03)	3.0(1)
C(14)	0.3156(03)	0.5060(02)	0.8535(03)	3.3(1)
C(15)	0.1894(03)	0.5393(02)	0.7667(03)	3.2(1)
C(16)	0.1436(03)	0.4643(02)	0.6634(02)	2.7(1)
C(17)	0.2457(03)	0.4541(02)	0.5934(03)	3.4(1)
C(18)	0.3726(03)	0.4214(02)	0.6802(03)	3.5(1)
C(19)	0.3533(03)	0.3222(02)	0.7350(03)	3.0(1)
C(20)	0.4156(03)	0.4968(02)	0.7826(03)	3.8(1)

B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Table XR-18. Bond distances (Å) and bond angles (degrees) of compound **178**. Estimated σs refer to the last digit.

Bond Distances (Å)

atom	atom	distance	atom	atom	distance
S1	O1	1.491(2)	S1	C1	1.865(3)
S1	C11	1.860(2)	C1	C2	1.515(4)
C1	C6	1.530(4)	C11	C12	1.535(3)
C1	C11	1.505(3)	C11	C16	1.529(3)
C2	C3	1.538(4)	C12	C13	1.538(4)
C2	C9	1.532(4)	C12	C19	1.522(4)
C3	C4	1.524(5)	C13	C14	1.526(4)
C4	C5	1.535(5)	C14	C15	1.524(4)
C4	C10	1.513(5)	C14	C20	1.518(5)
C5	C6	1.523(4)	C15	C16	1.533(4)
C6	C7	1.533(4)	C16	C17	1.532(4)
C7	C8	1.533(4)	C17	C18	1.527(4)
C8	C9	1.525(5)	C18	C19	1.529(4)
C8	C10	1.518(5)	C18	C20	1.527(5)

Bond Angles (Degrees)

atom	atom	atom	angle	atom	atom	atom	angle
O1	S1	C1	111.2(1)	O1	S1	C11	111.2(1)
C4	C5	C6	109.7(3)	C1	S1	C11	47.7(1)
S1	C1	C2	113.7(2)	S1	C1	C6	114.2(2)
S1	C1	C11	66.0(1)	C2	C1	C6	110.1(2)
C2	C1	C11	122.3(2)	C1	C6	C5	108.9(2)
C6	C1	C11	122.3(2)	C1	C6	C7	109.7(2)
C1	C2	C3	108.7(2)	C1	C2	C9	109.9(3)
C5	C6	C7	109.3(3)	C3	C2	C9	108.4(3)
C6	C7	C8	109.6(3)	C7	C8	C10	109.2(3)
C2	C3	C4	110.0(3)	C7	C8	C9	108.8(3)

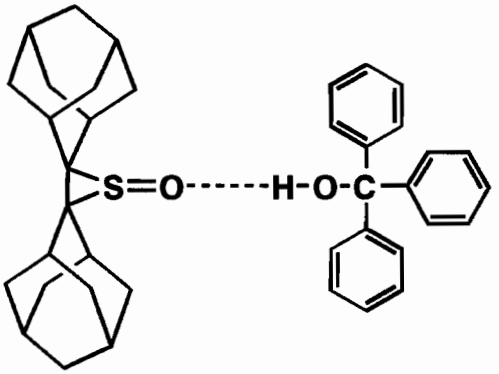
Table XR-18. continued

atom	atom	atom	angle	atom	atom	atom	angle
C9	C8	C10	109.8(3)	C5	C4	C10	109.6(3)
C2	C9	C8	110.3(3)	C13	C14	C15	109.8(2)
C13	C14	C20	109.3(3)	C4	C10	C8	110.0(3)
C15	C14	C20	109.3(3)	C14	C15	C16	110.0(2)
S1	C11	C1	66.3(1)	S1	C11	C12	114.8(2)
S1	C11	C16	112.8(2)	C1	C11	C12	122.2(2)
C1	C11	C16	122.4(2)	C11	C16	C15	108.7(2)
C12	C11	C16	110.2(2)	C11	C16	C17	109.2(2)
C11	C12	C13	108.4(2)	C11	C12	C19	109.9(2)
C15	C16	C17	108.9(3)	C13	C12	C19	109.1(2)
C16	C17	C18	110.3(2)	C17	C18	C19	108.8(3)
C17	C18	C20	109.1(3)	C19	C18	C20	109.9(3)
C12	C19	C18	109.9(2)	C14	C20	C18	109.9(2)

APPENDIX VII

X-RAY STRUCTURE DETERMINATION OF

Adduct 235



- **Crystal Data for the Structure Determination of 235** **(Table XR-19)**
- **Atomic Coordinates and Temperature Factors for 235** **(Table XR-20)**
- **Bond Distances and Bond Angles for 235** **(Table XR-21)**

Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer controlled by TEXRAY software using the θ/2θ scan mode.

Table XR-19. Crystal data for the structure determination of **235**

Chemical Formula	$C_{39}H_{44}O_2S$
Formula Weight	576.84
X-ray crystal dimension (mm)[a]	0.40 x 0.17 x 0.35
Radiation	CuK_α
Crystal system	triclinic
Space group	P -1 (#2)
Lattice constants	
a (Å)	10.588(2)
b (Å)	14.602(1)
c (Å)	10.521(2)
V (Å^3)	1536.7(5)
Z	2
F (000)	620
Density (calc'd) (g cm^{-3})	1.247
μ (mm^{-1})	1.148
λ (Å)	1.54178
2θ max (°)	140
No. of reflections measured	5930
No. of unique reflections	5589
No. of reflections with $I_{net} > 3.0\sigma(I_{net})$	3447
For significant reflections	RF = 0.065[b], R_w = 0.071[c], G_oF = 2.30[d]
Maximum shift / σ ratio	4.03
Deepest hole in D-map (e / Å^3)	-0.41
Highest peak in D-map (e / Å^3)	0.370
Method of structure determination	solved by direct methods
Method of structure refinement	NRCVAX system programs

[a]cell dimensions were obtained from 25 reflections with 2θ angles in the range 55.00-60.00°.

[b]$RF = \Sigma(F_o-F_c) / \Sigma(F_o)$

[c]$R_w = (\Sigma[wF_o-F_c)^2 / \Sigma (wF_o^2)])^{1/2}$

[d]$G_oF = (\Sigma[wF_o-F_c)^2 / (\#\text{ reflections} - \#\text{ parameters})])^{1/2}$

Table XR-20. Atomic coordinates (x, y, z) and temperature factors (B_{eq}) for adduct **235**. Estimated σs refer to the last digit.

Atomic Parameters x, y, z and B_{eq}
E. S. DS. refer to the last digit printed

atom	x	y	z	B_{eq}
S(1)	0.39525(10)	0.33773(08)	0.75762(12)	3.85(4)
O(1)	0.3361(03)	0.3409(02)	0.6142(03)	5.0(1)
O(2)	0.0938(03)	0.3684(02)	0.4785(03)	3.6(1)
C(1)	0.5802(03)	0.3568(03)	0.7879(04)	2.8(1)
C(2)	0.6367(04)	0.3994(03)	0.6783(04)	3.1(2)
C(3)	0.6289(05)	0.5023(03)	0.6784(05)	3.8(2)
C(4)	0.7065(04)	0.5587(03)	0.8101(05)	3.8(2)
C(5)	0.6467(05)	0.5158(03)	0.9191(05)	3.9(2)
C(6)	0.6541(04)	0.4131(03)	0.9201(04)	3.5(2)
C(7)	0.7827(04)	0.3955(04)	0.7039(05)	3.9(2)
C(8)	0.8600(04)	0.4518(03)	0.8367(05)	3.9(2)
C(9)	0.8511(05)	0.5543(03)	0.8344(05)	4.2(2)
C(10)	0.8004(05)	0.4079(04)	0.9439(05)	4.2(2)
C(11)	0.5069(04)	0.2541(03)	0.7742(04)	3.3(2)
C(12)	0.4820(05)	0.1870(03)	0.6498(05)	4.1(2)
C(13)	0.5957(06)	0.1348(04)	0.6627(06)	5.5(2)
C(14)	0.5975(06)	0.0796(04)	0.7803(07)	5.9(3)
C(15)	0.6219(06)	0.1470(04)	0.9037(06)	5.4(2)
C(16)	0.5089(05)	0.1995(04)	0.8924(05)	4.4(2)
C(17)	0.3770(05)	0.1240(04)	0.8725(07)	5.7(2)
C(18)	0.3533(06)	0.0584(04)	0.7492(07)	6.2(3)
C(19)	0.3490(06)	0.1138(04)	0.6311(06)	5.8(2)
C(20)	0.4667(07)	0.0066(04)	0.7613(09)	6.8(3)
C(21)	-0.1363(04)	0.3061(03)	0.3906(04)	3.0(1)
C(22)	-0.1426(05)	0.3955(03)	0.3563(05)	4.0(2)
C(23)	-0.2634(05)	0.4170(04)	0.3104(06)	5.2(2)
C(24)	-0.3821(05)	0.3487(04)	0.2932(06)	5.2(2)
C(25)	-0.3758(05)	0.2613(04)	0.3287(06)	5.1(2)

Table XR-20. continued

atom	x	y	z	B_{eq}
C(26)	-0.2565(04)	0.2400(04)	0.3756(05)	4.2(2)
C(31)	-0.0067(04)	0.2221(03)	0.5516(04)	2.8(1)
C(32)	0.0285(04)	0.2661(04)	0.6786(04)	3.6(2)
C(33)	0.0210(05)	0.2144(04)	0.7826(05)	4.7(2)
C(34)	-0.0167(05)	0.1171(04)	0.7622(05)	4.7(2)
C(35)	-0.0536(05)	0.0723(04)	0.6373(05)	4.3(2)
C(36)	-0.0445(04)	0.1237(03)	0.5323(05)	3.6(2)
C(41)	0.0324(04)	0.2269(03)	0.3234(04)	3.0(1)
C(42)	0.1612(05)	0.2138(03)	0.3388(05)	4.0(2)
C(43)	0.1966(05)	0.1652(04)	0.2407(05)	4.7(2)
C(44)	0.1058(06)	0.1260(04)	0.1263(05)	4.9(2)
C(45)	-0.0210(06)	0.1375(04)	0.1100(05)	5.6(2)
C(46)	-0.0571(05)	0.1863(04)	0.2076(05)	4.6(2)
C(50)	-0.0032(04)	0.2803(03)	0.4351(04)	3.0(1)

$\mathbf{B_{eq}}$ is the mean of the principal axes of the thermal ellipsoid.

Table XR-21. Bond distances (Å) and bond angles (degrees) for adduct **235**. Estimated σs refer to the last digit.

Bond Distances (Å)

atom	atom	distance	atom	atom	distance
S(1)	O(1)	1.509(3)	C(16)	C(17)	1.541(6)
S(1)	C(1)	1.868(4)	C(17)	C(18)	1.499(8)
S(1)	C(11)	1.867(4)	C(18)	C(19)	1.526(8)
O(2)	C(50)	1.433(4)	C(18)	C(20)	1.542(9)
C(1)	C(2)	1.521(5)	C(21)	C(22)	1.389(6)
C(1)	C(6)	1.518(5)	C(21)	C(26)	1.389(6)
C(1)	C(11)	1.512(5)	C(21)	C(50)	1.521(5)
C(2)	C(3)	1.522(6)	C(22)	C(23)	1.376(6)
C(2)	C(7)	1.525(6)	C(23)	C(24)	1.391(7)
C(3)	C(4)	1.524(6)	C(24)	C(25)	1.366(7)
C(4)	C(5)	1.534(6)	C(25)	C(26)	1.361(7)
C(4)	C(9)	1.512(6)	C(31)	C(32)	1.377(6)
C(5)	C(6)	1.520(6)	C(31)	C(36)	1.392(6)
C(6)	C(10)	1.533(6)	C(31)	C(50)	1.541(5)
C(7)	C(8)	1.531(6)	C(32)	C(33)	1.378(6)
C(8)	C(9)	1.522(7)	C(33)	C(34)	1.377(7)
C(8)	C(10)	1.522(7)	C(34)	C(35)	1.361(7)
C(11)	C(12)	1.518(6)	C(35)	C(36)	1.387(6)
C(11)	C(16)	1.521(6)	C(41)	C(42)	1.393(6)
C(12)	C(13)	1.547(7)	C(41)	C(46)	1.372(6)
C(12)	C(19)	1.535(7)	C(41)	C(50)	1.527(6)
C(13)	C(14)	1.521(8)	C(42)	C(43)	1.378(7)
C(14)	C(15)	1.513(8)	C(43)	C(44)	1.363(7)
C(14)	C(20)	1.515(8)	C(44)	C(45)	1.364(7)
C(15)	C(16)	1.545(7)	C(45)	C(46)	1.379(7)

Table XR-21. continued

Bond Angles (Degrees)

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	S(1)	C(1)	109.8(2)	S(1)	C(11)	C(1)	66.1(2)
O(1)	S(1)	C(11)	109.7(2)	S(1)	C(11)	C(12)	112.7(3)
C(1)	S(1)	C(11)	47.7(2)	S(1)	C(11)	C(16)	115.4(3)
S(1)	C(1)	C(2)	113.6(3)	C(1)	C(11)	C(12)	122.5(4)
S(1)	C(1)	C(6)	113.0(3)	C(1)	C(11)	C(16)	121.6(4)
S(1)	C(1)	C(11)	66.1(2)	C(12)	C(11)	C(16)	110.4(4)
C(2)	C(1)	C(6)	110.7(3)	C(11)	C(12)	C(13)	108.9(4)
C(2)	C(1)	C(11)	122.0(3)	C(11)	C(12)	C(19)	109.8(5)
C(6)	C(1)	C(11)	122.4(3)	C(13)	C(12)	C(19)	108.8(5)
C(1)	C(2)	C(3)	110.1(4)	C(12)	C(13)	C(14)	109.0(5)
C(1)	C(2)	C(7)	108.0(3)	C(13)	C(14)	C(15)	109.6(5)
C(3)	C(2)	C(7)	108.8(4)	C(13)	C(14)	C(20)	110.4(6)
C(2)	C(3)	C(4)	110.2(4)	C(15)	C(14)	C(20)	110.3(6)
C(3)	C(4)	C(5)	108.9(4)	C(14)	C(15)	C(16)	109.8(5)
C(3)	C(4)	C(9)	109.6(4)	C(11)	C(16)	C(15)	108.4(4)
C(5)	C(4)	C(9)	109.4(4)	C(11)	C(16)	C(17)	110.4(4)
C(4)	C(5)	C(6)	110.2(4)	C(15)	C(16)	C(17)	107.2(5)
C(1)	C(6)	C(5)	110.2(4)	C(16)	C(17)	C(18)	110.4(5)
C(1)	C(6)	C(10)	107.7(4)	C(17)	C(18)	C(19)	110.3(5)
C(5)	C(6)	C(10)	109.1(4)	C(17)	C(18)	C(20)	109.2(6)
C(2)	C(7)	C(8)	109.9(4)	C(19)	C(18)	C(20)	109.5(6)
C(7)	C(8)	C(9)	109.1(4)	C(12)	C(19)	C(18)	109.6(5)
C(7)	C(8)	C(10)	108.8(4)	C(14)	C(20)	C(18)	108.5(5)
C(9)	C(8)	C(10)	111.0(4)	C(22)	C(21)	C(26)	117.2(4)
C(4)	C(9)	C(8)	109.3(4)	C(22)	C(21)	C(50)	121.2(4)
C(6)	C(10)	C(8)	109.3(4)	C(26)	C(21)	C(50)	121.5(4)
C(21)	C(22)	C(23)	120.9(5)	C(31)	C(50)	C(41)	111.0(3)
C(22)	C(23)	C(24)	120.6(5)	C(21)	C(50)	C(41)	111.9(3)
C(23)	C(24)	C(25)	118.4(5)	C(24)	C(25)	C(26)	121.1(5)
C(21)	C(26)	C(25)	121.8(5)	C(32)	C(31)	C(36)	117.9(4)

Table XR-21. continued

atom	atom	atom	angle	atom	atom	atom	angle
C(32)	C(31)	C(50)	120.8(4)	C(36)	C(31)	C(50)	121.3(4)
C(31)	C(32)	C(33)	120.9(5)	C(32)	C(33)	C(34)	120.6(5)
C(33)	C(34)	C(35)	119.4(5)	C(34)	C(35)	C(36)	120.3(5)
C(31)	C(36)	C(35)	120.8(5)	C(42)	C(41)	C(46)	116.4(4)
C(42)	C(41)	C(50)	119.6(4)	C(46)	C(41)	C(50)	123.9(4)
C(41)	C(42)	C(43)	121.3(5)	C(42)	C(43)	C(44)	121.1(5)
C(43)	C(44)	C(45)	118.4(5)	C(44)	C(45)	C(46)	120.9(5)
C(41)	C(46)	C(45)	121.9(5)	O(2)	C(50)	C(21)	105.7(3)
O(2)	(50)	C(31)	109.2(3)	O(2)	C(50)	C(41)	109.5(3)
C(21)	C(50)	C(31)	109.5(3)				