# INVESTIGATIONS TOWARDS AN OVERALL MECHANISM FOR SULFUR EXTRUSION. THE IMPORTANCE OF DIATOMIC SULFUR.

By

## CHARLES R. WILLIAMS

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of

## **Doctor of Philosophy**

Department of Chemistry McGill University Montreal, Quebec Canada

**©** June 1991

À

## Charles R. Williams

#### Department of Chemistry

# INVESTIGATIONS TOWARDS AN OVERALL MECHANISM FOR SULFUR EXTRUSION. THE IMPORTANCE OF DIATOMIC SULFUR.

## ABSTRACT

Several reaction systems have been investigated as possible sources of diatomic sulfur  $(S_2)$ . Dialkoxy disulfides have been shown to thermally decompose with the formation of sulfur likely as  $S_2$  which was successfully trapped in modest yield. Several other systems have been shown to decompose with a likely  $S_2$  intermediate.

The chemistry of the chloro(triphenylmethyl)sulfides was studied. The X-ray crystal structures of the first chlorodisulfide and chlorotrisulfide were obtained. The chlorotriphenylmethyl sulfides were found to decompose in the presence of 1,3-dienes to yield products which are consistent with the trapping of diatomic sulfur. The reactions of the chloro(triphenylmethyl)sulfides were examined and used to prepare a series of mixed sulfides containing 1-4 sulfurs. A novel extrusion of sulfur in the reaction of chloro(triphenylmethyl)monosulfide with thiocarbonyl compounds was investigated. The thermal decomposition of the sulfides as solids and in solution were examined.

The solvent dependent desulfurization of sulfenic sulfonic thioanhydrides was investigated in the anticipation of discovering a diatomic sulfur intermediate. The extrusion was shown to involve the concatenation of sulfur atoms until a stable sulfur ring could be extruded.

The X-ray crystal structure of bis(triphenylmethyl)disulfide was determined and was discussed in relation to other hindered disulfides.

# ETUDE D'UN MECHANISME GENERAL D'EXTRUSION D'ATOME DE SOUFRE. L'IMPORTANCE DU SOUFRE DIATOMIQUE.

### <u>RESUME</u>

Différentes classes de réaction ont été étudiées en tant que source possible de soufre diatomique. Il a été montré que les dialkoxy bisulfures se décomposent sous l'effet de la température et conduisent vraisemblablement à la formation de  $S_2$  qui a pu être piégé avec un rendement modeste. La décomposition d'autres classes a montré la présence d'un intermédiaire semblant être  $S_2$ .

La chimie des chloro(triphénylméthyl)sulfures a été étudiée. Les structures cristallines des premiers chlorodisulfures et chlorotrisulfures ont été obtenues par rayon X. En présence de diènes-1,3, le chloro(triphénylméthyl)sulfures se décompose en produits qui sont semblables à ceux obtenus lors du piégeage du soufre diatomique. La réactivité du chloro(triphénylméthyl)sulfure a été étudiée et utilisée pour préparer differents types de sulfures mixtes de 1 à 4 atomes de soufre.

Par l'addition de composés thiocarbonylés, une nouvelle méthode d'extrusion de soufre du chloro(triphénylméthyl)sulfure a été établie. La décomposition thermique des sulfures, à l'état solide et en solution, a été étudiée.

Précédemment à l'identification de l'intermédiaire de soufre diatomique, l'effet du solvent sur la désulfurisation des sulfénic sulfonic thioanhydrides a été examiné. L'extrusion de soufre entraîne la concaténation d'atome de soufre jusqu'a ce qu'un cycle stable puisse être extrudé

La structure cristalline du bis(triphénylméthyl)bisulfure a été obtenue par rayon X et comparée à d'autres bisulfures stériquement encombrés.

#### <u>ACKNOWLEDGEMENTS</u>

I wish to thank Professor David N. Harpp without whose guidance and encouragement this project would not have been completed.

I would like to thank Professor A. Shaver for fruitful discussions of sulfur chemistry and Professor J. Chin for a discussion of kinetics. I would also like to thank Dr. D. Gray for the use of his computer in drawing of the structures.

I would like to thank Dr. F. Sauroil for exceptional guidance in the use of the NMR spectrometers, Dr. J. Finkenbine who obtained the mass spectra and Steve Barnett who acquired the Raman spectra.

The work of Dr. J. Britten who acquired the X-ray crystal structures is gratefully acknowledged.

For external work I would like to thank Professor Dr. R. Steudel, at the Institut für Anorganische und Analytische Chemie, Berlin, Germany who obtained the HPLC chromatograms of the sulfur extrusions experiments. The elemental analyses obtained from the laboratory of Dr. Charles Larsen at the University of Copenhagen, Denmark are acknowledged.

I would especially like to thank Dr. Patti Folkins who proofread most of this manuscript. I thank all those who made life in Room 240 livable: Dr. Patti Folkins, Mr. Warren Chew, Dr. Dominic Ryan, Gerard Derbesy, C.J. Li and Sylvie Tardif. I thank all of my friends at McGill who made my years in Montreal a time to remember. I would like to thank Dr. Steve Bodzay and Dr. Jeff McCarthy for cheering me up on many a "blue" day. I would like to thank Gerard Derbesy for translating the abstract into French.

Finally I would like to express my gratitude to Anita Bezeau whose friendship made the last couple of years a success, and without whose encouragement I would never have finished.

ų

Charles R. Williams

## TABLE OF CONTENTS

,

ì

k

- A

1.	Introduction	
	1.1 Sulfur Extrusion	1
	1.2 Singlet Sulfur Atoms	2
	1.3 Concatenation of Sulfur Atoms	6
	1.4 Solvent Dependent Extrusions	11
	1.5 Diatomic Sulfur S <sub>2</sub>	13
	1.6 Methods of S <sub>2</sub> Formation and Examples of Isolation	19
2.	Diatomic Sulfur (S <sub>2</sub> )	
	2.1 Introduction	28
	2.2 Experiments Towards the Identification of Diatomic Sulfur Precursors	32
	2.2.1 Sulfur Transfer Reagents	
	2.2.2 Thermal Decomposition of Dialkoxydisulfides	34
	2.2.3 4-Methoxycarbonylsulfenic Sulfonic Thioanhydrides	39
	2.2.4 3,5-Di-t-butyl-4-hydroxybenzene Sulfenyl	
	Chloride Reaction With Amines	44
	2.2.5 Reaction of Xanthic Acid Disulfides With Amino Disulfides	45
	2.2.6 Conversion of Tetramethylthiuram Disulfide to N,N-Dimethylcarbamyl Chloride	46
	2.2.7 Thermolysis of 2-Methyl-2-propyltetrasulfide	46
	2.3 Structure of the Addition Adducts	47
3.	Attempts to Elucidate the Mechanism of Sulfur Extrusion	
	from 4-Tolylsulfenic-4-tolylsulfonic thioanhydride	
	3.1 Introduction	53
	3.2 Mechanistic Proposals	54
	3.3 Differentiation between 146 and 147	
	3.3.1 General Techniques	58
	3.3.2 <sup>19</sup> F NMR Spectroscopy	59
	3.4 Attempted Trapping of S <sub>2</sub> From 4-Tolylsulfenic-4-tolylsulfonic Thioanhydride	60
	3.5 HPLC Analysis	61

Page

4. Chloro(triphenylmethyl)sulfides: Structure and Chemistry	
4.1 Introduction	66
4.2 Synthesis	68
4.3 Crystallographic Analysis	70
4.4 Spectroscopic Analysis	77
4.5 Thermal Decomposition	
4.5.1 In The Solid State	80
4.5.2 In Solution	82
4.5.3 Rate Studies on the Thermal Decomposition	
4.5.4 A Probable Mechanism For The Decomposition	
of Chloro(triphenylmethyl)di and Trisulfide	95
4.6 Reaction of the Chloro(triphenylmethyl)sulfides	
4.6.1 Nucleophilic Displacements	99
4.6.2 With 1,3-Dienes	104
4.6.3 Reaction of Chloro(triphenylmethyl)monosulfide and Thiocarbonyls	116
4.6.4 Reaction of Chloro(triphenylmethyl)disulfide and	
Thiocarbonyls; Attempted Preparation of a Thioozonide	124
4.6.4.1 NMR Analysis	125
4.6.4.2 Ultaviolet-Visible Spectroscopy	127
4.6.4.3 IR Analysis	127
4.6.4.4 Analysis With <sup>19</sup> F NMR Spectroscopy	128
4.6.4.5 Thermal Decomposition	128

## 5. Bis(triphenylmethyl)sulfides

đ

×.

á.

5.1	Introduction	131
5.2	Synthesis	132
5.3	Spectroscopic Analysis	134
5.4	Crystallographic Analysis	137
5.5	Thermal Decomposition	139
5.6	A Probable Mechanism for the Thermal Decomposition	138
5.7	Reaction of Bis(triphenylmethyl)trisulfide with Triphenylphosphine Dibromide	144

**Conclusion and Claims to Original Work** 

6. Experime	ental	
6.1 Gene	ral Procedures	147
6.2 Expen	rimental Procedures	150
6.2.1 E	Diatomic Sulfur Precursor Preparation and Trapping Experiments	150 158
6.2.2 S	ulfenic Sulfonic Thioanhydrides	
6.2.3 S	Synthesis of Chloro(triphenylmethyl)sulfides	162
6.2.4 (	Crystallography of the Chloro(triphenylmethyl)sulfides	164
6.2.5 F	Preparation of Substituted Triphenylmethanes	167
6.	2.5.1 Preparation of Thiols	168
6.	2.5.2 Preparation of Substituted Chloro(triphenylmethyl)monosulfides	171
6.2.5.3 Preparation of Substituted Chloro(triphenylmethyl)disulfides		171
6.	2.5.4 Preparation of Substituted Triphenylchloromethanes	173
6.2.6 F	Reaction of Chloro(triphenylmethyl)sulfides	
6.	2.6.1 With Nucleophiles	175
6.	2.6.2 With 1,3-Dienes	180
6.	2.6.3 Reaction of Chloro(triphenylmethyl)monosulfide	
	With Thiocarbonyl Compounds	183
6.	2.6.4 Reaction of 162b With Thiocarbonyl Compounds	
	Attempted Preparation of a Thioozinide	186
6.2.7 P	Preparation and Reaction of Bis(triphenylmethyl)sulfides	188
Appendix	Atomic Coordinates and Temperature Factors	194

101 ۰**.**- 146

~ ه\_ ه

## **INDEX OF TABLES**

4 cz. 4

1

ŗ

No.	Title	Page	
1.	Summary of Report 153 Isolation Procedures		
2.	4-Substituted Dialkoxydisulfides (124): Melting Points and		
	Decomposition Temperature	38	
3.	<sup>1</sup> H and <sup>13</sup> C NMR Chemical Shifts of the Trapped Adducts of <sup>1</sup> S <sub>2</sub>	48	
4.	Experimental and Calculated Data from the HPLC Analysis		
	for the Sulfur Extrusion From 146 in Ethanol	63	
5.	Summary of Physical Properties for the Chloro(triphenylmethyl)sulfides	69	
6.	Selected Bond Lengths and Angles From The X-ray Structures		
	of the Chloro(triphenylmethyl)sulfides	71	
7.	Molecules With Sulfur-Sulfur Double Bonds	76	
8.	Summary of the <sup>13</sup> C NMR Chemical Shifts for the Chloro(triphenylmethyl)sulfides	78	
9.	Summary of the Raman Signals for the Chloro(triphenylmethyl)sulfides	80	
10.	10. Product Distribution for the Decomposition of Chloro(triphenylmethyl)sulfides		
	at Ambient Temperature for 48 h in Various Solvents	83	
11.	Summary of Physical Data for Monosubstituted Triphenylmethanes	85	
12. Calculated Kates and Rate Constants for the Thermal			
	Decomposition of (173a) in Chloroform-d Solution	88	
13.	Summary of the <sup>13</sup> C NMR Chemical Shifts for the		
	Butyl(triphenylmethyl)sulfides (177)	100	
14.	Summary of S <sub>2</sub> Trapping Experiments of 2,3-Dimethyl		
	1,3-butadiene with Chloro(triphenylmethyl)disulfide (162b)	106	
15.	Summary of S <sub>2</sub> Trapping Experiments of 2,3-Dimethyl		
	1,3-butadiene with Chloro(triphenylmethyl)disulfide (162b). Isolation of 107 and 127	108	
16.	<sup>13</sup> C NMR Chemical Shifts and Assignments for the Addition of Chloro-		
	(triphenylmethyl)disulfide (162b) and 4,4'-Dimethoxythiobenzophenone (193)	125	
17.	<sup>1</sup> H NMR Chemical Shifts for 200 From the Reaction of Chloro-		
	(triphenylmethyl)disulfide (162b) and 4,4'-Dimethoxythiobenzophenone (193)	126	
18.	Summary of the <sup>13</sup> C NMR Chemical Shifts for the		
	Bis(triphenylmethyl)sulfides	135	
19.	Selected Bond Lengths and Angles for 167b	137	
20.	Product Distribution from the Thermolysis of the Bis(triphenylmethyl)sulfides,		
	From the <sup>13</sup> C NMR Spectra	139	
21.	<sup>19</sup> F and <sup>13</sup> C Chemical Shifts of Bis(mono-4-flourotriphenylmethyl)sulfides	141	
22.	Comparison of Sulfur-Sulfur Bond Dissociation Energies	141	
23.	Crystal Data and Collection parameters	165	

## **INDEX OF FIGURES**

.

ł

r 1

ł

No.	Title	Page
1.	<sup>1</sup> H NMR Spectra for the Thermal Decomposition of 4-Nitrobenzyloxydisulfide (124a).	36
2.	Mass Spectral Fragmentation Pattern for	
	Methoxycarbonylsulfenyl 4-Tolylthioanhydride (129a).	43
3.	Mass Spectral Fragmentation Pattern for	
	1,2,3,4-Tetrathia-6,7-dimethyl-6-cyclooctene (127).	51
4.	<sup>1</sup> H NMR Spectra for the Desulfurization of 1,2,3,4-Tetrathia-6,7-	
	dimethyl-6-cyclooctene (127) with Triphenylphosphine (143).	52
5.	Plot of Natural Logarithm k' vs X + 1 for the Sulfur Extrusion	
	from 146 in Ethanol. k' = Capacity factor for the HPLC	62
6.	ORTEP Diagram of Chloro(triphenylmethyl)monosulfide (162a).	72
7.	ORTEP Diagram of Chloro(triphenylmethyl)disulfide (162b).	73
8.	ORTEP Diagram of Chloro(triphenylmethyl)trisulfide (162c).	74
9.	The Change in the <sup>1</sup> H NMR signal for the Tolyl Protons over Time for the	
	Decomposition of Chloro(mono-4-methyltriphenylmethyl)disulfide (173a)	87
10.	Plot of Concentration vs Time for the Decomposition of	
	Chloro(mono-4-methyltriphenylmethyl)disulfide (173a) at 30°C	91
11.	Plot of Concentration vs Time for the Decomposition of Chloro(mono-4-	
	methyltriphenylmethyl)disulfide (173a) at 40°C. The Effect of Inhibition and Initiation	92
12.	Plot of Concentration vs Time for the Effect of the Addition of Elemental	
	Sulfur on the Decomposition of (173a)	93
13.	Plot of Natural Logaithm of the Rate Constants vs 1/T for the Decomposition of (173a)	94
14.	<sup>1</sup> H NMR Spectrum of a Mixture of Disulfide 107 and Tetrasulfide 127 from the	107
	Decomposition of Chlorodisulfide 162b with 2,3-Dimethyl-1,3-butadiene 109.	
15.	<sup>1</sup> H NMR Spectra for the Addition of 162b to 2,3-Dimethyl-1,3-butadiene (109) Over 4	
	Days. The Spectra Ranging from 2.25-4.5 ppm.	112
16.	<sup>19</sup> F NMR Spectra for the Addition Reaction Between 4,4'-Dimethoxythiobenzophenone	
	(193) and Chloro(mono-4-fluorotriphenylmethyl)monosulfide (172b).	122
17.	<sup>19</sup> F NMR Spectra for the Addition Reaction Between Bis(4-tolyl)trithiocarbonate	
	(194) and Chloro(mono-4-fluorotriphenylmethyl)monosullide (172b).	123
18.	<sup>19</sup> F NMR Spectra for the Addition Reaction Between 4,4'-Dimethoxythiobenzophenone	
	(193) and Chloro(mono-4-fluorotriphenylmethyl)disulfide (162b).	130
19.	Plot of <sup>13</sup> C Chemical Shift for the Quaternary Carbon vs Number of Sulfur Atoms.	
	For Chloro(triphenylmethyl)sulfide (162) and Bis(triphenylmethyl)sulfides (167).	136
20.	ORTEP Diagram of Bis(triphenylmethyl)disulfide (167b).	138

Å	angstrom
Ac	acetyl
b. <b>p.</b>	boiling point
bu	butyl
cm	centimeter
đ	doublet
dđ	doublet of doublets
EI	Electron Impact
ct	ethyl
eV	electron Volt
FT	fourier transform
g	gram
GC	Gas chromatography
h	hour
HPLC	high performance liquid chromatography
IR	infrared
m	meta
m.p.	melting point
me	methyl
mg	milligram
min	minute
mL	millilitre
mm	millimeter
MS	mass spectrometry
N	normality
NMR	Nuclear magnetic Resonance
0	ortho
p	para
Pet. Ether	petroleum ether
Ph	phenyl
ppm	parts per million
q	quartet
Rf	relative mobility
S	second
S	singlet

## **ABBREVIATIONS**

\*

1

---

t	tertiary
t	triplet
THF	tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	tetramethylsilane
Tr	triphenylmethyl (Trityl)
UV	Ultraviolet

## **CHAPTER 1**

### INTRODUCTION

### 1.1 Sulfur Extrusion

In the chemical sense, the term "sulfur extrusion" has been used to describe the loss of any moiety containing a sulfur atom from a molecule. Sulfur extrusion reactions have been successfully employed in organic synthesis, for example: Raney Nickel desulfurization,<sup>1</sup> and the Ramburg-Backlund rearrangement (loss of SO<sub>2</sub> to form alkenes).<sup>2</sup>

There are innumerable examples in the literature where one of the products in a chemical reaction is elemental sulfur.<sup>3</sup> The sulfur that is lost is often inappropriately represented as S, [S], S<sup>o</sup> or S<sub>1</sub> and the implication is often that atomic sulfur is produced in the process. The mechanism by which the sulfur is produced in these reactions is not well understood. Extrusion of elemental sulfur has been observed under many conditions: thermally, photochemically, base induced as well as solvent induced.

There have been four major reviews concerning sulfur extrusion in the literature but each was limited in scope. Two accounts which appeared in the 1960's by Dean and Stark<sup>4</sup> and Loudon<sup>5</sup> examined extrusions which resulted in stable aromatic systems. More recently a review by Radl<sup>6</sup> reported extrusions which resulted in the formation of five-membered ring heterocycles and one by Guziec and Sanfilippo<sup>7</sup> studied examples of the extrusion of sulfur, selenium and tellurium. No review examined the mechanism by which sulfur is produced in the extrusion reactions

<sup>1.</sup> J. Bougault, E. Cattelain and P. Chabrier, Comp. Rend., 208, 657 (1939); Bull. soc. chim. France, 7, 781 (1940).

<sup>2.</sup> For example see: S. Yamada, H. Ohsawa, T. Suzuki and H. Takayama, J. Org. Chem., 51, 4934, (1986); W. L. Mock, J. Am. Chem. Soc., 97, 3666 (1975).

<sup>3.</sup> C. R. Williams and D. N. Harpp, Sulfur Reports, 10, 103 (1990).

<sup>4.</sup> B. P. Stark and A. J. Duke, "Extrusion Reactions", Pergamon Press, Oxford, England, 1967, p. 72.

<sup>5.</sup> J. D. Loudon, "Organic Sulfur Compounds", N. Kharasch (Ed.), Pergamon Press, Oxford, 1961, Vol. 1, p. 299.

<sup>6.</sup> S. Radl, Janssen Chim. Acta, 5, 3 (1987).

<sup>7.</sup> F. S. Guziec, Jr and L. J. Sanfilippo, Tetrahedron, 44, 6241 (1988).

except to say that the driving force for the extrusion is the formation of stable aromatic systems. The following sections will examine and relate the mechanistic information on the loss of sulfur found in the chemical literature.

### 1.2 Singlet Sulfur Atom

In several instances, sulfur loss in organic reactions has been specifically proposed to proceed through a cheletropic loss of a singlet sulfur atom which could then combine to form elemental sulfur  $(S_8)$ . Under most conditions, formation of a singlet sulfur atom is not a reasonable pathway for the loss of sulfur to occur. The energy of formation for a singlet sulfur atom  $S(^1D_2)$  has been determined to be 66.3 kcal/mol.<sup>8,9</sup> The high energy value for this species suggests that decomposition pathways involving a singlet sulfur atom cannot be operative for the many observed sulfur extrusions that occur under mild conditions.<sup>3</sup> The sulfur loss must proceed through a transient species of lower energy such as diatomic sulfur  $(S_2)$  or longer-chain fragments.<sup>10</sup> These transient species could then combine to form elemental sulfur, ultimately resulting in an overall lower energy pathway for the extrusion reaction.

In many examples of sulfur extrusion, thiiranes are the proposed intermediates. Thiiranes (or episulfides) are the sulfur analogues of oxiiranes (epoxides) and they undergo many of the normal reactions observed for oxiiranes, such as nucleophilic ring opening<sup>11</sup> or olefin formation with phosphorus nucleophiles.<sup>12</sup> However, thiiranes will extrude sulfur under various conditions to form elemental sulfur (Scheme 1) whereas an analogous extrusion of oxygen is not found in the chemistry



Scheme 1

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

1.04

. .

<sup>8. &</sup>quot;JANAF Thermochemical Tables", Dow Chemical Co., Midland Mich., 1966, plus later supplements to 1976.

<sup>9.</sup> K. J. Miller, K. F. Moschner and K. T. Potts, J. Am. Chem. Soc., 105, 1705 (1983).

<sup>10.</sup> D. N. Harpp, Perspectives in the Organic Chemistry of Sulfur; B. Zwanenburg, A. J. H. Klunder, (Ed.), Elsevier, Amsterdam, 1987, p 1-22.

<sup>11.</sup> H. R. Snyder, M. Stewart and J. B. Ziegler, J. Am. Chem. Soc., 69, 2637 (1947).

of oxiranes. There are many instances where thiiranes decompose directly to olefins and elemental sulfur.<sup>13</sup> The mechanism for the thermal decomposition of thiirane to olefin and sulfur is often proposed to be a simple cheletropic loss of one sulfur atom.

A recent study by Lutz and Biellmann<sup>14</sup> has indicated that this may not be the case. They found that the loss of sulfur from the decomposition of (1) did not have first-order kinetics (as would be expected for sulfur atom formation), thus a more complex mechanism may be involved, perhaps with a bridged sulfur species (2).



13. (a) C. G. Moore and M. Porter, J. Chem. Soc., 2062 (1958).

(b) C. O. Guss and D. L. Chamberlain, Jr., J. Am. Chem. Soc., 74, 1342 (1952).

(c) 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., 2665 (1960).

(c) M. A. Youtz and P. P. Perkins, J. Am. Chem. Soc., 51, 3508 (1929).

(d) M. Mousseron, M. Bousquet and G. Marett, Bull. Soc. Chim. France, 84 (1948).

(e) D. Seyferth, W. Tronich, K. S. Marmor and W. E. Smith, J. Org. Chem., 37, 1537 (1972).

(f) H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, 3, 833 (1920); H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, 3, 840 (1920); A. Schönberg, *Ber.*, 58, 1793 (1925); A. Schönberg and L. von Vargha, *Ann.*, 483, 176 (1930); A. Schönberg and L. von Vargha, *Ber.*, 64B, 1390 (1931); A. Schönberg, K. Fateen and M. A. Sammour, *J. Am. Chem. Soc.*, 79, 6020 (1957); G. P. Hagen and R. M. Burgison, *J. Amer. Pharm. Assoc.*, 39, 7 (1950).

(g) T. Sato, Y. Goto, T. Tohyama, S. Hayashi and K. Hata, Bull. Chem. Soc. Japn., 40, 2975 (1967).

(h) G. A. Tolstikov, B. M. Lerman and L. I. Umanskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1367 (1982); Chem. Abstr., 97 162438d (1982).

(i) Y. Gao and B. Sharpless, J. Org. Chem., 53, 4114 (1988).

- (j) W. Ando, A. Itami, T. Furuhata and N. Tokitoh, Tetrahedron Lett., 1787 (1987).
- 14. E. Lutz and J.-F. Biellmann, *Tetrahedron Lett.*, 2789 (1985); this process is being investigated in detail in our laboratory; W. Chew and D. N. Harpp (unpublished results).

i

An earlier study of sulfur extrusion in solution examined the pyrolysis<sup>15</sup> of *cis*and *trans*-1,2-diethenylthiirane, (3) and (4) respectively. It was found that a competition between the observed sulfur extrusion and the thermal synthesis of thienocyclobutadiene (5) occurred. Pyrolysis of the thiiranes at  $100^{\circ}$ C resulted only in formation of the corresponding desulfurized olefins 6 and 7.



The reaction initially exhibited second order kinetics but changed to first order as the reaction proceeded. These kinetic studies indicate that the extrusion of sulfur from thiiranes has a more complica'ed mechanism than the simple cheletropic loss of an atom of sulfur.

Thermal sulfur loss from dithiins to form thicphenes<sup>16</sup> (Schemes 2 and 3) and from thicpins to form stable aromatic systems<sup>4,5</sup> (Scheme 4) was thought to also proceed exclusively through loss of a singlet sulfur atom.



Scheme 2

Scheme 3

<sup>15.</sup> K. P. C. Vollhardt and R. G. Bergman, J. Am. Chem. Soc., 95, 7538 (1973).

<sup>16.</sup> For example see: W. E. Parham and V. J. Traynelis, J. Am. Chem Soc., 77, 68 (1955) or R. Grigg, R. Hayes and J. L. Jackson, J. Chem. Soc. (D), 1167 (1969).



#### Scheme 4

Mueller<sup>17</sup> attempted to trap atomic sulfur in the reaction of  $\alpha$ -chloro- $\beta$ -(acetylthio)propionitrile (8) and diethylamine with an alkene, but was unsuccessful. He proposed that this particular reaction proceeded through a thiirane intermediate which spontaneously lost atomic sulfur. Other researchers attempted to trap atomic sulfur in the sulfur loss which occurred when a phosphothiolate (9) was oxidized with a peroxy acid but were also unsuccessful.<sup>18</sup> Thermal decomposition of 5substituted-1,2,3,4-thiatriazoles (10) in the presence of olefins gave no evidence for episulfide formation; however photolysis of the same species in the presence of olefins did produce the corresponding thiiranes, suggesting atomic sulfur formation. Under similar conditions the photolysis of isothiocyanates  $(11)^{19}$  resulted in the formation of sulfur atoms which were successfully trapped as thiiranes. The results from the photolysis experiments were not surprising as the normal method for producing sulfur atoms is the photolysis of carbon oxysulfide (COS).<sup>20</sup> These results indicated that sulfur atoms would not form thermally. Therefore the mechanistic proposals involving a singlet sulfur atom formation in thermal extrusions are likely incorrect.



<sup>17.</sup> W. H. Mueller, J. Org. Chem., 34, 2955 (1969).

N. A.

<sup>18.</sup> L. Field, N. E. Heimer, R. I. McNoil, R. A. Neal, J. Swinson and J. R. Van Wazer, Sulfur Lett., 1, 135 (1983).

<sup>19.</sup> R. Jahn and U. Schmidt, Monatsh Chem., 109, 161 (1978)

<sup>20.</sup> K. Gollnick and E. Leppin, J. Am. Chem. Soc., 92, 2217 (1970); E. Leppin and K. Gollnick, J. Am. Chem. Soc., 92, 2221 (1970).



#### 1.3 Concatenation of Sulfur Atoms

One possibility that has been proposed for the mechanism of sulfur extrusion is the concatenation of sulfur atoms with the formation and extrusion of a stable sulfur species. The initial step in such an extrusion would occur through the reaction between two sulfur species with the transfer of a sulfur atom to form a thiosulfoxidelike intermediate 12.



Intermediate 12 could then further react with other molecules until the sulfur chain (13) was six or eight atoms long and could cyclize to  $S_6$  or, more likely,  $S_8$ . The original concept can be credited to Foss.<sup>21</sup> A similar proposal was made by Davis<sup>22</sup> to account for the formation of elemental sulfur in acidified solutions of thiosulfate. Very recently, in an unrelated study of a novel reaction of sulfur cation radicals in solution, results were obtained that indicated a similar concatenation.<sup>23</sup> The formation of 5,6-diphenyl-1,2,3,4-tetrathietane (14) was observed when cis- or trans-2,3-diphenylthiiranes (15) were mixed with a catalytic amount of tris(pbromophenyl)aminium hexachloroantimonate in dichloromethane. The mechanistic<sup>23</sup> proposal was that the formation of a radical species was followed by the abstraction of a sulfur atom from an identical thiirane molecule forming the two-sulfur species 16 and alkene 17. The two-sulfur species would further abstract

<sup>21.</sup> O. Foss, Acta Chem. Scand., 4 (1950); O. Foss in "Organic Sulfur Compounds," N. Kharasch (Ed.), Pergamon Press, New York (1961), p. 75-77.

<sup>22.</sup> R. E. Davis, J. Am. Chem. Soc., 80, 3565 (1958).

<sup>23.</sup> M. Kamata, K. Murayama, T. Suzuki and T. Miyashi, J. Chem. Soc., Chem. Commun., 827 (1990).

sulfur atoms until an anionic chain of four sulfur atoms 18 was obtained, which then cyclized. The formation of 14 was confirmed by X-ray analysis.



The formation of sulfides by the loss of sulfur from polysulfides has been shown to readily occur (Scheme 5). A common explanation for the observed conversion is the loss of sulfur from the thiosulfoxide-like intermediate,<sup>24,25,26,27</sup> most probably formed *via* a rearrangement of the sulfide chain. The formation of a thiosulfoxide has been proposed in solvent mediated,<sup>24</sup> photo-induced<sup>25</sup> and in thermallymediated extrusions.<sup>26</sup> The branch-bonded arrangement is known and several stable derivatives containing it have been isolated and characterized.<sup>28,29</sup> The formation of thiosulfoxides as intermediates has been supported by recent results of Strausz.<sup>30</sup>

<sup>24.</sup> B. I. Stepanov, V. Ya. Rodionov and T. A. Chibisova, J. Org. Chem. USSR, 10, 78 (1974).

<sup>25.</sup> G. A. R. Brandt, H. J. Emeléus and R. N. Haszeldine, J. Chem. Soc., 2198 (1952).

<sup>26.</sup> R. N. Haszeldine and J. M. Kidd, J. Chem. Soc., 3219 (1953).

<sup>27.</sup> G. Höfle and J. E. Baldwin, J. Am. Chem. Soc., 93, 6307 (1971).

<sup>28.</sup> F. Seel and D. Gölitz, Chimia, 17, 207 (1964).

<sup>29.</sup> D. N. Harpp, K. Steliou and C. J. Cheer, J. Chem. Soc., Chem. Commun., 825 (1980).

<sup>30.</sup> M. Green, E. M. Cown and O. P. Strausz, J. Am. Chem. Soc., 106, 6938 (1984).



### Scheme 5

Allylic disulfides 19 were observed to rearrange to new disulfides at ambient temperature.<sup>25</sup> The rearrangements were again proposed to occur through the thiosulfoxide intermediate 20 via a 3,3-sigmatropic shift. For sterically hindered allylic disulfides only rearrangement to new disulfides was observed, while the less substituted disulfides rearranged to the corresponding sulfides 21 and sulfur.



A possible rationale for less substituted allylic disulfides rearranging to the sulfides and sulfur is the concatenation of sulfur atoms from the thiosulfoxide intermediate. The greater the steric repulsion, the lesser the chance for the sulfur atoms to come into close enough proximity for sulfur attack to occur. Once reacted, the sulfur species could extend to longer chains and ultimately lose elemental sulfur.

Husigen and Rapp,<sup>31</sup> in an unrelated experiment, successfully trapped molecules having a structure similar to the thiosulfoxide intermediate in the thermal decomposition of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (22). They proposed a mechanism involving a 1,3-dipolar cycloreversion to the thiobenzophenone-S-sulfide 23; in the absence of trapping agents further abstraction of sulfur atoms occurred

<sup>31.</sup> R. Huisgen and J. Rapp, J. Am. Chem. Soc., 109, 902 (1987).

to form a species that could cyclize and ultimately form thiobenzophenone (24) and cyclooctasulfur  $(S_8)$ .



Miller and Potts<sup>9</sup> carried out a theoretical study on the reaction of thieno[3,4c]thiophenes (25) with dicyanoacetylene as a model for cycloadditions involving derivatives of this ring system. They concluded that extrusion of sulfur as an atomic species from the addition product (Diels-Alder adduct) was energetically unfavorable. Extrusion of sulfur as  $S_6$  or  $S_8$  was found to be an energetically more favorable process. Their mechanistic proposal involved a bridged sulfide intermediate 26 which could react with a second molecule to form a compound with two sulfur atoms. The molecule would then further react until it contained a chain of six or eight sulfur atoms and then would cyclize with the elimination of the stable  $S_6$  or,  $S_8$  ring.



A more recent paper by Gleiter<sup>32</sup> summarized the thermal stabilities of monocyclic thiepins 27. By studying the loss of sulfur from thiepins using photoelectron spectroscopy Gleiter reached a similar conclusion as that obtained by Miller and Potts. The possibility of a species involving the concatenation of sulfur atoms from the thianorcaradiene (thiirane) intermediate 28 was proposed with 29, as a possible intermediate. This species would ultimately lose elemental sulfur (S<sub>8</sub>, *vide infra*).

ſ

<sup>32.</sup> R. Gleiter, G. Krennrich, D. Cremer, K. Yamamoto and I. Murata, J. Am. Chem. Soc., 107, 6874 (1985).



4

. .

Concatenation has also been proposed to account for the formation of elemental sulfur in the decomposition of nitrile N-sulfides (30),<sup>33</sup> in the observed sulfur loss during the oxidation of a phosphothiolate 9 with a peroxy acid<sup>18</sup> and in the formation of elemental sulfur when dipyrido[1,2-*a*:1',2'-*c*]imidazolium-11-thiolate 31 was refluxed with hydrobromic acid.<sup>34</sup> Matturo<sup>35</sup> recently concluded that a similar mechanism must be involved in the extrusion of sulfur from the addition adduct of dimethylthiophene and singlet oxygen. He proposed that the mechanism involved a concatenation of sulfur atoms or sulfur fragments such as S<sub>2</sub> or S<sub>3</sub>. All these examples indicate or suggest that the concatenation of sulfur is the likely mechanism for the formation of elemental sulfur. There is also a strong case for the thiosulfoxide as an intermediate.



<sup>33.</sup> R. K. Howe and J. E. Franz, J. Org. Chem., 39, 962 (1974); R. K. Howe and B. R. Shelton, J. Org. Chem., 46, 771 (1981).

<sup>34.</sup> J. T. Edward and R. H. Sheffler, J. Org. Chem., 50, 4855 (1985).

<sup>35.</sup> M. G. Matturro, R. P. Reynolds, R. V. Kastrup and C. F. Pictroski, J. Am. Chem. Soc., 108, 2775 (1986).

## 1.4 Solvent Dependent Extrusion

In the extrusion of a singlet sulfur atom no charged intermediate should be formed. In the absence of a charged intermediate solvent polarity would not be important in the mechanism and therefore should not have a great effect on the kinetics of extrusion. If the mechanism of extrusion occurs through a charged intermediate, as proposed by Miller and Potts<sup>9</sup> and Gleiter,<sup>32</sup> then a solvent effect should be observed. There have only been a limited number of examples where a solvent effect on the extrusion of sulfur has been observed. The initial example was noted by Twiss<sup>36</sup> on *O*-ethylcarbonyltetra- and trisulfides, (32) and (33). Upon stirring in ethanol the sulfides were found to decompose to the disulfide 34 and elemental sulfur. The conversion of bis(2,4-dinitrophenyl)disulfide (35) to the sulfide 36 has been observed in ethanol.<sup>24</sup> The authors proposed a thiosulfoxide intermediate for the conversion.



Markley and Dunbar<sup>37</sup> noted that aminothiosulfonates 37 decomposed to the aminosulfonates 38 slowly at ambient temperatures and rapidly at high temperatures in polar solvents. A similar conversion has been noted by Harpp<sup>38</sup> in the solvent mediated extrusion of sulfur from sulfenic sulfonic thioanhydrides 39. In polar solvents these compounds extruded one atom of sulfur to form the

ſ

<sup>36.</sup> D. Twiss, J. Am. Chem. Soc., 49, 491 (1927).

<sup>37.</sup> L. D. Markley and J. E. Dunbar, J. Org. Chem., 37, 2512 (1972).

<sup>38.</sup> D. N. Harpp, D. K. Ash and R. A. Smith, J. Org. Chem., 44, 4135 (1979).

corresponding thiosulfonates 40.



Kinetic studies into these and other reactions should provide a clear indication of the mechanism involved in sulfur extrusion. With the sulfenic sulfonic thioanhydrides, extrusion creasover experiments suggested that two molecules were involved in the sulfur extrusion reactions but the results were not clear. Other investigations have given mixed results as to the mechanism of sulfur extrusion. Roth<sup>39</sup> obtained erratic results in attempted rate studies on the thermal extrusion of sulfur from 4-(phenacylthio)-2(1H)-pyrimidinones (R = H, R' = Br) (41) to form 4(3H)-(benzoylmethenyl)-2(1H)-pyrimidinones (42). Thiohydroxylamine-Smonothiocarboxylates 43 are unstable and were slowly converted into Oalkylthiocarbamates 44 and sulfur at room temperature.<sup>40</sup> The mechanism and rate of the extrusion was extensively studied and was found to be a intramolecular decomposition.<sup>41</sup>



39. B. Roth, R. Laube, M. Y. Tidwell and B. S. Rauckman, J. Org. Chem., 45, 3651 (1980).

40. R. Gösl, Angew Chem. Int. Ed. Engl., 1, 268 (1962).

41. A. Holm and G. M. Jensen, Acta Chem. Scand., 25, 339 (1971).

#### 1.5 Diatomic Sulfur S<sub>2</sub>

The diatomic nature of elemental oxygen has been known for many years. Its ground state was long ago confirmed to be the triplet state with one of the excited states being the singlet spin-paired species. Singlet oxygen chemistry is well developed and has been extensively studied.<sup>42</sup> S<sub>2</sub> is isovalent with O<sub>2</sub> and has a similar basic electronic structure. As with oxygen, the ground state is the triplet and the molecule is therefore paramagnetic. The singlet state has been calculated to be 13 kcal above the ground state. The electronic spectra and electronic states have been well reviewed by Barrow;<sup>43</sup> Freeman, Jones and Rogstad<sup>44</sup> measured the rotational Raman spectrum of sulfur dimer; while Rice and Ingallis<sup>45</sup> recorded the absorption spectra.

The S<sub>2</sub> molecule has been produced thermally. The thermal decomposition of carbonyl sulfide<sup>46</sup> between 1550 and 3200 K gives mainly S<sub>2</sub>. When the reaction was studied above 4500 K, the S<sub>2</sub> produced was found to dissociate back into sulfur atoms.<sup>47</sup> S<sub>2</sub> has also been observed to be formed in the reaction of sulfur atoms with thiirane.<sup>48</sup> In the analytical determination of sulfur dioxide the characteristic blue color observed has been attributed to the formation of S<sub>2</sub>. A similar result was obtained when a sample of SO<sub>2</sub> was shock heated.<sup>49</sup> S<sub>2</sub> has also been identified in the products of the low temperature photolysis of disulfur dichloride.<sup>50</sup>

The energy of dissociation of  $S_2$  was determined to be 101 Kcal/mol and the sulfur sulfur bond distance measured at 1.887 Å. The stability of  ${}^{1}S_2$  is expected to be less than that of singlet oxygen. Singlet oxygen is reported to have a half-life ranging from about 2  $\mu$ sec in water to 1000  $\mu$ sec in Freon 11.<sup>50</sup>

The extrusion of diatomic sulfur in an organic reaction was first proposed in

<sup>42.</sup> H. H. Wasserman and R. W. Murray, "Singlet Oxygen," Academic Press, New York, 1989.

<sup>43.</sup> R. F. Barrow and R. P. du Parcq, "Elemental Sulfur," B. Meyer (Ed.), Interscience, New York, 1965.

<sup>44.</sup> P. A. Freeman, W. J. Jones and A. Rogstad, J. Chem. Soc. Faraday Trans. II, 71, 286 (1975).

<sup>45.</sup> F. O. Rice and R. B. Ingalls, J. Am. Chem. Soc., 81, 1856 (1959).

<sup>46.</sup> A. J. Hay and R. L. Belford, J. Chem. Phys., 52, 3545 (1970); H. G. Schecker and H., G. Wagner, Int. J. Chem. Kinetics, 1, 541 (1969).

<sup>47.</sup> T. Higahihara, K. Saito and I. Murakami, Bull. Chem. Soc. Japan, 53, 15 (1980).

<sup>48.</sup> R. B. Klemm and D. D. Davis, Int. J. Chem. Kinetics, 5, 149 (1973).

<sup>49.</sup> B. P. Levitt and D. B. Sheen, J. Chem. Soc., Trans Faraday Soc., 63, 540 (1967).

<sup>50.</sup> B. Meyer and J. J. Smith, UCRL report no. 18060 (1968).

1965 in the photoinduced dimerization of O-ethyl thioacetate (45) to form 2,3diethoxy-2-butene (46).<sup>51</sup> There have been earlier reports where, although  $S_2$  was not indicated, the mechanistic proposals appeared to preclude the formation of sulfur in any other form except diatomic sulfur as detailed below. These mechanistic proposals indicate that  $S_2$  may be an important intermediate in the extrusion of sulfur. In 1928 Staudinger and Freudenberger<sup>52</sup> studied the photolytic decomposition of thioketones to the corresponding ketones and elemental sulfur. They proposed a six-membered ring intermediate 47. The intermediate ring structure could undergo a cyclic reversion forming two molecules of the ketone and diatomic sulfur (which could combine to form elemental sulfur).

Thompson<sup>53</sup> proposed a similar six-membered transition state (49) in the decomposition of dialkoxy disulfides containing an  $\alpha$  hydrogen 48 to the corresponding aldehyde, alcohol and sulfur.



<sup>51.</sup> U. Schmidt, and K. H. Kabitzke, Angew. Chem. Int. Ed. Engl., 3, 641 (1964); U. Schmidt, K. Kabitzke, I. Boie and C. Osterroht, Chem. Ber., 98, 3819 (1965).

~~

<sup>52.</sup> H. Staudinger and H. Freudenberger, Ber., 61, 1576 (1928).

<sup>53.</sup> Q. E. Thompson, M. M. Crutchfield, M. W. Dietrich and E. Pierron, J. Org. Chem., 30, 2692 (1965).

Hansen and Petersen<sup>54</sup> proposed a six-membered transition state in the conversion of the dithiocarbamic acid (50) to N-alkyl-N'-4-pyridylthioureas (51). The formation of  $S_2$  was proposed but no confirmatory evidence was presented.



There are examples where thicketones dimerize with the formation of olefins and elemental sulfur (Scheme 6).52,55



Scheme 6

These extrusions may have resulted from a head-to-head dimerization to form the 1,2-dithietane species which could then lose sulfur as  $S_2$  with concomitant formation of olefin. 1,2-Dithietenes may also dimerize, through a dithioketone intermediate, with the formation of 1,4-dithiins and sulfur in the form of  $S_2$  (Scheme 7).



Scheme 7

- 54. E. T. Hansen and H. J. Petersen, Synth. Commun., 14, 537 (1984).
- 55. (a) W. Manchot and C. Zahn, Ann., 345, 315 (1906);

Ĵ

- (b) S. K. Mitra, J. Indian Chem. Soc., 9, 633 (1932); Chem. Abstr., 27, 3922 (1933).
- (c) H. Staudinger and H. Freudenberger, Ber., 61, 1386 (1928).
- (d) F. Arndt and P. Nachtwey, Ber., 56, 2406 (1923).
- (e) F. Arndt, E. Scholz and P. Nachtwey, Ber., 57, 1903 (1924).

The loss of sulfur has been proposed to occur via a Diels-Alder addition of one molecule of the 1,2-dithietane and a molecule of the 1,2-dithiin.

Davis and Skibo<sup>56</sup> studied the thermal decomposition of N,N'-thiodiamines 52. In the absence of trapping reagents the isolated products were an azobenzene 53, an arylamine and sulfur. The initial step in the decomposition was proposed to be the formation of the arylamine and an N-thiosulfinylaniline via a hydrogen transfer. In the presence of a 1,3-diene, the N-thiosulfinylaniline was successfully trapped as a Diels-Alder adduct. The azobenzene was proposed to result from a head-to-head dimerization of the N-thiosulfinylaniline 54 to form the four-membered ring intermediate 55. This intermediate would lose two atoms of sulfur likely as S<sub>2</sub> to form 53.



Cava studied<sup>57</sup> the photolysis of dithiolone 56, which upon irradiation formed the 1,4-dithiin 57. The authors proposed that loss of carbon monoxide to form acenaphthenedithione (58) was the first step in this transformation. The epimeric 1,2-dithietane 59 can undergo a Diels-Alder reaction with the dithione to give the proposed bridged disulfide 60 which would lose sulfur in the form of S<sub>2</sub>. Once again the formation of S<sub>2</sub> was presented but not confirmed. The reaction reported by Cava has been proposed in the dimerization of other 1,2-dithioketones to form

1. p

<sup>56.</sup> F. A. Davis and E. B. Skibo, J. Org. Chem., 41, 1333 (1976).

<sup>57.</sup> A. Orahovatz, M. I. Levinson, P. J. Carroll, M. V. Lakshmikantham and M. P. Cava, J. Org. Chem., 50, 1550 (1985).

1,2-dithiins.

Ĭ



(58) (59)

(60)

Pastor<sup>58</sup> discovered that treatment of the sterically hindered sulfenyl chloride, 3,5-di-t-butyl-4-hydroxybenzenesulfenyl chloride (61), with an amine resulted in dimerization. The dimerization occurred with the loss of sulfur to form 3,3',5,5'-tetra-t-butyldiphenylquinone (62). Once again the proposed mechanism involved the head-to-head dimerization of a thioketone to form a 1,2-dithietane intermediate, which could eliminate S<sub>2</sub>.



58. S. D. Pastor, J. Org. Chem., 45, 5260 (1984).

The reaction of a dithioamine 63 and alkyl xanthic acid disulfides 64 under basic conditions yielded N,N-disubstituted thionocarbamates  $66.^{59}$  When this reaction was conducted in the absence of base the alkoxythiocarbonyl iminodisulfides 65 were successfully isolated. These disulfides were unstable, and upon standing at room temperature for several days, decomposed to thionocarbamate and sulfur. The authors proposed that this decomposition resulted from a nucleophilic attack by the lone-pair of electrons on nitrogen on the thiocarbonyl carbon concomitant with the elimination of two atoms of sulfur in the form of S<sub>2</sub>.



There are numerous example where  $S_2$  has been shown in the literature but these examples were not trapped or considered as precursors for trapping. We are attempting as part of the work described trying to exploit these opportunities for the trapping of  $S_2$ . There were also several instances where the generation of  $S_2$  was proposed to occur through transition states other than rings. The presence of  $S_2$  was proposed as one of the initial products in the photolysis of triphenylmethanethiol (67),<sup>60</sup> in the reaction between a ketoimine 68 and phenylisothiocyanate (69),<sup>61</sup> and in the reaction of sulfur diimides 70 with 1,2,4-trithiaborolanes 71 to form 1,4dithia-2,6-diaza-3,5-diborinanes (72) and sulfur.<sup>62</sup>

<sup>59.</sup> J. J. D'Amico, F. G. Bollinger and A. B. Sullivan, Int. J. Sulfur Chem., 8, 229 (1973).

<sup>60.</sup> J. K. S. Wan, J. Chem. Soc., Chem. Commum., 429 (1967).

<sup>61.</sup> R. F. Hudson and H. Dj-Forudian, Phosphorus and Sulfur, 4, 9 (1978).

<sup>62.</sup> C. Habben, A. Meller, M. Noltemeyer and G. M. Sheldrick, J. Organomet. Chem., 288, 1 (1985); C. Habben and A. Meller, Z. Naturforsch, 39b, 1022 (1984).



In 1987 Ando<sup>63</sup> reported the synthesis of novel fused cyclopolysulfides 73 and selenapolysulfides 74. He proposed that the photoinduced decomposition of 73 and 74 occurred through a diatomic sulfur intermediate.



## 1.6 Methods of S<sub>2</sub> Formation and Examples of Isolation

Methods for the formation of singlet diatomic sulfur have gained prominence due to the importance of the S<sub>2</sub> unit in many natural products such as the gliotoxins 75.<sup>64</sup> The importance of S<sub>2</sub> in drug synthesis has been reviewed by Steliou.<sup>65</sup> Attempts at forming many possible S<sub>2</sub> precursors were investigated by Smith<sup>66</sup> with no positive results.

and the second

<sup>63.</sup> W. Ando, H. Sonobe and T. Akasaka, Tetrahedron Lett., 28, 6653 (1987).

<sup>64.</sup> A. Taylor, Microbial toxins VII, S. Kadis, A. Ciegler and J. S. Ajl (Ed.), Academic, New York, (1971) p 337-376.

<sup>65.</sup> K. Steliou, Y. Gareau, G. Milot and P. Salama, "Phosphorus, Sulfur and Silica," C. T. Pedersen and J. Becher (Eds.), Gordon and Breach, Science Publishers Inc., England, (1989), pp 209-241.

<sup>66.</sup> D. L. Smith, University Microfilms, Ann Arbour, Michigan 71-11, 451 (1973).



(75)

The first successful trapping of  $S_2$  was reported by Jahn and Schmidt in 1975.<sup>67</sup> They isolated the addition adduct 77 of 1,2-dimethylenecyclohexane 76 and  $S_2$ formed during the photolysis of *O*-ethylthioacetate. The isolated yield of 77 was only 2%. The other isolated products were thiophenes 78 and 79. The addition chemistry of singlet oxygen with a 1,3-diene is well developed and documented;<sup>52</sup> it was believed that similar results would be obtained from singlet sulfur. Evidence for the production of  $S_2$  has been obtained through trapping experiments with 1,3dienes. In the absence of 1,3-dienes,  $S_2$  concatenates to elemental sulfur,  $S_8$ . The successful isolation of 1,2-dithiins confirmed the formation of  $S_2$  as an intermediate in the sulfur loss mechanism. Reactions of "activated" elemental sulfur with dienes have also been studied.<sup>68</sup> These reactions resulted in the formation of several sulfurated products including the 1,2-dithiin. The isolation of other sulfuration products in sulfur extrusion reactions indicated that the sulfur may not only be lost as  $S_2$  but also in other forms of activated sulfur, the structure of which are unknown.



Steliou<sup>69</sup> reported the first synthetically useful diatomic sulfur precursor in 1984. The reaction of triphenylmetal trisulfides 80 with triphenylphosphine

<sup>67.</sup> R. Jahn and U. Schmidt, Chem. Ber., 108, 630 (1978).

<sup>68.</sup> J. A. Elvidge, S. P. Jones and T. L. Peppard, J. Chem. Soc., Perkin Trans I, 1089 (1982); R. Steudel, Top. Curr. Chem., 102, 149 (1982).

<sup>69.</sup> K. Steliou, Y. Gareau and D. N. Harpp, J. Am. Chem. Soc., 106, 799 (1984).

dibromide (81) delivered  $S_2$ , which was successfully trapped as a Diels-Alder adduct. There was no evidence at this time to support whether the  $S_2$  was delivered to the diene from an intermediate such as 82 or if  $S_2$  was formed in solution as a discrete species. One mechanistic proposal involved a thioozonide structure 82 acting as the  $S_2$  source. Such a structure would be similar to the oxygen analogue (formed from the reaction of the phosphine with ozone) which is a known singlet oxygen source.<sup>70</sup> A six-membered transition state 83 was also proposed in the formation of  $S_2$ .



Two diatomic sulfur precursors were reported almost simultaneously in 1987. Schmidt and  $G\ddot{o}rl^{71}$  examined 5,5-dimethyl-1,2-dithia-3,7-diselenacyclopentane (84) as a stable source of S<sub>2</sub>. When heated to reflux in chlorobenzene, diatomic sulfur was successfully trapped as a Diels-Alder adduct along with the formation of 4,4-dimethyl-1,2-diselenacycyclopentane (85).



<sup>70.</sup> P. D. Bartlett and C. M. Lonzetta, J. Am. Chem. Soc., 105, 1984 (1983).

<sup>71.</sup> M. Schmidt and U. Görl, Angew. Chem. Int. Ed. Engl., 26, 887 (1987).

Steliou<sup>72</sup> has reported the most synthetically useful preparation of diatomic sulfur to date. 2,2'-Dibenzoylbiphenyl (86), when heated under sulfurization conditions, formed 2,2'-bis(thiobenzoyl)biphenyl (87) which spontaneously lost  $S_2$  to give (with C-C bond coupling) 9,10-diphenylphenanthracene (88). When the reaction was conducted in the presence of a diene, diatomic sulfur was successfully trapped. The cyclic disulfides were isolated in good yield.



The most recent synthetically useful preparation of  $S_2$  war published by Harpp and MacDonald<sup>73</sup> in 1988. The reaction of dicyclodienylmetal pentasulfides (89) with triphenylphosphine dibromide (81) produced  $S_2$  which was successfully trapped with 1,3-dienes. The intermediate in the formation of  $S_2$  could once again be the thioozonide (82). The yields of the Diels-Alder adducts are summarized below in Table 1.

n #

<sup>72.</sup> K. Steliou, P. Salama, D. Brodeur and Y. Gareau, J. Am. Chem. Soc., 109, 926 (1987).

<sup>73.</sup> D. N. Harpp and J. G. MacDonald, J. Org. Chem., 53, 3812 (1988).



In 1987, Ando<sup>74</sup> published a reported preparation of  $S_2$  from an epidithio intermediate 90 formed in the reaction of 9,10-dihydro-9,10-(1,3-epidithio-2methano-2-*p*-methoxyphenyl-1-oxide)propanoanthracene (91) with perchloric acid. It was not clear whether the Diels-Alder adducts were isolated or detected. The yields were based on isolated by-products making this claim tentative. This procedure had been attempted several years previously but was unsuccessful.<sup>66</sup>

N.

<sup>74.</sup> W. Ando, Y. Kumamoto and N. Tokitoh, Tetrahedron Lett., 28, 4833 (1987).

Bartlett and Ghosh<sup>75</sup> attempted to trap  $S_2$ <sup>in</sup> the conversion of pentathiepins 92 to trithiolanes 93 but were unsuccessful.



Nicolaou<sup>76</sup> reported that the first stable 1,2-dithietane, dithiatropazine (94) will transfer sulfur to suitable acceptors forming the alkene 95. The successful isolation of the species that would result from the trapping of singlet diatomic sulfur was described. He successfully isolated the trapped adduct from 2,3-diphenyl-1,3-butadiene in a 25% yield. The formation of S<sub>2</sub> may not be the sole mechanistic pathway as the tetrasulfide was also isolated, 28%. These reactions were conducted in a tenfold excess of 94.



<sup>75.</sup> P. D. Bartlett and T. Ghosh, J. Org. Chem., 52, 4937 (1987).

<sup>76.</sup> K. C. Nicolaou, C.-K. Hwang, M. E. Duggan and P. J. Carroll, J. Am. Chem. Soc., 109, 3801 (1987).

The presence of diatomic sulfur was observed by Rapoport<sup>77</sup> in the conversion of 3-ethyl-2-methyl-1-monothiomaleimide (96) to the oxygen analogue, 3-ethyl-2-methyl-1-maleimide (97). The proposed six-membered transition state 98 was similar to 47 as proposed by Staudinger and Freudenberger in the air oxidation of thioketones.<sup>63</sup> Proton NMR evidence was obtained to support the formation of trapped diatomic sulfur but yields were too low to be isolated.



In 1986<sup>78</sup> the presence of dinitrogen sulfide (N<sub>2</sub>S) in the thermal decomposition of 1,2,3,4-thiatriazoles to a cyanate, nitrogen and sulfur was confirmed with the use of infrared spectroscopy (Scheme 8).



Scheme 8

The reaction was later studied with photoelectron spectroscopy and  $S_2$  was identified as one of the decomposition products.<sup>79</sup> The  $S_2$  was proposed to result from a dimerization of two dinitrogen sulfide molecules to ultimately give two molecules of nitrogen and one ot  $S_2$  (Scheme 9 and 10).





<sup>77.</sup> J. E. Bishop, S. A. Dagham and H. Rapoport, J. Org Chem., 54, 1876 (1989).

ſ

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

<sup>78.</sup> C. Wentrup, S. Fischer, A. Maquestiau and R. Flammang, J. Org. Chem., 51, 1908 (1986).


Scheme 10

More recently Constabel and Towers<sup>80</sup> have proposed that singlet sulfur was the toxic product of Thiarubine A (99), a 1,2-dithiin, although there is no evidence for this claim. The results showed that light enhanced conversion of 99 to the thiophene 100 caused toxic effects that were greater than those resulting from Thiarubine A or thiophene alone. This proposal was based on the fact the singlet oxygen had been shown to be the toxic species generated from peroxides.<sup>81</sup>



26

<sup>80.</sup> C. P. Constabel and G. H. N. Towers, Planta Medica, 55, 35 (1989).

<sup>81.</sup> C. S. Foote, Acc. Chem. Res., 1, 104 (1968); T. Matsuura, Tetrahedron, 33, 2869 (1977); A. Naqui, B. Chance, and E Cadenas, Ann. Rev. Biochem., 55, 137 (1986).

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

1

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 all the synthetically useful preparations, 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. This work will consider several compounds of this type as viable  $S_2$ precursors.

# **CHAPTER 2**

#### **DIATOMIC SULFUR** $(S_2)$

#### 2.1 Introduction

- 15 Ba

The generation of  $S_2$  provides a logical one-step synthetic procedure for the preparation of cyclic disulfides *via* Diels-Alder additions to 1,3-dienes. Myrcene disulfide (101) was successfully synthesized from myrcene (102),<sup>82</sup> by Steliou<sup>72</sup> and Schmidt and Görl.<sup>71</sup>



Steliou has used  $S_2$  methodology to prepare a series of substituted 1,2-dithiins derivatives 103 and 104, several of which exhibited anti-viral and anti-HIV activity.<sup>65</sup>



82. J. A. Elvidge, S. P. Jones and T. L. Peppard, J. Chem. Soc. Perkin Trans. I, 1089, (1982).

The most difficult step in the synthesis of bridged bicyclic disulfides like gliotoxin (75) was the formation of the S-S bond.<sup>83</sup> Diatomic sulfur methodology may offer an accessible synthetic route for this class of compounds. Attempts to prepare egosterol endodisulfide (105) from ergosterol (106) (a 1,3-diene) using known S<sub>2</sub> methodology were attempted but were unsuccessful.<sup>84</sup>







The four known synthetic procedures<sup>69,71-73</sup> for the generation of  $S_2$  described in Chapter 1 all have experimental limitations which must be considered. These limitations make the widespread application of these methodologies difficult.

Schmidt and Görl<sup>71</sup> synthesized 5,5-dimethyl-1,2-dithia-3,7-diselena-

-

<sup>83.</sup> Y. Kishi, T. Fukayama and S. Nakatsuka, J. Am. Chem. Soc., 95, 6490, 6492 (1973).

<sup>84.</sup> Y. S. Tsantrizos, P. L. Folkins, J. F. Britten, D. N. Harpp and K. K. Ogilvie, Unpublished results.

cyclopentane (84). This compound, although stable was difficult to prepare and isolate, as the synthesis required high dilution conditions. The high temperature at which the formation of  $S_2$  was maximized (140°C) may be destructive to some substrates.

The major limitation of the two procedures<sup>69,71</sup> which require the use of triphenylphosphine dibromide (81) is this reagent. Compound 81 is light and moisture sensitive and reactive towards a wide variety of functionalities. The triarylmetal trisulfides (82)<sup>69</sup> are also difficult to prepare.

The procedure of Steliou,<sup>72</sup> which gives the highest yield of cyclic disulfides, must be conducted in the absence of most functionalities. The procedure used to produce the  $S_2$  uses an excellent method for the conversion of ketones to thioketones.<sup>85</sup> The major sulfurating reagent, hexamethyldisilathiazine has a vile odor and readily reacts with moisture to produce hydrogen sulfide. Boron trichloride is a strong Lewis acid and readily conjugates with oxygen or other donor atoms to hamper  $S_2$  formation.

Confirmation for the generation of  $S_2$  was the successful isolation of cyclic disulfides in the presence of 1,3-dienes. There was not, however, a standard procedure for the calculation of "percent yield" in the four methodologies reported. Steliou was interested in the development of a method for the preparation of cyclic disulfides and his experiments were performed using an excess of  $S_2$  precursor.<sup>86</sup> Yields were based on the amount of diene in the reaction mixture, in this way high yields of disulfides were obtained. The trapping experiments of Harpp and MacDonald<sup>73</sup> and Schmidt and Görl<sup>71</sup> used the diatomic sulfur precursor as the limit ng reagent. Harpp and MacDonald<sup>73</sup> used an excess of diene while Schmidt and Görl<sup>71</sup> used either an excess or equimolar amount of diene. Ando<sup>74</sup> also reported the trapping of  $S_2$  but the results obtained were inconclusive because the yields were based on isolated side products and not the isolated disulfides.

There are four reaction systems reported which successfully generated singlet diatomic sulfur  $(S_2)$  in synthetically useful yields.<sup>69,71-73</sup> The formation of  $S_2$  as a intermediate has also been proposed in a number of systems (see introduction) but, such an intermediate was only confirmed in two instances. In the thermal

. .

<sup>85.</sup> K. Steliou and M. Mrani, J. Am. Chem. Soc., 104, 3104 (1982).

<sup>86.</sup> K. Steliou, University of Montreal, private communication.

decomposition of 5-substituted-1,2,3,4-thiatriazoles,<sup>77,78</sup> the presence of  $S_2$  was confirmed by photoelectron spectroscopy, and in the conversion of 3-ethyl-2-methyl-1-monothiomaleimide (96) to 3-ethyl-2-methylmaleimide (97),<sup>79</sup> the  $S_2$  was successfully trapped as a Diels-Alder adduct.

Ż

Tan I

The central theme of this work is the identification of  $S_2$  as an intermediate in the extrusion of sulfur. In this respect several systems which resulted in the formation of elemental sulfur were examined for the formation of  $S_2$ . Other systems which could be induced to eliminate diatomic sulfur under appropriate conditions were synthesized and studied. The successful identification of  $S_2$  was realized when signals in the <sup>1</sup>H NMR spectrum corresponding to cyclic disulfides 1,2-dithia-4,5dimethyl-4-cyclohexene (107) or 1,2-dithia-4,5-diphenyl-4-cyclohexene (108) were observed when the reaction was conducted in the presence of 2,3-dimethyl-1,3butadiene (109) or 2,3-diphenyl-1,3-butadiene (110) respectively. Once  $S_2$  was identified the reaction conditions were modified so that the yield of cyclic disulfide was maximized. It was hoped that the reaction could then be considered as a viable source of  $S_2$  to be added to the list of those already known.



There are many systems for which it is possible to visualize a sulfur-sulfur bond being lost as an  $S_2$  unit. Of the many known examples of sulfur extrusion<sup>3</sup> in a

chemical process (Chapter 1) it is reasonable to assume that a few of these extrusions could proceed through an  $S_2$  intermediate.

Reported below are those systems which were only considered as possible sources of  $S_2$ . Those systems which were further investigated as to the chemistry and mechanism of the extrusion are included separately in later Chapters.

## 2.2 Experiments Towards the Identification of Diatomic Sulfur Precursors

## 2.2.1 Sulfur Transfer Reagents

"Sulfur Transfer Reagents" are mild reagents for the transfer of one or two atoms of sulfur to suitable substrates. The transfer of two atoms of sulfur could conceivably under the correct conditions be in the form of  $S_2$ . There were several examples where these reagents did not give the desired product but, instead, elemental sulfur was isolated along with an unexpected product. Two of these examples were investigated to determine if  $S_2$  was an intermediate in the formation of the elemental sulfur.

One such example was the reaction of N,N'-dithiobisbenzimidazole<sup>87</sup> (111) with 1,2-diphenylhydroazobenzene (112) in benzene which yielded a mixture of azobenzene (113), benzimidazole (114) and elemental sulfur (Scheme 11).



Scheme 11

The mechanism of sulfur formation was originally thought to be the transfer of two sulfur atoms to form a four-membered ring intermediate (115). This species could conceivably lose  $S_2$  via a 2,2-cycloreversion to form azobenzene 113. A similar intermediate was proposed in the sulfur extrusion which resulted from the

87. D. N. Harpp, K. Steliou and T. H. Chan, J. Am. Chem. Soc., 100, 1222 (1978).

photolysis of N, N'-thiodiamines (52).<sup>56</sup>

NAME.

ſ



Attempts at trapping the proposed  $S_2$  intermediate from the reaction of 111 and 112 using 2,3-dimethyl-1,3-butadiene (109) were unsuccessful. The trapping experiments were conducted initially in dichloromethane. A <sup>1</sup>H NMR spectra of the reaction mixture did not exhibit signals which corresponded to the trapped adduct of  $S_2$ . Filtration to remove the benzimidazole 114 gave a solution which was chromatographed on silica gel to yield sulfur and azobenzene 113. No trapped Diels-Alder adduct was detected on TLC or in the <sup>1</sup>H NMR spectra.

Changing to less polar solvents (benzene or carbon tetrachloride) had no effect on the isolated products. The trapping experiment was also conducted in dichloromethane- $d_2$  but once again no trapped adduct was isolated or identified.

The absence of successful  $S_2$  trapping indicates that the reaction may not proceed as proposed. The mechanism for the sulfur formation may not involve an  $S_2$  intermediate but a step-wise process. Such a mechanism is a feasible process for sulfur transfer reagents, as the less reactive transfer reagent N,N'-thiobisphthalimide (116), on reaction with thiol, can be halted after the addition of one equivalent the thiol to give mixed disulfide 117.<sup>88</sup>



The reaction of N,N'-dithiobisbenzimidazole<sup>87</sup> (111) with 2mercaptobenzathiazole (118) did not yield the expected tetrasulfide 119 but instead, disulfide 120 and elemental sulfur were isolated. It was again anticipated that the transfer of two sulfur atoms to form the tetrasulfide 119 as the intermediate. Tetrasulfide 119 could then decompose to yield disulfide 120 and sulfur.

<sup>88.</sup> D. N. Harpp and T. G. Back, Tetrahedron Lett., 5313 (1972).



(118) (119) (120)

Once again no evidence for the formation of  $S_2$  was obtained from trapping experiments. The reaction was attempted in several solvents (benzene, carbon tetrachloride and dichloromethane-d<sub>2</sub>) all of which gave negative results.

The lack of trapping in the above example indicated that the sulfur was not lost as an  $S_2$  intermediate. The loss more likely followed a step-wise process involving a thiosulfoxide intermediate. Such an intermediate has been used to account for the conversion of polysulfide to disulfides and monosulfides<sup>24-27</sup> (for a review of the thiosulfoxide structure see Chapter 1). Decomposition would first give the trisulfide 121 and then the disulfide 120 which is stable (Scheme 12).



Scheme 12

#### 2.2.2 Thermal Decomposition of Dialkoxydisulfides

Dialkoxydisulfides have been of interest in our laboratory for several years. It is ambiguous whether the structure is the "linear" or the branched sulfur species. Evidence for the branched species was obtained when disulfur difluoride  $(S_2F_2)$  was conclusively shown to exist as both the linear and the bridged isomers.<sup>89</sup> Harpp and Steliou<sup>90</sup> isolated the branch-bonded alkoxy disulfide O,O-bicyclohexyl-1,1'-diyl thiosulfite (122), from the reaction of 1,1'-dihydroxybicyclohexane (123) and N,N-thiobisbenzimidazole. It was expected that non-cyclic dialkoxydisulfides may exhibit a similar structure. The X-ray crystal structure of 4-nitrobenzyloxydisulfide (124a) has been determined and found to exhibit the linear OSSO structure.<sup>91</sup>

in the second

Ę



Thompson<sup>74</sup> proposed that primary dialkoxydisulfides decomposed with the transfer of a hydrogen atom to form the alcohol, aldehyde and sulfur (Scheme 13). From the proposed mechanism, the sulfur could only be formed as  $S_2$ .



Scheine 15

Thermal experiments on 4-nitrobenzyloxydisulfide<sup>92</sup> (124a), performed by heating a solid sample to the desired temperature, showed that this compound decomposed between 120°C and 150°C to form 4-nitrobenzylalcohol (125) and 4nitrobenzaldehyde (126). The presence of sulfur was confirmed by TLC. The <sup>1</sup>H NMR spectra for the decomposition of 124a are shown below in Figure 1 and clearly display the formation of 125 and 126. The lack of formation of other products indicate that the decomposition likely proceeds through the mechanism involving the formation of S<sub>2</sub>.

90. D. N. Harpp, K. Steliou and C. J. Cheer, J. Chem. Soc., Chem. Commun., 825 (1980).

<sup>89.</sup> R. L. Kuczkowski, J. Am. Chem. Soc., 86, 3617 (1964).

<sup>91.</sup> D. N. Harpp and S. Tardif, unpublished results.

<sup>92.</sup> The initial sample of 124a was obtained from S. Tardif.

Figure 1. <sup>1</sup>H NMR Spectra for the Thermal Decomposition of 4-Nitrobenzyloxydisulfide (124a). Z = 4-nitrobenzylalcohol (125); X = 4nitrobenzaldehyde (126).

۰,

۰<u>،</u>

**\*\* \*\*** 





When the decomposition was conducted in refluxing toluene the isolated compounds after chromatography were sulfur (89%), 125 (79%) and 126 (92%). The components were identified by comparison of the <sup>1</sup>H NMR spectra with those for the authentic compounds.

The decomposition of 124a appeared to proceed by the concerted mechanism proposed by Thompson.<sup>74</sup> The formation of  $S_2$  was therefore a distinct mechanistic possibility as the intermediate in the formation of elemental sulfur. In attempts to isolate the sulfur formed as  $S_2$ , the decomposition of 124a was repeated in the presence of 1,3-dienes. The results of these experiments are described below.

A sample of disulfide 124a and 2,3-diphenyl-1,3-butadiene 110 was fused at  $155^{\circ}$ C for 10 min. A <sup>1</sup>H NMR spectra of the fused mixture indicated signals which corresponded to addition adduct, 1,2-dithia-4,5-diphenyl-4-cyclohexene (108). Chromatography on silica gel resulted in the isolation of the addition adduct but in a yield of only 11%.

A sample of disulfide 124a was decomposed by refluxing in toluene in the presence of either 109 or 110. Reaction o<sup>f</sup> disulfide 124a in the presence of 2,3-dimethyl-1,3-butadiene 109 gave the trapped adduct 107 in a isolated yield of 17%.

The low yields were thought to result from the high temperature required for the decomposition. Careful decomposition studies showed that the decomposition of the 4-nitro derivative **124a** began on heating to 135°C. In order to find an alkoxy disulfide that was stable but decomposed at a lower temperature several other substituted benzyloxydisulfides were prepared. The melting points and temperature of decomposition for each alkoxydisulfide are summarized in Table 2. The temperature at which the thermal decomposition of the 4-methyl derivative **124d** occurred was not determined as the product was a liquid at room temperature making purification difficult.

ري<del>د</del>. بريد

-



Table 2.4-Substituted Dialkoxydisulfides (124):Melting Points and Decomposition Temperature.						
Compound	Substituent	Melting Point (°C)	Decomposition Temp. (°C)			
1 <b>24</b> a	NO <sub>2</sub>	93-95	135			
1 <b>24b</b>	Н	52-55	135-140			
1 <b>24c</b>	Cl	44-48	135-140			
124d	CH <sub>3</sub>	liquid				
124e	*CH30	34-36	115			
* Decomposes at -15°C after only 7 days						

Decomposes at -15 C after only 7 days.

The lower temperature at which the 4-methoxy derivative 124e was observed to decompose made it attractive as a possible  $S_2$  source. It was anticipated that since the 4-methoxy derivative decomposed at lower temperature, it might allow for a higher yield of the trapped adduct. The disulfide 124e and the diene 107 were refluxed in toluene with the reaction monitored by TLC. The decomposition was complete after 3 h. Chromatography gave a trace amount of sulfur and the cyclic disulfide 107 and the cyclic tetrasulfide 127 each in a yield of 21%.



Decomposition of 124e was repeated in the presence of the diene 110. Column

chromatography gave two isolated fractions which were identified each as mixtures of two components. The first fraction consisted of unreacted diene and the tetrasulfide while the second was identified as disulfide 108 and a fourth product which was thought to have the structure 128. The mixture was purified by TLC to yield the disulfide, tetrasulfide and what was proposed to be 128. The assignment of 128 was based on the fact that the <sup>1</sup>H NMR contained a singlet at 4.1 ppm and gave a electron-impact mass spectrum with a cluster near m/z = 470. The assignments are detailed in Chapter 6.



(128)

## 2.2.3 <u>4-Methoxycarbonylsulfenic Sulfonic Thioanhydrides</u>

In the structure of sulfenic sulfonic thioanhydrides there are two adjacent nonoxidized sulfur atoms (see Chapter 3). To take advantage of this interesting structure a modification of **39** was prepared.<sup>38</sup> The sulfenic tolyl substituent was replaced with methoxycarbonyl group, which in the presence of sodium methoxide might allow for the formation of sulfur as S<sub>2</sub> (see below). Several derivatives of **129** were synthesized by the condensation of methoxycarbonyl sulfenyl chloride<sup>93</sup> with the corresponding potassium thiosulfonate in a non-polar solvent. The preparation is analogous to that used for thioanhydride **40**.<sup>38</sup>

$$R = CH_{3}C_{6}H_{4}$$

$$R = CH_{3}C_{6}H_{4}$$

$$129b R = ClC_{6}H_{4}$$

$$129c R = CH_{3}$$

The 4-tolyl derivative 129a gave the cleanest preparation and it was therefore used for further study. This compound exhibited an interesting chemistry and the results are presented below.

In the presence of methoxide anion, thioanhydride 129a decomposed in

a la

<sup>93.</sup> A. Granata, "The Chemistry of Sulfenylthiocarbonates," Ph.D. Thesis, McGill University, (1977).

methanol to form dimethyl carbonate (130) (confirmed by GC), sodium 4tolylsulfonate (131) and sulfur (both of which were isolated). The identities of the isolated products were confirmed by comparison to the authentic compounds and the mass spectra. Sulfur was isolated almost quantitatively based on the formation of two atoms of sulfur per molecule of thioanhydride 129a, (92%). The only mechanism for the sulfur formation that appeared feasible was through a nucleophilic attack of the methoxide anion on the carbonyl carbon resulting in the generation of the sulfur as  $S_2$  (Scheme 14).



The reaction of 129a with sodium methoxide was repeated in benzene in the presence of 2,3-dimethyl-1,3-butadiene 109. The solvent was changed because methanol is not known to enhance pericyclic reactions and may cause conversion of the  $S_2$  to the triplet state as has been observed for singlet oxygen.<sup>42</sup> No trapped adduct 107 was isolated in this reaction although the formation of dimethylcarbonate 130 was once again confirmed (GC). The reaction was followed using <sup>1</sup>H NMR spectroscopy and no signals were observed which corresponded to the trapped Diels-Alder adduct.

The lack of successful trapping indicates that the decomposition likely does not proceed through  $S_2$  but instead follows a step-wise mechanism to form an intermediate which could eliminate a stable sulfur species ( $S_6$ ,  $S_7$ , or  $S_8$ ). The mechanism would be similar to that proposed for the sulfur loss from sulfenic sulfonic thioanhydrides (see Chapter 3). Such a mechanism is displayed below (Scheme 15) and would initially involve the nucleophilic attack of the methoxide anion to form carbonate 130 and the sulfur anion 132. The sulfur anion could react in a similar fashion with another molecule of 129a and eliminate the sulfonate and give the tetrasulfide. The tetrasulfide could then react with another methoxide anion and repeat the cycle. The reaction would continue until the sulfur chain was 6 or 8 sulfurs long when cyclization and formation of S<sub>6</sub> or S<sub>8</sub> could occur. The mechanism would be more favored as S<sub>2</sub> formation is highly endothermic whereas the formation of elemental sulfur as S<sub>6</sub> or S<sub>8</sub> is an exothermic process.<sup>10</sup> The stepwise mechanism for the sulfur loss is supported by the work of Miller and Potts,<sup>9</sup> Glieter<sup>32</sup> and by the work of Davis<sup>22</sup> on acidifed solutions of thiosulfonates.



Scheme 15

Í

Ash<sup>94</sup> had observed that the reaction of sulfenyl chlorides with potassium thiosulfonates could produce either the thioanhydride or the thiosulfonate by loss of a sulfur atom depending on the substitutents. Mass spectral analysis of 129a gave signals corresponding to both the thioanhydride and the thiosulfonate. From the NMR spectra it was impossible to confirm that the thioanhydride was indeed formed. The formation of 129a was confirmed from the correct elemental analysis and it was shown to consist of only one component from the <sup>13</sup>C NMR spectrum.

The mass spectral fragmentation scheme for 129a is presented below in Figure 2. The signal at m/z = 278 corresponded to the molecular ion. The signal observed at m/z = 246 could correspond to the thiosulfonate but elemental analysis and NMR spectroscopy indicated that the original sample of 129a was pure. The signal was therefore assigned to the loss of a sulfur atom from 129a in the mass spectrometer. A similar extrusion was observed by Ash<sup>94</sup> in mass spectral studies of 4-tolylsulfenic 4-tolylsulfonic thioanhydride.

All of the remaining mass peaks can be accounted for by direct fragmentation of 129a, except for the signal at m/z = 214. The signal at m/z = 214 resulted from the loss of 64 mass units from the molecular ion, which may correspond to either the loss of SO<sub>2</sub> or two sulfur atoms. Direct loss of SO<sub>2</sub> or the two sulfur atoms while retaining the structural integrity of the molecule was unlikely. A rearrangement of the molecule with the formation of S<sub>2</sub> seemed more likely. The loss of S<sub>2</sub> in the mass spectrometer is a known process.<sup>95</sup>

**^**41

<sup>94.</sup> D. K. Ash, "The Chemistry of Organic Trisulfide and Related Derivatives," Ph.D. Thesis, McGill University, (1973).

<sup>95.</sup> A. Müller and W. Jaegermann, Inorganic Chem., 18, 2631 (1979).

Figure 2. Mass Spectral Fragmentation Pattern for Methoxycarbonylsulfenyl 4tolylsulfonylthioanhydride (129a).

A

.









m/z = 246



# 2.2.4 3.5-Di-t-butyl-4-hydroxybenzenesulfenyl chloride (61) Reaction With Amines

Pastor<sup>58</sup> found that the chlorination of 3,3',5,5'-tetra-t-butyl-4,4'dihydroxyphenyldisulfide (133) provided the sterically hindered sulfenyl chloride, 3,5-di-t-butyl-4-hydroxybenzenesulfenyl chloride (61). Treatment of (61) with an amine resulted in a dimerization, with loss of sulfur to yield 3,3',5,5'-tetra-tbutyldiphenylquinone (62) (Scheme 16).



Scheme 16

Pastor<sup>58</sup> proposed that 61, in the presence of the amine, lost a molecule of HCl to form the monothioquinone (134) which would dimerize via a free-radical mechanism in a head to head fashion to form an intermediate 1,2-dithietane (135). The intermediate was then proposed to lose sulfur, presumably as  $S_2$  (Scheme 17).





1.3

The reaction described above appeared to be an excellent possibility for the formation of  $S_2$ . The proposed mechanism was similar to the one described by Steliou for the production of  $S_2$  from biphenyl 86.<sup>72</sup> The reaction of 61 with triethylamine was repeated in the presence of 2,3-dimethyl-1,3-butadiene 109. To limit the addition of the sulfur-chlorine bond to the diene, the amine and the diene were added simultaneously. The reaction was stirred in the dark at room temperature for 48 h and a <sup>1</sup>H NMR spectrum of the reaction mixture was then acquired. The spectra exhibited signals that were consistent with the trapping of  $S_2$  (the formation of 107) but the yield was low and the disulfide could not be isolated from the reaction mixture. There were signals in the <sup>1</sup>H NMR spectra which corresponded to the formation of the 1,2-addition product by the addition of the S-Cl bond to one of the double bonds.

## 2.2.5 Reaction of Xanthic Acid Disulfides with Amino Disulfides

5

į

It was observed that the reaction of xanthic acid disulfides 63 with amino disulfides 64 in the presence a basic catalyst gave compound 65 (Scheme 18).<sup>59</sup> In the absence of the catalyst, the amino xanthic disulfide 66 could be isolated. This compound was found to decompose to 65 after standing for a few days. The authors proposed that the sulfur was lost as  $S_2$ .



Scheme 18

The above reaction was repeated at 50°C in the presence of diene 109. The reaction was also prepared in the absence of diene to monitor the progress of the

reaction. The two reactions were monitored simultaneously by <sup>1</sup>H NMR spectroscopy. After 5 days, the spectra showed that the formation of a new compound was complete which was identified as 65 from the spectra data. The reaction containing diene 109 gave no signals which would correspond to trapping of diatomic sulfur. The sulfur must therefore be formed through a mechanism that does not involve the formation of diatomic sulfur. The decomposition was not further studied.

## 2.2.6 <u>Conversion of Tetramethylthiuram Disulfide to N.N-Dimethycarbamoyl</u> <u>Chloride</u>

Cava<sup>96</sup> found that the reaction between tetramethylthiuram disulfide (136) and sulfuryl chloride resulted in the formation of N,N-dimethycarbamoyl chloride (137) and chlorine. Since the decomposition involved two sulfur atoms it was thought that the sulfur could be lost as S<sub>2</sub> as indicated below (Scheme 19). Attempts to trap the sulfur formed as S<sub>2</sub> using diene 109 were unsuccessful. A <sup>1</sup>H NMR spectrum of the reaction mixture acquired at three separate steps throughout the reaction gave no signals corresponding to trapped adduct.



2.2.7 <u>Attempted Isolation of Diatomic Sulfur From the Thermolysis of 2-Methyl-2-</u> propyltetrasulfide

The decomposition of 2-methyl-2-propyltrisulfide and tetrasulfide 138 and 139 were investigated in our laboratory. The decomposition was shown to form 2-methyl-2-propanethiol, the sulfide with 1-5 sulfurs, and presumably isobutylene.<sup>97</sup> The decomposition was thought to proceed through a free radical mechanism. The formation of the thiol would result from the abstraction of a proton by the sulfur

96. K.-Y. Jen and M. P. Cava, J. Org. Chem., 48, 1449 (1983).

97. D. N. Harpp and R. Jackman, unpublished results.

46

radical and form sulfur as  $S_2$  (Scheme 20). To test this hypothesis sulfide 139 was heated with diene 109 at 70°C and 140°C for 48 h and the mixture analyzed by <sup>1</sup>H NMR spectroscopy. The spectra displayed no signals which could correspond to the trap of diatomic sulfur. The  $S_2$  may not be formed as a singlet but instead may be in the triplet form.



## 2.3 Structure of the Addition Adducts.

1

\*

The diatomic sulfur trapping experiments gave two different trapped adducts which were originally identified as the monomeric product, 1,2-dithia-4,5-dimethyl-4-cyclohexene 107 and a polymeric form with an unknown structure but was proposed to be 140.<sup>73</sup> There were difficulties in separating the trapped sulfur derivatives 107 and 140 thus a more detailed study of the two compounds were undertaken.



The <sup>1</sup>H NMR chemical shifts of the monomer was the basis for the identification of the successful generation of singlet diatomic sulfur.<sup>69,71-4,77</sup> As with the <sup>1</sup>H NMR spectra, the <sup>13</sup>C NMR spectra of the disulfide and "polymer" also

differed; the NMR chemical shifts are summarized below in Table 3. From the NMR and mass spectral data the polymer was tentatively identified as the cyclic tetrasulfide, 1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene (127). Nicolaou<sup>76</sup> reported the formation of cyclic di and tetrasulfides with identical structures as those below from the thermal decomposition of dithiatropazine (94) in the presence of diene 108.

с. A



Table 3. <sup>1</sup> H and <sup>13</sup> C NMR Chemical Shifts of the Trapped Adducts of ${}^{1}S_{2}$						
Compound	<sup>1</sup> H NMR shifts		<sup>13</sup> C NMR shifts		· • • • • • • • • • • • • • • • • • • •	
	CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>3</sub>	CH <sub>2</sub>	C (ene)	
Disulfide (107)	1.75	3.20	20.80	34.15	125.13	
Tetrasulfide (127)	1.79	3.64	18.13	42.78	130.29	

Harpp and Macdonald<sup>73</sup> demonstrated that 1,2-dithiane 141 in the presence of bis( $\gamma$ -cyclopentadienyl)titanium dichloride (142) decomposed; less than one-half survived at room temperature after 48 h. The major component of the decomposition mixture was a compound which gave <sup>1</sup>H NMR signals similar to those of a polymer. It was assumed that the electrophilic reagent 142 caused a dimerization of the 1,2-dithietane to a polymerized form. The lack of successful trapping in some reactions was thought to be a result of the disulfide 107 decomposing under the reaction conditions. To test this hypothesis samples of 107 were treated under a variety of conditions.



48

The disulfide 107 was unchanged after 48 h when heated to  $60^{\circ}$ C in the dark, with acetic acid in the dark at ambient temperature, and in ambient light at room temperature. A small amount of decomposition was observed from the <sup>1</sup>H NMR spectra when the disulfide was treated with sodium methoxide at  $60^{\circ}$ C in the dark and when heated to  $60^{\circ}$ C in ambient light. The sample heated in ambient light showed signals in the aromatic region of the <sup>1</sup>H NMR spectra, these signals likely corresponded to the formation of thiophene.

1

Ţ

The electron impact mass spectrum of 127 is discussed below and the fragmentation pattern displayed in Figure 3. The signal at m/z = 210 corresponds to the molecular ion. The molecule fragmented with the loss of two sulfur atoms to give a signal at m/z = 146. Further loss of two more sulfur atoms gave the signal at m/z = 82 which corresponds to the mass of the starting diene. <sup>1</sup>H NMR confirmed that no disulfide or diene were present in the original sample analyzed by mass spectroscopy.

The tetrasulfide 127 was desulfurized by the addition of triphenylphosphine (143). The initial spectrum shows that the sample consists almost entirely of tetrasulfide (indicated by t) with a small amount of disulfide impurity (indicated by t). The addition of one equivalent of 143 resulted in a mixture consisting of roughly one-half tetrasulfide and one-half disulfide as determined by <sup>1</sup>H NMR. The addition of two equivalents of phosphine yielded a mixture consisting of triphenylphosphine sulfide (144) and 107. There was no evidence for the formation of the corresponding trisulfide 145 by the removal of one sulfur atom from the tetrasulfide. In our laboratory we have previously had difficulty in the synthesis of seven-membered ring cyclic trisulfides.<sup>98</sup> The trisulfide 145 must form but its desulfurization to the disulfide 107 must be favored over that of the tetrasulfide 127. The <sup>1</sup>H NMR spectra for the desulfurizations are shown in Figure 4. In the presence of excess phosphine 143 no further desulfurization occurred (Scheme 21).

<sup>98.</sup> D. N. Harpp, R. A. Smith and K. Steliou, J. Org. Chem., 46, 2072 (1981).



**"**"

15<sup>44</sup>164

Scheme 21

Figure 3. Mass Spectral Fragmentation Pattern for 1,2,3,4-Tetrathia-6,7-dimethyl-6-cyclooctene (127).

-

\*



51

Figure 4. <sup>1</sup>H NMR Spectra for the Desulfurization of 1,2,3,4-Tetrathia-6,7dimethyl-6-cyclooctene (127) by Triphenylphosphine (143). t = Tetrasulfide 127; d = disulfide 107

۰<u>ـ</u>



52

# CHAPTER 3

## ATTEMPTS TO ELUCIDATE THE MECHANISM OF SULFUR EXTRUSION FROM 4-TOLYLSULFENIC-4-TOLYLSULFONIC THIOANHYDRIDE

#### 3.1 Introduction

ź

The chemistry of 4-tolylsulfenic-4-tolylsulfonic thioanhydride (146) is unique. This compound extruded one atom of sulfur when dissolved in polar solvents forming the corresponding 4-tolylthiosulfonate (147) (Scheme 22).<sup>38</sup> The extrusion was observed in methanol, ethanol, 2-propanol, glacial acetic acid, 1:1 acetonewater, acetonitrile (wet) and dimethylformamide (wet and dry). When 146 was dissolved in non-polar solvents no extrusion was observed.



Scheme 22

Initial experiments on this system showed that crossover may have occurred between different molecules during the extrusion which indicated an intermolecular reaction. Labelling experiments showed that the central sulfur atom was extruded. These observations led to a mechanistic proposal involving a thiosulfene intermediate 148. However such a species is unlikely as work on other systems has shown that several mechanisms contribute to observed sulfur extrusion.<sup>3</sup>



(148)

## 3.2 Mechanistic Proposals

From the earlier experimental results<sup>38</sup> and the known examples of sulfur extrusion,<sup>3</sup> two possible mechanisms for the observed extrusion can be proposed. The first mechanism, proposal 1, is shown below (Scheme 23). The initial step involves a nucleophilic attack by the central sulfur of a molecule of 146 on a central sulfur atom of a second molecule of 146, with concomitant cleavage of the sulfur-sulfur bond to form charged intermediates. Such intermediates would be stabilized by polar solvents. The formation of 147 would then result from an attack of the sulfornate anion as shown in Scheme 23. This results in the formation of a bridged sulfur species such as 149, which has a thiosulfoxide like structure. Intermediate 149 could then further react in a similar fashion until the sulfur chain that is formed allows the sulfur to be extruded as a stable species. The sulfur lost may be in the form of S<sub>2</sub> or stable sulfur rings (S<sub>6</sub>, S<sub>7</sub> or S<sub>8</sub>). Attempts to trap S<sub>2</sub> in the extrusion were unsuccessful and have been discussed (see below).



#### Scheme 23

The above mechanism is supported by the fact that a neutral sulfur atom undergo nucleor, hilic reactions; for example sulfides react with methyl iodide to

54

form the corresponding methyl sulfonium salts (150) (Scheme 24).99





Another example of a nucleophilic reaction of a neutral sulfur atom is the equilibrium between two molecules of sulfenyl halide and the dimeric halonium ion (151) (Scheme 25).<sup>100</sup> Convincing <sup>1</sup>H NMR evidence for the formation of 151 was offered. The forward reaction would result from the nucleophilic attack of one molecule of the sulfenyl halide on the sulfur of the second sulfenyl halide.



Scheme 25

The initial nucleophilic sulfur attack in the proposed mechanism would be it rate determining. Rate studies on the extrusion of sulfur from 146 would allow for an evaluation of the mechanistic proposal. A kinetic study may also give insight into the mechanism by which the sulfur is formed. It may also give information by which the mechanism can be extended to other solvent assisted extrusions.

The initial step in the second mechanistic possibility, proposal 2, involves the cleavage of the S-S bond in 146 to form the thiosulfonate ion and the sulfenium ion

3

<sup>99.</sup> A. Cahours, Compt. rend., 76, 133 (1873)

<sup>100. (</sup>a) G. Capozzi, V. Lucchini and G. Modena, Chem. Ind. (Milan), 54, 41 (1972); (b) G. Capozzi, V. Lucchini, G. Modena and F. Rivetti, J. Chem. Soc., Perkin Trans. II, 361 (1975): (c) G. Capozzi, V. Lucchini, G. Modena and F. Rivetti, J. Chem. Soc., Perkin Trans. II, 900 (1975); (d) G. Capozzi, O. DeLucchi, V. Lucchini and G. Modena, Synthesis, 677 (1976).

(Scheme 26, step 1).<sup>101</sup> The sulfenium ion would be solvated while the thiosulfonate ion undergoes further reactions. The formation of both ions would be stabilized by polar solvents. In non-polar solvents no stabilization of sulfenium ion would occur and the reaction would not be favored. The initial cleavage of the S-S bond would be the slowest step.

۰. <sup>۱</sup>

In the second step of proposal 2 the thiosulfonate anion reacts with a proton to form the thiosulfonic acid (Scheme 26, step 2a). The proton would be obtained from the solvent or may be presence in the form of a water contaminant. The extrusion was observed in dry DMF but it is difficult to determine the extent of dryness. The negatively charged anionic sulfur of the thiosulfonate ion could react with the positively charged sulfur of the the thiosulfonic acid to lengthen the sulfur chain by one sulfur atom. The reaction would continue until the sulfur chain was six to eight sulfur atoms long. Cyclization of the intermediates forms sulfur rings, the sulfonate anion and regenerates the proton. The sulfonate reacts with the proton or with sulfenium ion to generate thiosulfonate 147.

An alternative to step 2a involves the reaction of the thiosulfonate ion with a molecule of 146 to lengthen the sulfur chain by one sulfur. The reaction continues until the sulfur chain is seven to nine sulfur atoms long. Cyclization forms the sulfur rings and a molecule of 147. All of the above steps are reversible.

Davis<sup>22</sup> proposed a similar mechanism to account for the formation of elemental sulfur in an acidified solution of thiosulfate  $(S_2O_3^{2^2})$ . The thiosulfate would become protonated and a reaction similar to proposal 2 would result until the sulfur chain would cyclize. Recent work by Steudel<sup>102</sup> on the formation of sulfur allotropes in inorganic reactions supported the mechanism proposed by Davis.

<sup>101.</sup> This mechanistic possibility was suggested by Dr. Ralf Steudel.

<sup>102.</sup> R. Steudel and H.-J. Mäusle, Z. anorg. allg. Chem., 457, 165 (1979).

STEP	1					
	R—SO2—S—:	SR		R-SO2-S	+	⁺sR
	RS +	+	n Solv	 RS(Solv)n +		

STEP 2a

R-SO2-S +	н+	R-SO2-SH		
R-SO <sub>2</sub> -SH +	R-SO2-S	R-SO <sub>2</sub> -SSH	+	R 502
R-SO2-SSH +	R-SO2-S	R-SO2-SSSH	+	R502
	Etc. Until			
		+ B-SO."		+

R—SO <sub>2</sub> —S <sub>6</sub> —H	 S <sub>6</sub>	+	R—S02	+	н+
R-SO2-S7-H	 S7	+	R502	+	н+
R-SO2-S6-H	 S,	+	RSO2	+	н+

STEP 3

í

R-SO2	+	н+	 R—S0₂—H
RSO2S	;_ +	н+	 R-S02-S2-H

```
STEP 2b

R-SO_2-S^2 + R-SO_2-SSR \longrightarrow R-SO_2-SSSR + R-SO_2^2

R-SO_2-S^2 + R-SO_2-SSSR \longrightarrow R-SO_2-SSSSR + R-SO_2^2

etc Until

R-SO_2-S_{x+1}-R \longrightarrow S_x + R-SO_2-SR

(X = 0, 7, 0)
```

Scheme 26

\_ \_

## 3.3 Attempted Differentiation Between 146 and 147

## 3.3.1 General Techniques

. .

In anticipation that rate studies would give an insight into the mechanism of the extrusion of sulfur from 146 several experimental techniques were investigated to obtain a quantitative differentiation of 146 and 147. This would allow the loss of 146 or the formation of 147 to be followed over time. Rate studies have been reported using a wide variety of experimental techniques. Although no method was found feasible for the rate study of the conversion of 146 to 147; the results are presented below to indicate the difficulty involved in the differentiation.

Gas chromatography did not allow for a differentiation of 146 and 147. Both 146 and 147 (independently prepared) gave identical retention times on both packed and capillary columns. The identical retention times were thought to result from a decomposition of 146 to 147 under the chromatographic conditions. Heating a sample of 146 above 150°C resulted in decomposition to what appeared to be 147 as confirmed by <sup>13</sup>C NMR spectroscopy. The thermal experiment indicated that 146 was decomposing in the injection port of the gas chromatograph which is maintained at 240°C. The decomposition may have also occurred on the column which was heated to 240°C during the analysis. Attempts to obtain a separation at lower temperatures of both the injection port and columns were unsuccessful.

NMR Spectroscopy was found to be unsuitable as a technique for the kinetic analysis. The NMR spectra of 146 and 147 do show some differences in the <sup>1</sup>H NMR chemical shifts of the methyl protons but the difference is slight and does not allow for a quantitative identification. The splitting pattern of the aromatic protons of 146 and 147 differed but allowed only enough for a qualitative identification. The two compounds did exhibit different <sup>13</sup>C NMR spectra but this technique is not suitable for rate studies.

The  $^{33}$ S NMR spectra of many compounds have been recorded with sulfones giving the best signals.<sup>103</sup> The low natural abundance of the sulfur-33 isotope (0.76%) made signal acquisition difficult. Both the thioanhydride and thiosulfonate did not give observable  $^{33}$ S NMR signals. To ensure that the technique was conducted correctly, the spectra of several known sulfones were obtained and the

<sup>103.</sup> P. S. Belton, I. J. Cox and R. K. Harris, J. Chem. Soc. Faraday Trans. 2, 81, 63 (1985), R. Faure, E. J. Vincent, J. M. Ruiz and L. Léna, Org. Magn. Reson., 15, 401 (1981).

results agreed with those reported.

į,

Other spectroscopic techniques were also found unsuitable for the kinetic study. Both compounds gave near identical infrared spectra. There was a slight difference in the IR spectra but a quantitative separation was impossible. The uv-visible spectra of the compounds were identical.

# 3.3.2 <sup>19</sup>F NMR Spectroscopy

As a method to differentiate between 146 and 147 the use of  ${}^{19}$ F NMR spectroscopy was investigated. There are several advantages to  ${}^{19}$ F NMR spectroscopy including the 100% natural abundance of the fluorine-19 isotope, its spin of 1/2 and the large range of chemical shifts observed for fluorine compounds. The abundance of the  ${}^{19}$ F isotope make acquisition of a signal simple. The limitation of  ${}^{33}$ S NMR is the low natural abundance of the  ${}^{33}$ S isotope. For  ${}^{1}$ H NMR the chemical shift range is about 13 ppm while for  ${}^{19}$ F NMR the range is much larger, 200-300 ppm. This wide chemical shift range make small changes in chemical structure observable.  ${}^{19}$ F NMR should therefore allow for a differentiation between fluorinated derivatives of 146 and 147.

Attempts were made to prepare the fluorinated derivatives 4fluorobenzenesulfenyl-4-tolylsulfonyl thioanhydride (152) and 4-tolylsulfenyl-4fluorobenzenesulfonyl thioanhydride (153). It was anticipated that the <sup>19</sup>F NMR spectra of these compounds should have different chemical shifts from those of the corresponding thiosulfonates 154 and 155. Each thioanhydride was prepared following the same preparation that was used for thioanhydride 146 which involved the condensation of the potassium thiosulfonate 156 with the corresponding sulfenyl chlorides. The reaction did not give the expected thioanhydrides but instead yielded only the corresponding thiosulfonates 154 and 155.





The formation of 154 and 155 was not surprising as the earlier studies<sup>38</sup> showed that attempted formation of the 4-chloro derivatives yielded only the thiosulfonates. Confirmation of thiosulfonates 154 and 155 as the products of these reactions was obtained from the mass spectra; there was evidence for the formation of the thioanhydrides 152 and 153, however their signal was one one-thousandth of that for the corresponding thiosulfonate. The thioanhydrides likely formed but were unstable and immediately extruded a sulfur to form 154 or 155. Their identity was further confirmed by the fact that samples of the proposed thioanhydrides were unchanged when dissolved in ethanol for 48 h ( $^{13}C$ ,  $^{1}H$ , and  $^{19}F$  NMR).

# 2.2.1.3 <u>Attempted Trapping of S<sub>2</sub> from 4-Tolylsulfenic 4-tolylsulfonic</u> thioanhydrides 146

The initial mechanism (proposal 1) suggested the possibility of the formation of the sulfur in the extrusion went through an intermediate such as  $S_2$ . Attempts were made to trap the  $S_2$  intermediate and the results are presented below.<sup>104</sup>

The sulfur extrusion reaction of 146 was repeated in the presence of 2,3dimethyl-1,3-butadiene 107 to determine if  $S_2$  was generated. The solvent (ethanol) was removed under reduced pressure and a <sup>1</sup>H NMR spectrum of the reaction mixture acquired. There was no evidence for the successful trapping of  $S_2$  (a signal at 3.20 or 3.76 ppm). The reaction was repeated in the presence of excess diene and with the diene as the limiting reagent but no cyclic disulfide formation was indicated (TLC, <sup>1</sup>H NMR). The reaction was repeated in deuterated methanol and followed in the <sup>1</sup>H NMR. There were no signals which corresponded to the trapping of diatomic sulfur.

5.76

<sup>104.</sup> The initial 'apping experiments were conducted by J. Gavin MacDonald.

Two possible explanations may account for the lack of successful trapping of diatomic sulfur from the above extrusion. The reaction may not go through a mechanism which involves an  $S_2$  intermediate. This would lessen support for the mechanism proposed in Scheme 23 and support the alternative mechanism in Scheme 26. The second explanation is that any  ${}^{1}S_{2}$  formed may be quickly isomerized to the triplet state. The lifetime of  $O_2$  is significantly less in polar solvents than non-polar solvents.<sup>42</sup>

#### 3.5 High Performance Liquid Chromatography Analysis

Ĩ

HPLC analysis of the sulfur isolated from this extrusion of 146 preformed in ethanol showed that it consisted mainly of  $S_8$  with small amounts of  $S_6$  and  $S_7$ (combined 1% of the  $S_8$  mass). The sulfur was isolated as a semi-solid indicating a mixture of sulfur allotropes. The mixture is expected to convert to  $S_8$  over time as sulfur allotropes ( $S_x$ ) have been to do this at 20°C within a few days.<sup>105</sup> This is because the only stable allotrope of sulfur at STP is  $S_8$ . The analysis was done in a distant laboratory thus there was a delay of several days between the isolation of the sulfur sample and the analysis by HPLC for the identification of the sulfur allotropes.

The transformation of 146 into 147 was initially followed by HPLC to determine the nature of the sulfur formed in the extrusion  $(S_x)$  but unexpected results were observed. After 10 days signal were obtained which were assigned to compounds have the structure R-SO<sub>2</sub>-S<sub>x</sub>-R (X = 3...1). The assignments were made based on a straight line for the plot of the natural logarithmln k' vs x + 1. This plot is shown in Figure 5. The data from the chromatogram is summarized in Table 4. The straight line is not unexpected in that the introduction of addition sulfur atoms caused little structural change and thus the chromatography is dependent only on the molecular weight of each compound. If the compounds have a similar structure a linear plot should therefore result.

<sup>105.</sup> B. Meyer, Chem. Rev. 64, 429 (1964). The HPLC analysis was conducted by Professor R. Steudel (Berlin).
Figure 5. Plot of Natural Logarithm k' vs X + 1 for the Sulfur Extrusion From 146 in Ethanol. k' = capacity factor for the HPLC



~ 7e

Table 4. Ex for the Sulfi	perimental and Calculated or Extrusion From 146 in E	Data from the HPLC Ethanol	Analysis	
X <sup>a</sup>	Retention Time	k' ( <sup>b</sup> )	ln k'	
1	1.883	0.299	-1.21	
2	2.131	0.470	-0.756	
3	2.315	0.597	-0.516	
4	2.587	0.784	-0.243	
5	2.964	1.044	0.043	
6	3.470	1.393	0.332	
7	4.026	2.087	0.736	
8	4.745	2.272	0.821	
9	5.62	2.876	1.056	
10	6.78	3.67	1.302	
11	8.28	4.710	1.550	
<sup>a</sup> X = No of ( <sup>b</sup> ) k'	Sulfur atoms $(T_r - T_o) = \frac{T_o}{T_o}$	k' = capacity factor $T_o =$ dead time of the $T_r =$ retention time	e column	

1

:

From the chromatograms the largest component of the mixture was found to be, as expected, thiosulfonate 147. The formation of 147 would be accompanied by the formation of sulfur. As previously indicated, sulfur has been successfully isolated from a solution of 146 in ethanol by filtration. In the original analysis of this system by Ash, the only reaction products isolated were 147 and sulfur. The presence of other compounds was not determined.

The formation of other compounds beside 146 and 147 was confirmed by acquiring a <sup>13</sup>C spectrum of the reaction mixture obtained after stirring a sample of 146 in ethanol for 48 h. The spectrum displayed signals for the methyl carbons of 147, the starting material 146 and a third set of signals was assigned to the higher sulfides. The signals for 146 were the most intense indicating that it was the major component in the mixture.

The results of the HPLC analysis appear to favor the second mechanism (Scheme 26). Proposal 1 (Scheme 23) could still be considered presuming that the sulfur species isolated was formed by a rearrangement of the branched sulfur compound (Scheme 27).



Scheme 27

The major difference between the two proposed mechanisms is the acid catalysis of the second mechanism (Scheme 26). If the mechanism in Scheme 23 is correct the presence of acid should increase the rate of the reaction. The splitting pattern of the aromatic protons in the <sup>1</sup>H NMR spectra allow for a qualitative differentiation between 146 and 147 and thus was used to determine the effect of acid.

For this purpose two identical samples of 146 were prepared. One sample was dissolved in absolute ethanol while the second was dissolved in a solution of HCl in ethanol (made by bubbling dry HCl through absolute ethanol). The HCl ethanol solution of 146 developed a light yellow tinge after only 5 minutes. After 2 h an aliquot of each solution was removed from the reaction mixture. Each sample was treated in the identical fashion. The solvent was removed under reduced pressure and the residue dissolved in deutereochloroform and a <sup>1</sup>H NMR spectrum acquired. The sample of 146 distributed in the HCl-ethanol was almost totally converted to 147, while the sample in ethanol was virtually unchanged.

An acidified solution of potassium 4-tolylthiosulfonate (156) turned yellow after only 5 minutes. Filtration of the solution gave a yellow solid identified as sulfur (98%). Such a result is expected as 156 in the presence of acid should decompose via a mechanism similar to that presented in Scheme 26.



These results of the acid catalyst make the second mechanism (proposal 2) the most probable one. The lack of desulfurization of the nitro derivatives of 146 (in

1 m

the original work of Harpp, Ash and Smith<sup>38</sup>) can be accounted for by the fact that the electron withdrawing nitro groups would destabilize the formation of the sulfenium ion. All of the results support proposal 2 as the mechanism of sulfur extrusion.

# **CHAPTER 4**

# CHLORO(TRIPHENYLMETHYL)SULFIDES: STRUCTURE AND CHEMISTRY

#### 4.1 Introduction

The sulfur-chlorine bond has been the subject of several reviews<sup>106</sup> and has a rich and well studied chemistry.<sup>107</sup> Chlorosulfides are known to react with alkenes to give 1,2-addition products.<sup>106,108</sup> In the work presented here, the reaction of chloro(triphenylmethyl)disulfide with 1,3-dienes did not yield 1,2-addition products, instead a product consistent with the trapping of <sup>1</sup>S<sub>2</sub> was obtained. As a result a more detailed study of this disulfide and related compounds was essential to understand the mechanism and chemistry of this addition.

Chloromonosulfides (or sulfenyl chlorides) are a well known class of compounds that are easily synthesized by a variety of methods<sup>106,109</sup> and are relatively stable. The structures of a few chloromonosulfides have been investigated but these studies have been limited to mainly small molecules which allowed for easy spectroscopic analysis. The geometry of sulfur dichloride (SCl<sub>2</sub>) has been determined using microwave spectroscopy<sup>110,111</sup> and electron diffraction.<sup>112</sup> The structure of methanesulfenyl chloride<sup>113,114,115</sup> (157) was also investigated by microwave spectroscopy, while the trichloro- (158)<sup>116</sup> and trifluoro- (159)<sup>117</sup> derivatives were examined with electron diffraction. Electron diffraction has also been used to measure the geometry of benzenesulfenyl chloride (160).<sup>118</sup> The

- 107. K. D. Gundermann, Angew Chem. Int. Ed. Engl., 2, 674 (1963).
- 108. W. H. Mueller, Angew Chem. Int. Ed. Engl., 8, 489 (1969); E. Kuhle, Synthesis, 561 (1972).
- 109. D. N. Harpp, and P. Mathiaparanam, J. Org. Chem., 37, 1367 (1972).
- 110. J. T. Murray, W. A. Little, Q. Williams and T. L. Weatherly, J. Chem. Phys., 65, 985 (1976).
- 111. R. W. Davis and M. C. L. Gerry, J. Mol. Spectrosc. 65, 455 (1977).
- 112. Y. Morino, Y.Murata, T. Ito and J. Nakamura, J. Phys. Soc. Japan, 17, suppl. BII, 37 (1962).
- 113. A. Guarnieri, Z. Naturforsch, 23a, 1867 (1968).
- 114. A. Guarnieri, Z. Naturforsch, 25a, 18 (1970).
- 115. A. Guarnieri, L. Charpentier, and B. Kuck, Z. Naturforsch 28a, 1721 (1973).
- 116. N. V. Alekseev and F. K. Velichko, Zh. Strurkt. Khim., 8, 532 (1967).
- 117. H. Oberhammer, W. Gombler and H. Willner, J. Mol struct. 70, 273 (1981).
- 118. N. M. Zaripov, M. V. Popik and L. V. Vilkov, Zh. Strurkt. Khim. 21, 37 (1980), .

<sup>106.</sup> W. R. Hardstaff and R. F. Langler in "Sulfur in Organic and Inorganic Chemistry," A. Senning (Ed.), Marcel Dekker Inc., New Yotk, Vol. 4, (1982), p 193.

sulfur-chlorine bond length was found to range between 2.006(4)Å for sulfur dichloride<sup>112</sup> to 2.051(6)Å for benzenesulfenyl chloride. The carbon-sulfur bond length ranged from a low of 1.764(12)Å in benzenesulfenyl chloride to a high of 1.824(6)Å found in trifluoromethylsulfenyl chloride.<sup>117</sup> The C-S-Cl bond angle varied from a low of  $98.3(15)^{\circ}$  for trichloromethylsulfenyl chloride<sup>116</sup> to a high of  $103.0(4)^{\circ}$  for sulfur dichloride.<sup>112</sup> The compound of interest, chloro(triphenylmethyl)monosulfide,<sup>119</sup> has been known for more than seventy years and has been widely employed as a protecting group in amine chemistry.<sup>120</sup>



Chlorodisulfides (also known as chlorodisulfanes or thiosulfenyl chlorides) are less well known due to a lower stability. The preparation of a number of these compounds has been reported<sup>121</sup> but there is little structural information available. The structure of disulfur dichloride ( $S_2Cl_2$ ) was determined in 1969 by electron diffraction<sup>122</sup> and more recently by microwave spectroscopy.<sup>123,124</sup> The sulfurchlorine bond was longer than reported for any chloromonosulfide at 2.057(2)Å and the S-S-Cl angle was larger (108.2(3)°). Recently, the chemistry of the trifluorothio derivatives has received attention. The structure of chloro(trifluoromethyl)disulfide (161) has been studied using vibrational analysis.<sup>125,126</sup> Overall, the chlorodisulfides exhibited bond angles larger than that of the corresponding chloromonosulfides and

- 119. D. Voländer and E. Mittag, Chem. Ber., 46, 3450 (1913).
- 120. B. P. Branchaud, J. Org. Chem., 48, 3538 (1983).
- 121. E. K.Moltzen and A. Senning, Sulfur Lett., 4, 169 (1976).
- 122. B. Beagley, G. H. Eckersley, D. P. Brown and D. Tomlinson, J. Chem. Soc., Trans. Faraday Soc., 65, 2300 (1969).
- 123. C. J. Marsden, R. D. Brown and P. D. Godfrey, J. Chem. Soc. Chem. Commum., 399 (1979).
- 124. A. Yamazaki, K. Mogi, M. Koyama and I. Yamaguchi, J. Mol. Struct., 55, 185 (1979).
- 125. R. Minkwitz, R. Lekies, D. Lennhoff, J. Sawatzki, J. Kadel and H. Oberhammer, Inorg. Chem., 29, 2587 (1990).
- 126. C. O. Della Vedova, J. Raman Spectrosc., 20, 279 (1989).

longer sulfur-chlorine bonds. Chloro(triphenylmethyl)disulfide,<sup>127</sup> first synthesized in 1970, has received very little consideration. It was first employed as a reagent to prepare unsymmetrical trisulfides<sup>113</sup> and later used to prepare di- and trisulfides in the synthesis of fungal metabolites.<sup>128</sup>



# (161)

Chlorotrisulfides were unknown as isolated compounds but several have been prepared *in situ* and used to synthesize hydrotetrasulfides (RSSSSH). No effort was made to isolate the chlorotrisulfides.<sup>129</sup> Chlorotrisulfides and disulfides are proposed intermediates in the preparation of tetra- and trisulfides from sulfur chlorides and thiols. The probable reaction mechanism for the preparation of the tetrasulfide is shown below, (Scheme 28). In the absence of additional thiol, the reaction would stop following the formation of the chlorosulfide.



R-S<sub>3</sub>-Cl + R-SH ------- R-S<sub>4</sub>-R + HCl

### Scheme 28

#### 4.2 Synthesis

Chloro(triphenylmethyl)monosulfide (162a) was obtained by the direct chlorination of triphenylmethanethiol (163a) following the procedure of Vorländer and Mittig.<sup>119</sup> The higher sulfides (162b and 162c) were isolated from the condensation of the thiol 163a with an excess of the inorganic sulfur chloride at low temperature (-78°C) (Scheme 29). The disulfide 162b was purified by a simple

<sup>127.</sup> D. N. Harpp and D. K. Ash, Int. J. Sulfur Chem., A, 1, 211 (1971).

<sup>128.</sup> R. M. Williams and W. H. Rastetter, J. Org. Chem., 45, 2625 (1980).

<sup>129.</sup> H. J. Langer and J. B. Hyne, Can. J. Chem., 51, 3403 (1973).

recrystallization from hexanes. The reactants for the preparation of the trisulfide 162c were purified several times so that recrystallization of the product was unnecessary. Attempts to purify the trisulfide by recrystallization in low boiling pentane resulted in the isolation of triphenylchloromethane (164) and sulfur, this decomposition is discussed in detail in section 4.4.2. The tetrasulfide (162d) was prepared by the condensation of triphenylmethyl hydrodisulfide (163a)<sup>130</sup> and an excess of disulfur dichloride. The physical properties of the sulfides are summarized in Table 5.

Ł

Ĵ,



130. This compound was supplied courtsey of Mr. Gerard Derbersy.

### 4.3 Crystallographic Analysis

aber.

<u>م</u> ۲۰

The sulfides were crystalline compounds, and the X-ray crystal structures were obtained in hopes of obtaining a greater understanding of their reactivity.<sup>131</sup> Careful recrystallization of 162a and 162b from hexanes yielded crystals suitable for analysis. On initial precipitation from ether 162c gave proper crystals. A crystal of 162d suitable for analysis could not be obtained.

The crystals of compound 162c showed extensive decomposition (82%) after 12 hours and therefore no high angle data was obtained. A decay correction was applied to the data. Sulfides 162a and 162b exhibited no decomposition during X-ray analysis. Compound 162a gave structural data for two independent molecules which were nearly identical. For 162c the chosen enantiomorph gave R-factors 0.002 lower than the alternate solution. The ORTEP<sup>132</sup> drawings of 162a-162c are shown in Figures 6-8 respectively. Selected bond lengths and angles are given in Table 6.

The X-ray structures of bromo- and iodo(triphenylmethyl)monosulfide have been obtained.
 R. Minkwitz, U. Nass and H. Preut, Z. anorg. allg. Chem., 538, 143 (1986): R. Minkwitz, H. Preut and J. Sawatzki, Z. Naturforsch, 43B, 399 (1988).

<sup>132.</sup> C. K. Johnson, ORTEPII, Report OR NL-5138, Oak Ridge National Laboratory, Tennessee, USA, (1976).

**Table 6.** Selected Bond Lengths and Angles from the X-ray Structures of the Chloro(triphenylmethyl)sulfides. 

. . . . . . . . .

	Bond Leng	gths (Angstroms)	
Bond	Monosulfide <sup>a</sup> (162a)	Disulfide <sup>a</sup> (162b)	Trisulfide <sup>b</sup> (162c)
S-Cl	2.018(3)	2.073(2)	2.026(4)
S-S		1.975(2)	2.035(6)
			2.011(4)
C-S	1.854(6)	1.912(4)	1.88(1)
C(19)-C(6)	1.511(7)	1.529(6)	1.55(1)
C(19)-C(12)	1.546(8)	1.523(6)	1.53(1)
C(19)-C(18)	1.529(7)	1.538(5)	1.54(1)
Angle <sup>C</sup>	Bond Ang	les (deg.)	
Aligic			
S-S-Cl		108.44(8)	104.7(2)
S-S-S			107.3(2)
C-S-S		111.5(1)	107.9(3)
C-S-Cl	105.2(2)		
C(6)-C(19)-S	113.6(4)	110.6(3)	110.7(6)
C(12)-C(19)-S	109.6(4)	111.0(3)	110.1(6)
C(18)-C(19)-S	97.3(4)	97.5(3)	100.3(5)
S-S Dihedral		99.3(2)	-80.2(3)
			-102.4(3)
••••	••••••••••	•••••	••••••••••••••

<sup>a</sup> Gave a satisfactory sulfur analysis using an Antek Sulfur Analyzer.
 <sup>b</sup> Correct elemental analysis.

• •

<sup>c</sup> The angle is that of the central atoms listed. 

. . . .

71

1

í



··\*•











The sulfur-chlorine and carbon-sulfur bond distances for 162a were in the range of those obtained for other monosulfides as was the observed angle about the sulfur atom. The only crystal structure of a chloromonosulfide reported was the unusual  $\alpha$ chloro- $\alpha$ -chlorosulfenyl-4-nitro-2,5-dimethoxyphenylacetyl chloride<sup>133</sup> (165) which showed a sulfur-chlorine bond length of 1.98Å, a carbon-sulfur bond length of 1.84Å and an angle about the sulfur atom of 99.42°. These measurements are in agreement with those measured for 162a only slightly smaller. The smaller bond lengths and bond angles in 165 likely resulted from electronic effects from the strong withdrawing groups near the S-Cl bond.



Surprising structural features were found in the X-ray crystal analysis of the intermediate sulfur chloride 162b. The length of the sulfur chlorine bond, 2.073(2)Å, is to our knowledge the longest bond of this type ever reported. The length of the sulfur-sulfur bond is one of the smallest ever reported, with only disulfur dichloride and compounds with known sulfur-sulfur double bonds being shorter. A comparison of bond lengths for compounds with known sulfur-sulfur double bonds with 162b is given in Table 7. Disulfur dichloride is included because it is known to exhibit some double bond character. The disulfide bond length of 162b falls between that of disulfur dichloride and normal open-chain disulfides.

<sup>133.</sup> M. S. Simon, J. B. Rogers, W. Saenger and J. Gougoutas, Z. J. Am. Chem. Soc. 1967, 89, 5838

Table 7: Molecules with Sulfur-Sulfur Double Bonds.			
Compound	Bond length (Å)		
$F_2S=S$	1.860 <sup>88</sup>		
S=S=O	1.884 <sup>134</sup>		
F-S-S-F	1.888 <sup>88</sup>		
S = S	1.892 <sup>135</sup>		
$(RO)_2S=S$	1.901 <sup>136</sup>		
R-N=S=S	1.898 <sup>137</sup>		
$Ph_3NSN = S = S$	1.908 <sup>138</sup>		
CI-S-S-CI	1.931 <sup>122</sup>		
Disulfide 162b	1.975		
open chain CS-SC	2.02-2.06 <sup>139</sup>		

The observed angles about the sulfur atoms in 162b are two of the largest ever reported for a bivalent sulfur atom. The angle between C19-S-S is  $111.5(1)^{\circ}$  which is larger than the bond angles of S<sub>8</sub> (108°) but smaller than the O-S-S bond angle of S<sub>2</sub>O<sub>2</sub> (112.7°).<sup>140</sup> The large angle in the structure of S<sub>2</sub>O<sub>2</sub> led to a proposal of double bond character for the sulfur-sulfur bond. The short bond length coupled with the large sulfur dihedral angle suggested similar double bond character for 162b. The dihedral or torsional angle (99.3°) is also larger than that of open chain disulfides which are normally in the range of 85-95°.<sup>140</sup> The large dihedral angle is likely a result of steric hindrance. Snyder reported the dihedral angle of di-*tert*-adamantyl disulfide (166) to be  $110.5(9)^{\circ}$ .<sup>141</sup> The large dihedral was believed to be due to steric hindrance.

ra R

1.

<sup>134.</sup> D. J. Meschi and R. Meyers, J. Mol. Spectrosc., 3, 409 (1959).

<sup>135.</sup> S. C. Abrahams, Acta Crystallogr., 8, 611 (1955).

<sup>136.</sup> D. N. Harpp, K. Steliou and C. J. Cheer, J. Chem. Soc., Chem. Commun., 825 (1980).

<sup>137.</sup> F. Iwasaki, Acta Crystallogr. Sect. B., 35, 2099 (1979).

<sup>138.</sup> T. Chivers, R. T. Oakley, A. W. Cordes and P. Swepston, J. Chem. Soc., Chem. Commun., 35 (1980).

<sup>139</sup> I. Hargittai, "The Structure of Volatile Sulfur Compounds", Akadémiai Kiadó, Budapest, Hungary, 1985.

<sup>140.</sup> F. J. Lovas, E. Tiemann and D. R. Johnson, J. Chem. Phys., 60, 5005 (1974).

<sup>141.</sup> G. Rindorf, F. S. Jørgensen and J. P. Snyder, J. Org. Chem., 45, 5343 (1980).



The S-Cl, S-S and C-S bond lengths for 162c are in the range measured for normal chloromonosulfides and dialkyldisulfides.<sup>140</sup> The angles about the sulfur atoms, although large, are in the range for S<sub>8</sub>. The dihedral angles for the two S-S bonds differed greatly; the S-S adjacent to the triphenylmethyl group has a much larger dihedral angle than the S-S bond distant from the triphenylmethyl group. The reason for this difference is not known, but may be a result of the hindered rotation of the triphenylmethyl group. A similar structural arrangement of dihedral angles was observed in the X-ray crystal structures of organometallic trisulfides.<sup>142</sup>

All of the sulfides exhibit a distortion in the tetrahedral arrangement about the central carbon (C-19). This distortion may be attributed to an interaction between the electron pairs on the  $\alpha$ -sulfur and the  $\pi$ -clouds of the aromatic rings, which would be intensified by rotational constraints of the triphenylmethyl group.

# 4.4 Spectroscopic Analysis

Y

Like the results of the X-ray structure analysis, the <sup>13</sup>C NMR spectrum of 162b differed from that of 162a and 162c. The <sup>13</sup>C NMR chemical shifts relative to tetramethylsilane are reported in Table 8. The carbon atoms were identified by the following numbering system. The NMR signals for 162d were identified from a mixture with the decomposition product triphenylchloromethane (164). The chemical shifts for 164 are included here for comparison.

<sup>142.</sup> A. Shaver, McGill University, private communication.



**Table 8.** Summary of the <sup>13</sup>C NMR Chemical Shifts for the Chloro(triphenylmethyl)sulfides.

	<sup>13</sup> C-NM	R (ppm)		
C-1	C-2	C-3	C-4	C-5
72.21	141.76	128.19	129.87	127.90
77.60	142.17	128.08	130.58	127.65
74.36	142.60	128.10	130.12	127.48
73.92	142.45	128.12	130.12	127.44
81.32	145.19	127.68	129.63	127.68
	C-1 72.21 77.60 74.36 73.92 81.32	<sup>13</sup> C-NM C-1 C-2 72.21 141.76 77.60 142.17 74.36 142.60 73.92 142.45 81.32 145.19	<sup>13</sup> C-NMR (ppm) C-1 C-2 C-3 72.21 141.76 128.19 77.60 142.17 128.08 74.36 142.60 128.10 73.92 142.45 128.12 81.32 145.19 127.68	<sup>13</sup> C-NMR (ppm) C-1 C-2 C-3 C-4 72.21 141.76 128.19 129.87 77.60 142.17 128.08 130.58 74.36 142.60 128.10 130.12 73.92 142.45 128.12 130.12 81.32 145.19 127.68 129.63

The triphenylmethyl carbon (C-1) of 162b would be expected to resonate between that of 162a and 162c. It therefore should appear at about 73 ppm, hewever the signal was shifted about 4 ppm downfield from this expected value. The downshift of C-1 in 162b can be partially attributed to the rotational constraints of the triphenylmethyl group. Such a rotational barrier has been proposed to explain the unusual shifts observed for the thiol proton in the <sup>1</sup>H NMR spectrum of hydro(triphenylmethyl)disulfide as compared to the monosulfide and trisulfide.<sup>143</sup> Similar rotational constraints were not as prevalent in 162c, which was less hindered because of the extra sulfur atom.

A comparison of the  ${}^{13}$ C NMR spectra of sulfides and disulfides revealed that the  $\alpha$ -carbon is shifted downfield; with that of the disulfide being further downfield than that of the monosulfide.<sup>144</sup> The introduction of the second sulfur atom in 162b can account for some of the downfield shift for C-1 from the position of C-1 in 162a.

<sup>143.</sup> J. Tsurugi, Int. J. Sulfur Chem., B, 7, 199 (1972).

<sup>144.</sup> E. Pretsch, J. Siebl, W. Simon and T. Clerc, "Tables of Spectral Data For Structural Determination of Organic Compounds," Springler-Verlag, Berlin (1989), 2 ed, p C180.

The double bond character of the S-S bond in 162b may account for the remaining downfield shift. A carbon atom adjacent to carbon-carbon double bonds is shifted downfield and a similar effect should be observed in this system.

The UV-Visible spectrum of all three sulfides were determined in chloroform. Each sulfide exhibited two absorption maxima at 244 and 254 nm. The absorption band at 244 nm was assigned to the S-Cl bond as the intensity of the signal decreased over time due to decomposition and loss of the S-Cl bond.

The IR spectra showed a variety of diverse peaks but, due to the similarity a clear differentiation between the sulfides was vory difficult. The S-S and S-H stretches are weak in the IR and are not always observed. Each sulfide exhibited s. Tals corresponding to C-H aromatic and C-C double bond stretches and the C-H out-ot-, 'ane bends. The only observable difference in the spectra was the S-Cl stretching frequencies which corresponded closely to those observed in the Raman spectra. The S-Cl frequencies were as follows:  $162a = 487 \text{ cm}^{-1}$ ,  $162b = 482 \text{ cm}^{-1}$  and  $162c = 488 \text{ cm}^{-1}$ .

Raman spectroscopy has been used as a technique to obtain structural information; it was anticipated that the Raman spectra would give further insight into the molecular structure of the sulfides. The typical value for the usual S-S symmetrical stretch in a Raman spectrum is about 510 cm<sup>-1.145,146</sup> There also appears to be an approximate linear relationship between the frequency of the S-S shift and the dihedral angle.<sup>147</sup> The explanation for this was that as the dihedral angle decreased from 90° there was a greater  $p\pi$ - $p\pi$  interaction, which destabilized the S-S bond.<sup>147,148</sup> This effect was only observable for compounds with dihedral angles below 60°. The effect may also become important in compounds with dihedral angles above 90°. There appears to be no correlation of the Raman shift and the dihedral angles above 60°. The stretching frequency for the S-S bond of CF<sub>3</sub>SSCl has be determined to be 528<sup>125</sup> cm<sup>-1</sup> and 535<sup>126</sup> cm<sup>-1</sup> while that of disulfur dichloride<sup>149</sup> was found to be 540 cm<sup>-1</sup>. These agree with the value of 543 cm<sup>-1</sup> measured for **162b**. The stretching frequency for the S-Cl bond of CF<sub>3</sub>SSCl was

<sup>145.</sup> S. G. Frankiss, J. Mol. Structure, 3, 89 (1969).

<sup>146.</sup> H. E Van Wart, F. Cardinaux and H. A. Scheraga, J. Chem. Phys., 80, 625 (1976).

<sup>147.</sup> H. E Van Wart and H. A. Scheraga, J. Chem. Phys., 80, 1823 (1976).

<sup>148.</sup> H. E Van Wart, A. Lewis, H. A. Scheraga and F. D. Saeva, Proc. Natl. Acad. Sci. USA, 70, 2619 (1973).

<sup>149.</sup> E. B. Bradley, M. S. Mathur and C. A. Frenzel, J. Chem. Phys, 47, 4325 (1967).

found to be  $474^{125}$  cm<sup>-1</sup> and  $484^{126}$  cm<sup>-1</sup>. The S-Cl stretching frequency in 162b was assigned to the peak at 483 cm<sup>-1</sup>. The Raman signals are summarized below in Table 9.

The complex spectra of 162c may be a result of the presence of decomposition products. Decomposition of 162c has been observed at room temperature and is enhanced by light. The Raman spectra of various sulfur allotropes have been measured.<sup>150</sup> The most stable sulfur allotropes  $S_6$  and  $S_8$  both have a base peak at 472 cm<sup>-1</sup>. This signal may correspond to the signal at 470 cm<sup>-1</sup> in the spectra of 162c.

he Chloro(triphen	ylmethyl)sulfides.	
monosulfide	disulfide	trisulfide
(162a)	(162b)	(162c)
520	543	519
501	488	483
487	422	470
365	416	454
	402	449
	341	357
		346

### 4.5 <u>Thermal Decomposition of the Chlorosulfides</u>

#### 4.5.1 In the Solid State

Sulfides 162a, 162b and 162c were thermally unstable. Their stability appeared to decrease, as expected, with the increase in sulfur content of the molecule. Samples of each sulfide decomposed when heated for three minutes to their melting points. Each decomposition sample was analyzed by <sup>13</sup>C NMR spectroscopy; 162b

<sup>150.</sup> R. Steudel, D. Jensen, P. Göbel and P. Hugo, Ber Bunsenges, Phys. Chem., 118, 92 (1988).

and 162c yielded only triphenylchloromethane (164), while 162a gave a mixture of 164 and starting material (Scheme 30). Sulfur was successfully isolated from the decomposition mixtures by extraction into chloroform followed by filtration.

``

÷



### Scheme 30

HPLC analysis of 162b after it had been heated above its melting point revealed the presence of a variety of products indicating that decomposition The chromatogram showed peaks for occurred via a complex mechanism. chloromethane 164, S<sub>6</sub>, S<sub>7</sub>, S<sub>8</sub>, and S<sub>9</sub> rings and 10 other products, some of which were identified as bis(triphenylmethyl)sulfides (167) Assignments were made with a comparison of the chromatograms of a solution containing  $S_6-S_{10}$  rings and a solution of 167,  $Ph_3C-S_x-CPh_3$  (x = 3-12). The S<sub>6</sub>:S<sub>8</sub> and S<sub>7</sub>:S<sub>8</sub> concentration ratios were 0.31/1 and 0.33/1 respectively which are much higher than those obtained from liquid sulfur at 120°C (0.0054/1 and 0.033/1 respectively).<sup>151</sup> Therefore the equilibrium between various sulfur rings in liquid sulfur is not found in this case. The formation of the sulfides was not surprising, as they are identified in the decomposition in solution (see below) however, signals for these compounds were not observed in the <sup>13</sup>C NMR spectrum of the decomposition mixture. The lack of identification of the isomers of 167 from the <sup>13</sup>C NMR spectra indicates that they are in low concentration. The overall reaction is summarized below (Scheme 31).

<sup>151.</sup> R. Steudel, R. Strauss and L. Koch, Angew Chem. Int. ed. Engl., 24, 59 (1985); We are greatful to Professor Steudel for this analysis.



### Scheme 31

Sulfides 162b and 162c are also unstable in the solid state at room temperature. Both compounds exhibited a visible color change after 48 h. Analysis by <sup>13</sup>C NMR of the resulting solid showed it was a mixture of the sulfide and chloromethane 164. The decomposition was also enhanced by light as was proven in the following experiment. Two identical samples of 162c were prepared and kept under identical conditions except one was stored under ambient light while the second sample was kept in the dark. The sample maintained under ambient light showed decomposition after only 48 h as determined both visibly and through a comparison of the <sup>13</sup>C NMR spectra; the dark sample was unchanged.

#### 4.5.2 Thermal Decomposition in Solution

. \*\*\*

The disulfide 162b, trisulfide 162c and tetrasulfide 162d also decomposed in solution. A sample of 162b was stirred with silica gel in chloroform and the resulting mixture was chromatographed after 48 h to yield several compounds: bis(triphenylmethyl)sulfides (167), a trace amount of triphenylmethane (168), triphenylmethanol (169) (formed from the hydrolysis of 164 under the chromatographic conditions) and sulfur (Scheme 31). The hydrolysis of 164 to 169 was confirmed in a separate experiment by treating a sample of 164 under chromatographic conditions identical to those used for the purification of the decomposition mixture. The only compound isolated was 169. The hydrolysis of 164 on silica gel was incomplete with a more polar solvent for the chromatography, indicating that the decomposition occurs slowly on the silica gel.

The solvent used for the decomposition experiments had a profound effect on the composition of the isolated mixture. The decomposition of 162b was conducted in several solvents using the same quanity of material for each decomposition experiment (0.17 g, 0.50 mmol). The yields of the decomposition products are summarized below in Table 10.

Table 10. Product Distribution for the Decomposition of Chloro(triphenylmethyl)disulfide (162b) at Ambient Temperature for 48 h in Various Solvents.					•
Solvent	Solvent Dipole Moment Yield of Components mg (%) <sup>a</sup>				
	(Debye)	Sulfur <sup>b</sup>	(167) <sup>c</sup>	( <b>16</b> 9) <sup>b</sup>	
CCl <sub>4</sub>	0	12 (36)	112 (73)	43 (33)	
CHCl <sub>3</sub>	1.01	23 (71)	69 (45)	54 (42)	
$CH_2Cl_2$	1.62	27 (83)	76 (50)	57 (44)	
THF	1.63	25 (78)	89 (58)	49 (38)	
Acetone	2.88	30 (94)	8 (5.5)	127 (97)	_
<ul> <li><sup>a</sup> The yields are percent recovery.</li> <li><sup>b</sup> Yields determined assuming an ionic decomposition with conversion of 162b to any suffer and observations 164 (absorbing 164 by drolwing to any suffer and observations).</li> </ul>					

only sulfur and chloromethane 164 (chloromethane 164 hydrolyzed to triphenylmethanol 169).

<sup>c</sup> Yield determined assuming a radical mechanism to yield only a mixture of bis(triphenylmethyl)sulfides (167).

As anticipated, decomposition in polar solvents resulted in the formation of mostly chloromethane 164 and sulfur, while non-polar solvents yield mostly a mixture of bis(triphenylmethyl)sulfides (167). The differences in product distribution likely resulted from a competition between an ionic and a radical mechanism. Polar solvents which stabilize ions would enhance the cleavage of the carbon sulfur bond to give the triphenylmethyl cation and sulfur anion. The ions could then combine to yield sulfur and chloromethane 164. Less polar solvents would not favor the formation of ionic species thus a radical decomposition would be favored. The possibility of a radical mechanism will be discussed in Section 4.4.4. In intermediate solvent it is possible that both a radical and an ionic mechanism may account for the decomposition.

The decomposition of 162c in chloroform gave similar products as those

obtained for 162b. The decomposition products isolated for 162c were in yields similar to that found in the decomposition of 162b: sulfur (64%), 169 (35%) and a mixture of sulfides 167 (50%). The yields were determined as described above in Table 10.

The tetrasulfide 162d decomposed during <sup>13</sup>C NMR analysis. The major product of the decomposition was shown in the initial <sup>13</sup>C NMR spectra to be the chloromethane 164. An extensive decomposition study of the tetrasulfide was not performed as the pure compound could not be isolated.

In order to fully understand the decomposition of 162b in solution and for the purpose of investigating the reactions of the sulfides, several substituted triphenylmethanes were prepared. Each derivative was prepared by following known reactions. The thiols, monosulfides and disulfides were all synthesized following the procedures used to prepare the unsubstituted compounds. The chloromethanes were synthesized from the corresponding alcohols using a known procedure.<sup>152</sup> The melting points and important NMR shifts of these compounds are summarized in Table 11. All of the chlorodi- and monosulfides were light yellow to light orange. Only those compounds with substitution that was NMR observable were synthesized.

	170 X = OH	a R = 4-CH <sub>3</sub>
R	171 X = SH	$\mathbf{b} \mathbf{R} = 4 \mathbf{F}$
× – – ×	172 X = SCl	$c R = 2-CH_3$
	173 X = SSCl	$d R = 4-CH_3O$
$\checkmark$	174 X = Cl	

The derivatives exhibited surprisingly little physical difference. The mono-2methyl derivatives (Xc) displayed chemical shifts in the <sup>1</sup>H and <sup>13</sup>C NMR spectra that were further downfield than those of the parent compounds. These shifts likely resulted from the steric interaction between the 2-methyl group and the substituent (X). The <sup>13</sup>C NMR shifts of the triphenylmethyl carbons also act as a strong indicator of molecular structure. The chemical shifts were directly related to the electronegativity of the atom bonded to the carbon.

ĩ

<sup>152.</sup> N. N. Lichtin and M. J. Vignale, J. Am. Chem. Soc., 79, 579 (1957).

(X)	Substitution	m.p. (°C)	<sup>13</sup> C NMR (C-X)	<sup>1</sup> H NMR (X)
ОН				
(169)	Н	160-163	81 07	2 02
(170a)	4-CH <sub>3</sub>	79-81	\$1.57 \$1.85	2.82
(17 <b>0</b> b)	4-F	120.5-122	81 57	2.70
(170c)	2-CH <sub>3</sub>	93-96	83.03	2.04
(170d)	$4-CH_3O$	78-80	81.67	2.90 2.77
SH				
(163a)	Н	105.5-106.5	62.77	3.07
(1 <b>71a</b> )	4-CH <sub>3</sub>	61-64	62.62	3.06
(171b)	4-F	89-89.5	62.29	3.08
(171c)	2-CH <sub>3</sub>	116-117	63.06	3.05
(171d)	$4-CH_3O$	97-98	62.40	3.07
SCI				
<b>162a</b> )	H	135-137	72.21	
1 <b>72</b> a)	4-CH <sub>3</sub>	87-89	72.05	
1 <b>72b</b> )	4-F	107-109	71.61	
SSCI				
1 <b>62b</b> )	H	91-93	77.60	
173a)	4-CH <sub>3</sub>	76.5-77	77.59	
173b)	4-F	86.5-88	77.46	
1 <b>73c</b> ) <sup>a</sup>	2-CH <sub>3</sub>		79.16	
1 <b>73d</b> )	4-CH <sub>3</sub> O	86-87	77.47	
1				
164)	Н	110-112	81 32	
<b>74a)</b>	4-CH <sub>3</sub>	90.5-92	81 <i>A</i> 5	
(74b)	4-F	87.0-89 5	80. <del>4</del> 5 80.75	

12 JT 3.

.

# 4.5.3 Rate Studies of the Thermal Decomposition of 162b

÷.

Ň

The products isolated from the decomposition of 162b indicate that it may proceed through a complex mechanism. The mono-4-methyl and mono-4-fluoro derivative of 162b was used to further investigate the decomposition of the disulfide and other reactions of the monosulfide 162a and disulfides 162b (see below). The decomposition and reactions of these derivatives could be followed by <sup>1</sup>H NMR.

NMR spectroscopy has been used in several investigations for the determination of reaction kinetics.<sup>153</sup> One limitation for the use of NMR for the purpose of studying reaction kinetics is that only a maximum of 3 half-lives can be followed due to the concentration limits of the instrument. In all the data reported there is an inherent 10% error factor due to measurement of the integration of the <sup>1</sup>H NMR signals.

A typical decomposition of chloro(mono-4-methyltriphenylmethyl)disulfide (173a) to mono-4-methyltriphenylchloromethane (174a) resulted in a upfield shift of 0.03 ppm for the aromatic tolyl protons which could be followed by <sup>1</sup>H NMR spectroscopy. This chemical shift difference allowed the rate of disappearance of 173a or the appearance of 174a. The change over time for the tolyl protons for a typical decomposition is shown in Figure 9.

The data is limited because of several constraints: namely the unavailibility of a large number of deuterated solvents suitable for the decomposition and the concentration limits of the instrument. Several NMR solvents were not suitable as disulfide 162b reacts with any nucleophilic solvent. At low concentration of 173a, the signal to noise ratio of the instrument become significant and a clean separation of the tolyl protons of 173a and 174a cannot be obtained. Due to the limitation above, an exhaustive kinetic study was not conducted but a few experiments were examined to give an insight into the mechanism of the decomposition.

<sup>153.</sup> D. H. R. Bartlett and K. E. Howard, J. Chem. Soc., 155 (1949).

Figure 9. The Change in the <sup>1</sup>H NMR Signal for the Tolyl Protons Over Time for the Decomposition of Chloro(mono-4-methyltriphenylmethyl)disulfide (173a).

·.~



The decomposition of 173a was examined at three temperatures. The plot of concentration vs time for the kinetic runs at 30°C as determined from the NMR data is presented in Figure 10. The initial rate method was used to calculate the rate constants.<sup>154</sup> The initial concentration, initial rates and rate constants are given in Table 12.

Table 12. Calculated Rates and Rate Constants for the ThermalDecomposition of (173a) in Chloroform-d solution.					
temp	רעח #	conc	Initial rate	Rate Constant k	
(°C)		M	Ms <sup>-1</sup> x 10 <sup>5</sup>	s <sup>-1</sup> x 10 <sup>4</sup>	
30	30A	0.070	0.90	1.30	
	30B	0.097	1.05	1.08	
	30C	0.112	1.81	1.61	
40	40A	0.019	2.00	2.78	
	40B	0.072	2.11	2.93	
	40C	0.150	3.31	2.21	
	40D	0.210	5.00	2.38	
50	50A	0.104	2.58	2.78	
	50B	0.104	3.13	3.00	

The HPLC analysis of 162b in solution indicated that this compound contained some impurities. These impurities may have acted as a catalyst, or may have been directly involved in the decomposition. The mono-4-methyl derivative (173a) prepared by the same method as 162b is also expected to have similar impurities. The effect of a nucleophile on the decomposition can be observed when the decomposition of 162b is repeated in unpurified chloroform (containing 0.75% ethanol as a stabilizer). Decomposition was visibly much quicker in unpurified chloroform as compared to purified chloroform. The impuri es may have an effect on the rate of decomposition but the effect could not be quantized.

The decomposition of 173a was enhanced by the addition of a radical initiator

ſ

<sup>154.</sup> T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry," Harper and Row. New York, 2 ed., 1981, p175.

and slowed by the addition of a radical inhibitor, thus suggesting a radical mechanism. The addition of 3-chloroperoxybenzoic acid (initiator) (175) increased the rate by almost ten-fold while the addition of 4-t-butylcatechol (inhibitor) (176) slowed the reaction by three-fold. The plot of the natural logarithm of the concentration vs time for the decomposition of 173a in the presence of inhibitor and initiator is presented in Figure 11.



Sulfur was found to be a contaminant in 173b. The mono-4-methyl derivative (173a) prepared by the same method as 162b is expected to have similar impurities. An experiment was conducted to see if the presence of sulfur had any effect on the decomposition reaction. Two identical samples were prepared but elemental sulfur (S<sub>8</sub>) was added to one. The sample containing sulfur did not exhibit a rate enhancement but the decomposition showed a minor inhibited effect (initial rate 1.7 times slower then the sample with no sulfur). The comparison of the two rate profiles is shown in Figure 12. The inhibiting effect on the rate of decomposition of 173a by elemental sulfur was not surprising as this effect of sulfur on some radical reactions has been well documented.<sup>155</sup> This experiment was not conclusive as the sulfur added was S<sub>8</sub> while sulfur exists in many allotropes<sup>105</sup> and one or more of these allotropes may have been catalyzing the decomposition.

Arrhenius parameters can be determined from the plot of ln k vs 1/T. The energy of activation ( $E_{act}$ ) was found to be 8 kcal/mol. The low energy of activation indicates that the bond being broken is relatively weak. The entropy of activation ( $\Delta S^{\mp}$ ) was determined from the Arrhenius plot to be -52 e.u.. The large  $\Delta S^{\mp}$  gives an indication the the transition state is relatively stable.

P. D. Bartlett and D. S. Trifan, J. Polymer Sci., 20, 457 (1956); P. D. Bartlett and H. Kwart, J. Am. Chem. Soc., 72, 1051 (1950); P. D. Bartlett and H. Kwart, J. Am. Chem. Soc., 72, 1051 (1950); J. L. Kice, J. Polymer Sci., 19, 132 (1956).

From a comparision of the initial rates to the concentration the order of the reaction was determined. The decomposition displayed an erratic order of 1.5 at  $30^{\circ}$ C and 0.8 at  $40^{\circ}$ C. At lower temperatures the decomposition exhibits an induction period ...aking determination of the initial rates difficult. These orders suggest that a complex mechanism may be involved in the decomposition.

Figure 10. Plot of Concentration vs Time for the Decomposition of Chloro(mono-4methyltriphenylmethyl)disulfide (173a) at 30°C.



~

\* "\*

Figure 11. Plot of Concentration vs Time for the Decomposition of Chloro(mono-4methyltriphenylmethyl)disulfide (173a) at 40°C. The Effect of Inhibition and Initiation.

No.

-



Figure 12. Plot of Concentration vs Time for the Effect of the Addition of Elemental Sulfur on the Decomposition of (173a)

1.





\_\_\_\_\_

ĺ

ŗ



# 4.5.4 <u>A Probable Radical Mechanism for the Decomposition of</u> the Chloro(triphenylmethyl)disulfides and Trisulfides.

A radical mechanism can be proposed for the decomposition of the chloro(triphenylmethyl)sulfides (162a, 162b and 162c) to triphenylchloromethane (164). This mechanism is supported by the following observations:

1. The identification of 164, several bis(triphenylmethyl)sulfides 167, and sulfur as decomposition products.

2. Rate studies on the decomposition of chloro(mono-4methyltriphenylmethyl)disulfide (173a) showed induction periods which were more pronounced at lower temperatures.

3. The rate of the decomposition was speeded by the introduction of a radical initiator or slowed by the introduction of a radical inhibitor.

It is possible to propose three initiation pathways for such a decomposition to occur.

The mechanism shown below (Scheme 32) involves scission of the carbon sulfur bond of the disulfide to form a chloroperthiyl radical ( $\cdot$ SSCI) and a triphenylmethyl radical ( $Ph_3C \cdot$ ).

# Scheme 32

The second pathway (Scheme 33) is similar except that the initial scission occurs at the sulfur chlorine bond to form a chlorine radical (Cl $\cdot$ ) and a triphenylmethylperthill radical (Ph<sub>3</sub>CSS $\cdot$ ).

#### Scheme 33

Finally a mechanism involving the scission of the sulfur-sulfur bond to form the triphenylmethylthiyl radical ( $Ph_3CS$ ) and the sulfur-chlorine radical ( $\cdot$ S-Cl)

(Scheme 34).

#### Scheme 34

The distribution of the decomposition products indicated that Scheme 33 was most likely the correct mechanism since any free-radical mechanism must account for all the observed products. The bis(triphenylmethyl)sulfides 167 could have been formed by either radical termination reactions or by the attack of a triphenylmethylperthiyl radical on another sulfide. The tetrasulfide 167d could have been formed by the combination of two triphenylmethylperthiyl radicals. The trisulfide 167c could have been formed by the radical attack of the triphenylmethylperthiyl radical on the  $\alpha$ -sulfur of the chlorodisulfide or a previously formed sulfide. The radical reactions that lead to these observed products are shown below (Scheme 35).



#### Scheme 35

Further evidence supporting this proposed mechanism (Scheme 33) comes from a semi-empirical study by Bergson<sup>156</sup> on the interaction between lone-pair electrons and the application of these results to the structure and reactivity of sulfur chains. Radical species with two sulfur atoms (R-SS•) were found to be more stable than those with one sulfur atom (R-S•). This conclusion was based on the observation that the energy required to break the sulfur-sulfur bond in a disulfide was higher

í

<sup>156.</sup> G. Bergson, Ark. Kem., 18, 409 (1962).

than that required to break a sulfur-sulfur bond within compounds containing more than two sulfur atoms.

It was shown that the methaneperthial radical  $(CH_3S_2\bullet)$  does not add to cyclohexene whereas the methanethial radical  $(CH_3S\bullet)$  adds readily.<sup>157</sup> This lack of reactivity is consistent with the idea that  $CH_3S_2\bullet$  is a significantly more stable, and thus less reactive, radical than  $CH_3S\bullet$ .

Support for this radical mechanism can also be found in decomposition studies of other disulfides. The photolysis of t-butyldisulfide,  $^{158,159}$  which gave a mixture of products has been proposed to occur via a radical mechanism (Scheme 36). The identified products were proposed to form from the initial scission of one sulfurcarbon bond to give the t-butyl ((CH<sub>3</sub>)<sub>3</sub>C•) and the t-butylperthiyl ((CH<sub>3</sub>)<sub>3</sub>CS5•) radicals. Coupling of two perthipler radicals gave the tetrasulfide while the trisulfide formed from the attack of a perthipler radical on a second disulfide. The butane and isobutylene formed as a result of a hydrogen abstraction by the t-butyl radical. Bennett and Brunton<sup>160</sup> have acquired an ESR spectrum which was attributed to the t-butylperthipler radical, from the photolysis of chloro(t-butyl)disulfide at -86°C in toluene.



Scheme 36

A variety of other reactions proposed to involve radical mechanisms also lend

<sup>157.</sup> I. Kende, T. L. Pickering and A. V. Tobolsky, J. Am. Chem. Soc., 87, 5582 (1965).

<sup>158.</sup> D. Grant and J. Van Wazer, J. Am. Chem. Soc., 86, 3012 (1964).

<sup>159.</sup> G. W. Byers, H. Gruen, H. N. Scott and J. A. Kampmeier, J. Am. Chem. Soc., 94, 1016 (1972).

<sup>160.</sup> J. E. Bennett and G. Brunton, J. Chem. Soc. Chem. Commun, 62 (1979). These results are supported by molecular calculation on the bond energies of disulfides, M. D. Ryan, "Organopolycalcogenides, New Bond Energy Results and Synthesis Via The First Selenium Transfer Reagent," Ph.D. Thesis, McGill University (1988).
support to Scheme 33. Free-radicals have been proposed in the decomposition of methanesulfenyl chinesel (157) and methanesulfur trichloride,<sup>161</sup> however, electron spin resonance studies of the decompositions were inconclusive. Zack and Shreeve<sup>162</sup> have proposed a radical mechanism for the addition reaction of chloro(trifluoromethyl)disulfide (161) with olefins, to yield 1,2-addition products. addition was observed to involve the chlorine radical The and trifluoromethylperthiyl radical (CF<sub>3</sub>CSS•). Haszeldine and Kidd observed that bis(trifluoromethyl)trisulfide decomposed irradiation by upon a radical mechanism.<sup>163</sup>

٤

ſ

Many free-radical reactions exhibit induction periods.<sup>164</sup> The induction period observed for the decomposition of the chlorodisulfides in this study provided further evidence for the involvement of a radical mechanism. The induction period indicates that decomposition of the chlorodisulfide proceeds through such a mechanistic pathway, and that a steady state concentration of radicals must be obtained before the decomposition can occur.

It is also possible to envision the triphenylmethylperthiyl radical (Ph<sub>3</sub>CSS•) undergoing two types of decomposition, a  $\beta$ -elimination or an  $\alpha$ -scission. The  $\beta$ -elimination would form singlet diatomic sulfur and the triphenylmethyl radical while the  $\alpha$  scission would form triplet diatomic sulfur and the triphenylmethyl radical. These mechanisms have been discussed previously in connection to the generation of singlet sulfur (Section 37).

$$Ph_{3}C - S - S \cdot Ph_{3}C \cdot + \cdot S - S \cdot$$

$$Ph_{3}C - S - S \cdot Ph_{3}C \cdot + S = S$$

#### Scheme 37

- 162. N. R. Zack and J. M. Shreeve, J. Chem. Soc., Perkin Trans. 1, 614 (1975).
- 163. R. N. Hazeldine and J. M. Kidd, J. Chem. Soc., 3219 (1953).
- 164. E. S. Swinbourne, "Analysis of Kinetic Data," Thomas Nelson and Sons Ltd, Don Mills, (1971).

<sup>161.</sup> I. B. Douglass, R. V. Norton, R. L. Weichman and R. B. Clarkson, J. Org. Chem., 34, 1803 (1969).

## 4.6 Reactions of the Chloro(triphenylmethyl)sulfides

The reactivities of compounds containing S-Cl bonds have been extensively studied.<sup>107</sup> It was therefore not considered necessary to do an exhaustive study of the sulfides 162a, 162b and 162c but, a few representative reactions were investigated. Many of the reactions were carried out only to show the typical reactivities of these chlorosulfides and hence they are presented only to show this fact. If there were no unexpected results the reaction was discussed as succinctly as possible.

#### 4.6.1 Nucleophilic Displacements

100

. .

The chlorosulfides 162a, 162b and 162c underwent normal displacement reactions with a variety of nucleophiles. Reaction with butylmagnesium chloride gave the corresponding butyl(triphenylmethyl)sulfide (177) (Scheme 38). The reaction of 162b also led to the formation of a small amount of bis(triphenylmethyl)tetrasulfide 167d, as confirmed by comparison of the <sup>13</sup>C NMR spectrum with that of the authentic compound.<sup>165</sup> The reaction of 162a gave the expected sulfide but in a modest yield (17%) as compared to 162c and 162b.

# $Ph_3C - S_x - CI + Bu - MgCI - Ph_3C - S_x - Bu + MgCl_2$ Scheme 38

Displacement of the chlorine atom of 162 with butyllithium also yielded sulfides 177 (Scheme 39). The substitution did not appear to be 100% site selective as the product of 162b disulfide 177b was contaminated with a small amount of monosulfide 177a confirmed by the <sup>13</sup>C NMR spectrum.

PhyC-Sy-Cl + Bu-L PhyC-Sy-Bu + LiCl

## Scheme 39

Harpp and  $Ash^{21}$  have previously prepared unsymmetrical trisulfides by the condensation of thiols with 162b. Therefore the reaction of 162a and 162c with thiols should yield di- and tetrasulfides, respectively. This was investigated by

165. T. Nakabayashi, J. Tsurugi and T. Yabuta, J. Org. Chem., 29, 1236 (1964).

carrying out a representative reaction. The sulfides were condensed with a sample of 1-butanethiol (Scheme 40). The reaction of 162a and 162b gave sulfides 177 identical to those obtained in the reaction of 162b and 162c with either butyllithium of butylmagnesium chloride, as expected. The reaction of 162c yielded the tetrasulfide (177d).

-----

1

## Scheme 40

The <sup>13</sup>C NMR shifts for the isolated butyl(triphenylmethyl)sulfides (177) are summarized below in Table 13. The arbitrary numbering of the carbon atoms is for ease of assignment and begins at the terminal methyl and proceeds consecutively. The introduction of an additional sulfur atom resulted in a downfield shift for <sup>13</sup>C NMR signals for the carbons  $\alpha$  to the sulfur atoms, as expected.



Table 13. Summary of the <sup>13</sup> C NMR Chemical Shifts for the Butyl(triphenylmethyl)sulfides (177) (X = $\#$ of S atoms)									
x	X <sup>13</sup> C NMR shifts (ppm)								
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
1	13.62	22.12	30.65	31.69	<b>66.3</b> 1	145.06	127.75	129.57	126.45
2	13.53	21.46	30.84	36.38	70.79	143.86	127.68	130.07	126.75
3	13.60	21.53	31.01	39.31	73.19	143.55	127.85	130.42	127.11
4	13.62	21.49	30.98	38.86	73.50	143.08	127.93	130.28	127.19

The monosulfide (177a) was also prepared by the reaction of 164 with 1butanethiol (Scheme 41).<sup>166</sup> The <sup>1</sup>H and <sup>13</sup>C NMR spectra were identical to those obtained from the reaction of 162a and either butyllithium or butylmagnesium chloride.

ì

#### Scheme 41

The condensation of 162b and 162c with triphenylmethanethiol (163a) also gave the expected products (Scheme 42). The reaction of 162b gave bis(triphenylmethyl)trisulfide (167c) (80%) while 162c yielded bis(triphenylmethyl)tetrasulfide (167d) (88%). These compounds are examined in detail in Chapter 5. No reaction was observed between 162a and 163a, presumably due to steric interactions.

$$Ph_3C - S_1 - CI + Ph_3C - SH - Ph_3C - S_1 - CPh_3 + HCI$$

## Scheme 42

The reaction of O-ethylxanthic acid potassium salt 178 with each sulfide 162b and 162c gave the mixed sulfide 179 and shown below (Scheme 43).



It was anticipated that an easy route for the formation of the 177d would be the condensation of a sulfur chloride with hydro(triphenylmethyl)di- or trisulfides 180. There is one example where hydrosulfides were synthesized from chlorosulfides using hydrogen sulfide gas.<sup>167</sup> The major limitation of this method was the large

<sup>166.</sup> E. von Meyer and P. Fischer, J. Prakt. Chem., [2], 82, 521 (1910); Chem. Abstr., 5, 1595 (1910).

<sup>167.</sup> H. J. Langer and J. B. Hyne, Can. J. Chem., 51, 3403 (1973).

excess of hydrogen sulfide gas required (4 moles of  $H_2S$  for 0.02 moles of hydrosulfide produced). It was thought that perhaps that the hydrosulfides could be produced from the sulfides by the nucleophilic displacement of the chlorine with an excess of sodium hydrosulfide (Scheme 44).

ł

1

 $Ph_3C - S_x - Cl + NaSH - Ph_3C - S_{(x+1)} - H + KCl$ 

#### Scheme 44

The reaction did not yield the hydrosulfides, but instead gave mixtures. Reaction of 162a gave a mixture with the major products being bis(triphenylmethyl)trisulfide (167c), and appreciable concentrations of 164 and 169. Reaction of 162b gave a mixture of bis(triphenylmethyl)tri- (167c), penta-(167e) and hexasulfides (167f). The largest component of the mixture 166e, was isolated by recrystallization. Reaction of 162c also gave a complex mixture but bis(triphenylmethyl)heptasulfide (167g) was isolated. The products isolated indicate that the hydrosulfide was likely formed but, then underwent a reaction with a second molecule of the chlorosulfide (Scheme 45). This proposal is supported by the reaction of the chlorosulfides with 163a yielded the bis(triphenylmethyl)sulfides (167) (see above).

 $Ph_3C-S_{(x+1)}-H + Ph_3C-S_x-CI - Ph_3C-S_{(2x+1)}-CPh_3 + HCI$ 

#### Scheme 45

The reaction with potassium phthalimide (181) with the sulfides 162b and 162c which yielded the corresponding phthalimido sulfides (182) (Scheme 46). The structure of 182a was identified from the <sup>13</sup>C and <sup>1</sup>H NMR spectra and confirmed by elemental analysis.



Reactions of 162b were studied further because of the ease of purification of this compound. Reduction of 162b with lithium aluminium hydride formed the thiol. The formation of hydrogen sulfide was also evident as detected by its strong odor. These products would form by the reduction of the sulfur-sulfur and sulfur-chlorine bonds respectively. Substitution also occurs with ethoxide anion. In the presence of excess ethoxide 162b decomposed with the formation of ethyl(triphenylmethyl)ether (183), confirmed by comparison to an independently synthesized compound.<sup>168</sup>



(183)

The difference in reactivities between 162a and 162b and 162c is likely a result of steric effects of the triphenylmethyl group. These effects would be large for 162a, and smaller for 162b and 162c as the introduction of sulfur atoms would place a place a greater distance between the reactive S-Cl group and the triphenylmethyl group.

168. J. F. Norris and R. C. Young, J. Am. Chem. Soc., 46, 2582 (1924)

103

#### 4.6.2. Reaction of Chloro(triphenylmethyl)sulfides (162) With 1.3-Dienes.

ų.

Í,

When in solution chlorodisulfide 162b slowly decomposed with the formation of sulfur and triphenylchloromethane (164), along with several other products (see above). It is reasonable to propose the loss of two sulfur atoms from 162b to yield 164 involves the generation of  $S_2$  as the intermediate sulfur species.



For the purpose of determining whether  $S_2$  was generated in the decomposition of 162b; a sample of 2,3-dimethyl-1,3-butadiene 109 and disulfide 162b were refluxed in chloroform-d for 2 h and a <sup>1</sup>H NMR spectrum of the reaction mixture acquired. The spectrum exhibited signals which corresponded to the trapping of  $S_2$ with characteristic peaks for 1,2-dithia-4,5-dimethyl-4-cyclohexene (107), at 1.75 and 3.20 ppm. The reaction was repeated on a larger scale in chloroform. Silica gel chromatography of the mixture with 20% chloroform in hexanes gave an isolated product which was consistent with a compound originally proposed to be a polymeric trap (140) of  $S_2$ , with <sup>1</sup>H NMR signals at 3.76 and 1.79 ppm.<sup>169</sup> The polymeric species 140 was identified as the cyclic tetrasulfide, 1,2,3,4-tetrathia-6,7dimethyl-6-cyclooctene (127). The structural assignment for tetrasulfide 127 was described in Section 2.3.



The successful isolation of the trapped adduct in any form was encouraging and the reaction was repeated several times until signals in the <sup>1</sup>H NMR spectrum

<sup>169.</sup> D. N. Harpp and J. G. MacDonald, unpublished results.

consistent with the isolation of the cyclic disulfide (107) (1,2-dithia-4,5-dimethyl-4cyclohexene) were identified. The disulfide was initially obtained as a mixture with tetrasulfide 127, as indicated by the <sup>1</sup>H NMR spectrum. Chromatography with 20% chloroform in hexanes on silica gel did not allow for the separation of the disulfide from the tetrasulfide. The overall reaction for the decomposition of disulfide 162b to form the two trapped adducts is shown below (Scheme 47).

1.....



#### Scheme 47

A <sup>1</sup>H NMR spectrum of the mixture of disulfide 107 and tetrasulfide 127 isolated from the decomposition of disulfide 162b is displayed in Figure 14. The signals at 3.20 and 1.75 ppm corresponded to 107 (indicated by d) while those at 3.76 and 1.79 ppm corresponded to 127 (indicated by t).

The decomposition was further investigated by varying the reaction conditions. The sulfuration products were isolated as the mixture and no attempt was made to separate the disulfide from the tetrasulfide until the yield was maximized. The reaction conditions and yields are summarized in Table 14.

The initial experiments were conducted with the diene in excess so that the generation of  $S_2$  could be confirmed. Once generation of  $S_2$  was demonstrated the diene was introduced as the limiting reagent (the  $S_2$  precursor was in excess) so that the maximum yield of the cyclic disulfide 107 could be obtained.

The introduction of a radical inhibitor did not greatly effect the yields of trapped adducts, but a lower disulfide to tetrasulfide ratio was observed. Harpp and Macdonald<sup>73</sup> reported that disulfide 107 could be was isolated by chromatography on alumina. Replacing alumina as the solid support did not allow for separation of the disulfide from the tetrasulfide in this work.

Ratio <sup>a</sup>	Solvent (°C)	Temp (h)	Time (%)	Yield <sup>b</sup> 107/12	Ratio 7	Comments	
1:3	CHCl <sub>3</sub>	40	12	23	1:3		
1:3	$CH_2Cl_2$	reflux	1	22	1:3		
1:3	C <sub>4</sub> H <sub>8</sub> O	reflux	1	20	1:6		
3:1	$CH_2Cl_2$	reflux	1	56	1:3.5	column silica	
3:1	$CH_2Cl_2$	reflux	1	52	1:4	column alumina	
3:1	CHCl <sub>3</sub>	reflux	1	44	1:6	with inhibitor	
3:1	C <sub>6</sub> H <sub>6</sub>	reflux	1	40	1:6	with inhibitor	
3:1	$CH_2Cl_2$	reflux	8	49	1:4		
3:1	$CH_2Cl_2$	rt	8	52	1:2.5		
3:1	$CH_2Cl_2$	rt	8	40	1:2.5	ambient light	
6:1	$CH_2Cl_2$	reflux	1	61	1:3.3		
6:1	$CH_2Cl_2$	reflux	12	52	1:3.3		
6:1	CH <sub>2</sub> Cl <sub>2</sub>	rt	12	58	1:2.5		
<sup>a</sup> Ratio - refers to the molar ratio of chloro(triphenylmethyl)disulfide (9)							
to 2,3-dimethyl-1,3-butadiene used in the reaction. b Yields are based on the mass of the disulfide expected.							

Table 14. Summary of  $S_2$  Trapping Experiments of 2,3-Dimethyl-1,3-butadiene with Chloro(triphenylmethyl)disulfide (162b)

\_

ſ

\_\_\_\_\_

106

Figure 14. <sup>1</sup>H NMR Spectrum of a Mixture of Disulfide 107 and Tetrasulfide 127 from the Decomposition of Chlordisulfide 162b with 2,3-Dimethyl-1,3-butadiene 109. d = disulfide 107 and t = tetrasulfide 127



The reaction was repeated in dichloromethane and the eluent used for the silica gel chromatography changed until a separation of the 107 from 127 was achieved. The separation was obtained with 5% chloroform in hexanes as the eluent, and the fractions collected from the chromatography were one-third the normal size.

٤,

Į

The major problem in obtaining a separation was the small difference in the  $R_f$  values ( $R_f$  difference 0.04; solvent system 5% chloroform in hexanes) for 107 and 127. This small difference in  $R_f$  further supports a similar structure for the two sulfuration products.

The reaction conditions were once again modified to obtain the maximum isolated yields of 107 and 127. The reaction conditions and yields are summarized in Table 15.

**Table 15.** Summary of  $S_2$  Trapping Experiments of 2,3-Dimethyl-1,3-but adiene with Chloro(triphenylmethyl)disulfide (162b). Isolation of 107 and 127.

Ratio <sup>a</sup>	Solvent	Temp	Time	Y	ïeld		
	(°C)	(h)		Disulfide	Tetrasulfide		
3:1	$CH_2Cl_2$	50	1	27	32		
3:1	$CH_2Cl_2$	50	2	29	35		
3:1	$CH_2Cl_2$	rt	18	26	33		
3:1	$CH_2Cl_2$	rt	18	23	36		
3:1	$CH_2Cl_2$	50	18	14	47		

<sup>a</sup> Ratio refers to the molar ratio of chloro(triphenylmethyl)disulfide to the diene used in the reaction.

The best yield of the cyclic disulf le was 29% which although not high was better than that obtained in the reaction of 89 and  $81.^{73}$  The minor differences in the isolated yields above can be attributed to chromatography.

From the known  $S_2$  procedures and the properties of 162b it is possible to propose three mechanisms which could lead to the formation of the trapped adducts

(Scheme 48-50).

A possible mechanism (Scheme 48) involves a concerted transfer of two sulfur atoms to the 1,3-diene with concomitant formation of chloromethane 164. The triphenylmethyl group is sterically hindered thus a concerted process is unlikely. It is unknown if  $S_2$  is actually formed as a discrete species in solution. A concerted transfer of the  $S_2$  unit is a distinct possibility in the four reported examples of successful  $S_2$  trapping



#### Scheme 48

The formation of  $S_2$  as a discrete species was the mechanism proposed in all of the reactions reported. The second mechanism (Scheme 49) involves the formation of diatomic sulfur as a discrete species in solution. Formation of free  $S_2$  has been proposed to account for the isolation of cyclic trisulfide from the reaction of  $S_2$  with hindered alkenes.<sup>170</sup>



#### Scheme 49

As indicated above, a concerted reaction of disulfide 162b is unlikely so a stepwise mechanism could account for the formation of the S<sub>2</sub> as a discrete species. The initial step would be homolysis of the sulfur-chlorine bond in 162b to yield the triphenylmethylperthiyl radical (see section 4.5) and the chlorine radical. The perthiyl radical could then undergo a  $\beta$ -elimination to form diatomic sulfur and the triphenylmethyl radical (such a cleavage is likely as the triphenylmethyl radical is very stable). Reaction of S<sub>2</sub> with the diene would yield the isolated products. The reaction of S<sub>2</sub> with dienes to yield tetrasulfide has only been indicated in two

170. K. Steliou, Y. Garneau, G. Milot, P. Salama, J. Am. Chem. Soc., 112, 7819 (1990).

instances. Nicholau<sup>76</sup> isolated a tetrasulfide in the reaction of dithiatropazine (94) with diene 110. Harpp and MacDonald<sup>73</sup> found that a polymeric species (now shown to be tetrasulfide 127) was isolated in the reaction of pentasulfide 89 and dibromide 81 in the presence of 2,3-dimethyl-1,3-butadiene 109. Tetrasulfide 127 has also been isolated in the decomposition of dialkoxydisulfides 124 (Section 2.3)

3

1

The third mechanismic possibility (Scheme 50), the most probable, involves the formation of the 1,4-addition product which would decompose to yield disulfide 107 and 164. The mechanism is supported by work of Mueller and Butler<sup>171</sup> on the reaction of sulferyl halides with 1,3-dienes.



Scheme 50

The reaction of sulfenyl halides to conjugated dienes, under kinetic control initially yields one or both of the 1,2-anti-adducts, 184 and 185 (Scheme 51). The 1,2-adducts would be in equilibrium with the thiiranium chloride intermediate (186). If the interconversion is slow, the thermodynamically more stable 1,4-addition adduct 187 would be formed. A similar mechanism likely occurs for the addition of chlorodisulfide 162b to 1,3-dienes as described below.



Scheme 51

171. W. H. Mueller and P. E. Butler, J. Org. Chem., 33, 2642 (1968).

110

The initial reaction between chlorodisulfide 162b and diene would involve the electrophilic attack of one double bond on the sulfur atom forming the corresponding 1,2-addition products 188 and 189 (as above). The 1,2-addition adducts could then rearrange to the more stable 1,4-addition adduct (190). Formation of the cyclic disulfide and tetrasulfide could be produced by the process displayed below (Scheme 52). The 1,4-addition adduct 190 could undergo a cleavage of the sulfur-carbon bond to form the stable triphenylmethyl cation and the sulfur anion. The sulfur anion could eliminate the chlorine atom to form the disulfide. If the sulfur anion reacted with a second molecule of 162b then the intermediate triphenylmethyl tetrasulfide (191) would be formed. Breaking of the sulfur carbon bond in 191 would give the sulfur anion which could once again eliminate the chlorine atom and give the tetrasulfide 127.



There is proton NMR evidence to support the proposal displayed below involving the 1,4-addition product (Scheme 52). Shown below in Figure 15 is the <sup>1</sup>H NMR spectra for the reaction of disulfide 162b with 2,3-dimethyl-1,3-butadiene 109 followed over 96 h. The 1,4-addition adduct is indicated by "a" and the cyclic disulfide 107 by the "d"; the spectra are arranged chronologically.

There was no signal in the initial spectra which corresponded to the cyclic disulfide. Over time the intensity of the signal assigned to the disulfide increased with a corresponding decrease in other signals which could be assigned to the 1,4-addition adduct 190 which are described below. From NMR shift tables<sup>172</sup> signals can be assigned to all of the protons for the two 1,2-addition products and the 1,4-addition product 190. The possible NMR assignments are displayed below.

. **m**a

<sup>172.</sup> E. Pretsch, J. Seibl, W. Simon and T. Clerc, "Tables of Spectral Data for Structure Determination of Organic Compounds," Springler-Verlag, New York, 2 ed., (1989), p H16.

Figure 15. <sup>1</sup>H NMR Spectra for the Addition of 162b to 2,3-Dimethyl-1,3-butadiene (109) Over 4 Days. The Spectra Ranging From 2.25-4.5 ppm. a = Proposed 1,4-Addition Adduct; d = Cyclic Disulfide 107

. .

ſ





The signal observed at 4.08 ppm in Figure 15 would correspond to a structure such as a  $\beta$ -chloroalkene (192) which is similar to the proposed 1,4-addition adduct. There is a signal observed at 4.04 ppm which would correspond to 192.



## Estimated Chemical Shifts for Structures Related to Scheme 52

ł,

and the second s



The shifts of the methyl groups for the 1,4-addition adduct are proposed to be at 2.28 and 2.34 ppm while signals are found at 2.33 and 2.41 ppm.

The assignment of the proton alpha to the  $Ph_3CSS$  group has to be considered carefully. The triphenylmethyl disulfide group has a profound effect on the shift of the proton on the carbons bonded directly to the sulfurs. The effect can be as seen in the <sup>1</sup>H NMR chemical shifts of the butyl(triphenylmethyl)sulfides (177). The addition of a sulfur atom converting the monosulfide to the disulfide results in a shift of 0.5 ppm upfield from 2.1 to 1.6 ppm. The proposed shifts from the chemical shift tables are based on alkyl sulfides with no effect for the additional sulfur atom or the effect of the triphenylmethyl group considered.

All of the above signals decreased in intensity with the corresponding increase in intensity of the signal assigned to the cyclic disulfide. The NMR chemical shifts indicate that the formation of the cyclic disulfide must occur through the 1,4addition product as the intermediate.

It was anticipated that the reaction of chloro(triphenylmethyl)trisulfide 162c with 1,3-dienes would be a direct route to the synthesis of cyclic trisulfides. The synthesis of cyclic trisulfides has not been successful in our laboratory using sulfur transfer reagents.<sup>173</sup> The reaction of 162c did not yield the trisulfide 145 but instead a 1:3 mixture of the 107 and 127 was isolated (35% yield) (Scheme 53). It would appear that the lack of formation of 145 is a direct result of stability. The trisulfide could not be obtained from the desulfurization of the tetrasulfide in the presence of triphenylphosphine (see Section 2.3).

There was no reaction between 162a and diene 109 even when the mixture was refluxed for 72 h. The lack of reactivity of 162a must result from the steric effects of the triphenylmethyl group.



Scheme 53

173. D. N. Harpp, R. A. Smith and K. Steliou, J. Org. Chem., 46, 2072 (1981).

#### 4.6.3 Reaction Between Chloro(triphenylmethyl)monosulfides and Thiocarbonyls.

Reactions of various chloromonosulfide: with thiocarbonyls usually led to the formation of the addition adducts,  $\alpha$ -chlorodisulfides, (Scheme 54).<sup>174</sup> However, when similar reactions were performed with 162a, no adducts were isolated (see below).



#### Scheme 54

When 162a and 4,4'-dimethoxythiobenzophenone (193) were mixed in chloroform at room temperature a yellow precipitate was observed almost immediately. The precipitate was identified as sulfur and was isolated in near quantitative yield (92%) as expected for the conversion of 162a to 164. Analysis of the reaction mixture using <sup>13</sup>C NMR spectroscopy showed the presence of only two components, the starting thioketone 193 and 164. The proposed reaction sequence is displayed below (Scheme 55). Silica gel chromatography of the reaction mixture resulted in the isolation of 193 and 169 in yields of 87% and 89% respectively. The hydrolysis of triphenylchloromethane (164) to triphenylmethanol (169) occurs during chromatography as independently verified.



<sup>174.</sup> The reaction of sulfenyl chlorides with various thioketones has been studied by Senning and co-workers For example see H. C. Hansen, B. Jensen and A. Senning, Sulfur Lett., 3, 181 (1985); H. C. Hansen, B. Jensen and A. Senning, Sulfur Lett., 6, 59 (1987).



Scheme 55

The reaction between 162a and 193 was further examined by high performance liquid chromatography. The chromatogram of the reaction mixture gave peaks which were identified to be sulfur allotropes  $S_7$ ,  $S_8$  and  $S_9$ . The precipitate formed in the reaction was only partially soluble in carbon disulfide and had a large melting point range, (95-125°C) indicating that it consisted partially of polymeric sulfur. The identification of the sulfur allotropes suggests that a concatenation of sulfur atoms occurred during the reaction; sulfur rings can be formed from sulfur chains.<sup>22,102</sup>

The scope of the reaction was investigated by substituting, bis(4-tolyl)trithiocarbonate (194) for 193. The reaction of 194 and 162a resulted in the precipitation of sulfur from the reaction mixture. The sulfur was once again isolated almost quantitatively for the conversion of 162a to 164, (89%) although its deposition appeared to be a slower process than in the reaction of 193 above. A <sup>13</sup>C NMR spectrum of the reaction mixture gave signals confirming the presence of starting material 194 and 164. Chromatography yielded 194 (83%) and 169 (75%), formed from the hydrolysis of 164.



In order to investigate the possibile formation of stable intermediates, the addition was conducted at low temperature (-78°C). On addition of thioketone 193 to 162a the blue of the thioketone dissipated to yield a red solution. During slow warming, the reaction did not appear to change until about -20°C, when the blue of the thioketone redeveloped. The sulfur precipitation was not observed until the solution reached temperatures of 0-5°C.

The regeneration of thicketone 193 or trithiccarbonate 194 indicate that the sulfur extrusion should be catalytic. In order to test this hypothesis, 193 was added to a large excess of 162a (75 equivalents). Once again a high yield of sulfur (98%) was isolated, as expected, in the conversion of 162a to 164. Chromatography gave the starting thicketone (67%) and the hydrolysis product 169 (85%).

Several experimental techniques were used to study these reactions. Substitution of chloro(mono-4-fluorotriphenylmethyl)monosulfide (172b) for 162a allowed the reactions to be followed using low temperature <sup>19</sup>F NMR spectroscopy, as 172b would be converted to mono-4-fluorotriphenylchloromethane (174b) under similar reaction conditions (Scheme 56).

1

118



### Scheme 56

The low temperature NMR experiments were conducted by preparing a solution of each reactant in deuterated dichloromethane and cooling to -78°C. A solution of the fluoro derivative 172b and the appropriate thicketone were mixed by shaking and quickly transferred to a 5 mm NMR tube at -78°C. The sample was then introduced into the spectrometer probe which had been previously cooled to -78°C. The spectrometer probe was slowly warmed to ambient temperature and spectra acquired at various temperatures following a 15 ...inute equilibration period at each temperature. The spectra for the reaction of 172b and thicketone 193 are presented in Figure 16 while those for the reaction of 172b with trithiocarbonate 194 are shown in Figure 17.

The reaction between 172b and 193, (Figure 16) showed three signals in the initial spectra obtained at -68°C. The large signal (designated by m) corresponded to the starting material monosulfide 172b; a smaller signal slightly upfield (designated by c) from this corresponded to chloromethane 174b; and a signal further upfield (designated by a) has been assigned to an addition complex. At - 50°C the signal corresponding to 172b had decreased while those for 1779 and addition complex have increased. A secondary signal near the addition complex was observed indicating a complex mixture. When the solution had reached -40°C all of 172b and the addition complex have been converted to 174b.

It is possible to envision two possible addition complexes 195 and 196 for this reaction. The salt 195 would be stabilized by resonance from the methoxy groups through the aromatic rings. Formation of an addition complex other than the salt would most likely involve the  $\alpha$ -chlorodisulfide (196). The reaction of other sulfenyl

chlorides with thiocarbonyl have been examined and an  $\alpha$ -chlorodisulfide isolated.<sup>174</sup> Spectral analysis indicates that the addition complex appears to be stable only below -40°C, but was not stable enough for the detection in the <sup>13</sup>C NMR spectrum. The mechanism by which this addition complex decomposes will be discussed below.



(195)

F and an

ſ

(196)

The reaction of 194 and 172b, Figure 17, appears to either occur via a different mechanism than the reaction of 193 and 172b or the intermediate formed is shortlived and not detectable on the NMR time-scale. The initial spectrum obtained at  $61^{\circ}$ C shows two signals, the larger one (designated by m) corresponding to 172b and a smaller signal (designated by c) for 174b. Upon warming the mixture, the concentration of 172b decreased with a corresponding increase in 174b. There was no evidence for the formation of an addition complex in the reaction mixture. At  $40^{\circ}$ C one-half of 172b had been converted to 174b. Total conversion did not occur until the mixture was warmed to  $-20^{\circ}$ C, There was a temperature dependent shift in the <sup>19</sup>F NMR spectra for the reaction of both 193 and 194 with 172b.

The mechanism for the decomposition of the addition complex (195 or 196) is an interesting one to consider. The <sup>19</sup>F NMR spectral analysis showed that the addition complex was only stable below -40°C but sulfur precipitation was not observed until about 0°C. These two observations suggest the formation of an intermediate with an extra sulfur atom, such as sulfide 197 or dithiirane 198.<sup>175</sup> A similar addition complex was proposed by Still<sup>176</sup> in the reaction between thioketones and sulfur dichloride. He proposed that 193 and sulfur dichloride formed a complex at low temperature which decomposed to regenerate thioketone 193 and sulfur. It was assumed that chlorine was also formed during the reaction.



A parallel set of decomposition intermediates may be 'ormed for the reaction of 194 with 172b but there was no evidence for the formation of an initial addition complex. The lack of resonance stabilization due to the introduction of the sulfur atoms in 194 may make the formation of such an addition complex unfavorable. The HPLC analysis supported the thiosulfine intermediate as concatenation would yield a mixture of stable sulfur allotropes, and should also result in the formation of polymeric sulfur.

Attempts were attempted to follow the addition of 162a to 193 using low temperature <sup>13</sup>C NMR spectroscopy. Neither the spectra of either addition products 197 or 198 or the proposed thiosulfine product could be identified from the  $^{13}C$  NMR spectra.

175. A. Senning, H. C. Hansen, M. F. Abdel-Megeed, W. Mazurkiewicz and B. Jensen, Tetrahedron, 42, 739 (1986).

176. I. W. J. Still, G. W. Kutney and D. McLean, J. Org. Chem., 47, 555 (1982).

Figure 16. <sup>19</sup>F NMR Spectra for the Addition Reaction Between 4,4'-Dimethoxythiobenzophenone (193) and Chloro(mono-4fluorotriphenylmethyl)monosulfide (172b). m = monosulfide 172b; c =chloromethane 174b; a = addition adduct.

ſ



Figure 17. <sup>19</sup>F NMR Spectra for the Addition Reaction Between Bis(4tolyl)trithiocarbonate (194) and Chloro(mono-4-fluorotriphenylmethyl)monosulfide (172b). m = monosulfide 172b; c = chloromethane 174b.

n, 24



123

# 4.6.4 Chloro(triphenylmethyl)disulfide: Attempted Preparation of a Thioozonide.

٠.

1

It was anticipated that the reaction of 162b and 193 would give an addition complex similar to that proposed above. It was hoped that the addition complex, once formed, would eliminate a molecule of 164 with the formation of a trisulfide which could cyclize to form a thioozonide (199). A thioozonide structure (82) has been proposed as the reactive intermediate in the formation of  $S_2$  from the reaction of triphenylphosphine dibromide (81) with either bis(triphenylmetal)trisulfides (80) or dicyclopentadienyltitanium pentasulfides (89) (see introduction). It was hoped that this reaction would be an entry into thioozonide chemistry and thus a singlet diatomic source. The structure of the addition complex is discussed below.



#### (199)

The reaction between 162b and thiocarbonyls differed from that of 162a above. Upon addition of a solution of 193 to a solution of 162b the blue color was immediately dissipated with formation of a red solution. When the reaction was conducted at low temperatures the red color was stable until the solution reached about 20°C when the blue was slowly regenerated in the reaction mixture. The temperature at which the addition complex decomposed was therefore much higher than that of the complex obtained in similar fashion from 162a. The greater stability would result from the addition of a third sulfur atom, which would greatly reduce the steric effects of the triphenylmethyl group.

The reaction was examined using a variety of spectroscopic techniques, <sup>13</sup>C, <sup>19</sup>F and <sup>1</sup>H NMR spectroscopy, UV and IR spectroscopy.

## 4.6.4.1 NMR Analysis

4000

s. 10

The  $^{13}$ C NMR chemical shifts of the isolated components plus those of the addition reaction mixture obtained at -40°C along with their structural assignments are reported in Table 16. The peak positions support the formation of an addition complex such as 200. If a salt formed then the shift likely would be observed at lower field.



C-1 77.60 C-2 142.16 C-3 128.08	72.51 142.73 129.97
C-2 142.16 C-3 128.08	142.73 129.97
C-3 128.08	129.97
C / 120 50	
0-4 150.58	130.36
C-5 127.65	127.58
C-6 233.27	
C-7 113.10	113.00
C-8 132.07	127.03
C-9 140.71	133.12
C-10 163.06	159.27
C-11 55.47	55.31

Several of the <sup>13</sup>C NMR signals confirmed the formation of the addition complex (200). The triphenylmethyl carbon (C-1) had shifted from its position of

77.60 ppm in 162b to 72.51 ppm in 200. This shift indicates that the sulfur-chlorine bond had been broken. The signal at 72.51 ppm corresponds to a triphenylmethyl carbon bonded to a three sulfur chain like in the similar compound, bis(triphenylmethyl)trisulfide (167c) and butyl(triphenylmethyl)trisulfide (177c) which had <sup>13</sup>C NMR shifts for C-1 at 72.55 and 73.19 ppm respectively. There was no signal corresponding to the thiocarbonyl carbon observed in the <sup>13</sup>C NMR spectrum of the reaction mixture.

- Carl

The <sup>1</sup>H NMR spectrum of the reaction mixture of 193 and 162b also indicated the formation of an addition complex. The upfield shift of the aromatic AB quartets and the methoxy protons resulted from an interruption in the resonance of the  $\pi$  system. Reaction at the C=S bond resulted in the disruption of the resonance between it and the aromatic rings. The <sup>1</sup>H NMR shifts are similar to those for bis(4-methoxyphenyl)methanethiol (201), which also does not show any conjugation between the aromatic rings through C-1. The <sup>1</sup>H NMR shifts of the isolated components and the addition complex obtained at -40°C are summarized below in Table 17.



17	n	1	1
(4	υ		,

 Table 17. <sup>1</sup>H NMR Chemical Shifts for 200 from the Reaction of Chloro(triphenylmethyl)disulfide (162b) and 4,4-Dimethoxythiobenzophenone (193).

 assignment
 starting material

assignment	starting material	addition complex	
CH <sub>3</sub> O	3.872	3.817	
aromatic	6.919 6.964	6.810 6.854	
aromatic	7.748 7.792	under Ph <sub>3</sub> peaks at 7.3 ppm	

When the reaction mixture was allowed to warm to room temperature a

complex <sup>1</sup>H NMR spectrum was obtained. Four signals corresponding to the methoxy protons were observed indicating a complex decomposition mechanism which will be discussed below.

#### 4.6.3.2 Ultraviolet-Visible Spectroscopy

The starting thicketone 193 exhibited two absorption maxima at 572 nm and 358 nm; from the changes in the two absorption maxima it was anticipated that the formation of the addition complex could be observed. Two sets of solutions of equal concentration of 162b and 193 were prepared. Due to the different extinction coefficients for the two adsorption maxima of 193 the spectra at 572 nm were examined with solutions in the concentration range of 4 X  $10^{-3}$  M while those obtained at 359 nm used solutions at concentrations 4 X  $10^{-5}$  M.

The solutions of higher concentration were used for the analysis from 450 to 800 nm. When equal concentrations of 162b and 193 were mixed, the signal at 572 which corresponded to 193, was eliminated with the formation of a new signal at 508 nm. When the mixture containing equal amounts of 162b and 193 was allowed to sit for 5 min and the spectrum reacquired, the signal at 508 nm disappeared. Similar samples prepared 15 min prior to analysis exhibited no signal at 508 nm. When excess 162b as a solid was added to 193 the signal at 508 nm is once again observed. These results indicated that the addition complex was formed and had an absorption at 508 nm but quickly decomposed. Samples prepared which had less than one equivalent of the 162b showed a linear reduction of the absorbance at 572 nm when mixed with 27. Due to the instability of the new signal, an exhaustive study was not undertaken but the spectra were taken as further confirmation for the formation of the addition adduct.

#### 4.6.3.3 IR Analysis

: ~15-

The experiments for the IR analysis of the formation of the addition complex between 162a and 193 were conducted in solutions of carbon tetrachloride. The change in the spectra was only observable above 850 cm<sup>-1</sup> due to the strong absorption of carbon tetrachloride below this wave number. Several strong signals for 193 are observed at 1035, 1168, 1255, 1303, 1506 and 1599 cm<sup>-1</sup>. The addition of 162b to a solution of 193 showed an effect on several of the signals for 193. The signal at 1168 cm<sup>-1</sup> was shifted to 1179 cm<sup>-1</sup> while the signal at 1599 cm<sup>-1</sup> was shifted to 1606 cm<sup>-1</sup> and the signal at 1506 cm<sup>-1</sup> was greatly reduced in intensity. The shift in the signal for C=C at 1599 cm<sup>-1</sup> most likely resulted for the interruption in the conjugated  $\pi$  system of 193 by the formation of the addition complex

## 4.6.3.4 <u>Analysis Using <sup>19</sup>F NMR Spectroscopy</u>

The formation of the addition complex was studied using the mono-4-fluoro derivative of 162b, chloro(mono-4-fluorotriphenylmethyl)disulfide (173b). The reaction mixture was prepared as for 172b above and the spectra obtained are presented in Figure 18. The addition complex (indicated by a) was formed even when the solution was analyzed at  $-78^{\circ}$ C. Also observed was a small signal corresponding to the starting material disulfide 173b (indicated by d). No change in the spectra was observed until the solution was warmed to about 0°C. At this temperature new signals appeared which were assigned as decomposition products of the addition complex. One signal corresponded to the chloromethane 174b (indicated by c). It was impossible to identify the other decomposition products from the <sup>19</sup>F NMR spectra.

#### 4.6.3.5 Thermal decomposition

When the reaction mixture containing 193 and 162b was warmed to ambient temperature the blue color of 193 redeveloped. This was an indication that a decomposition of 200 had occurred. This decomposition was conducted in the presence of 2,3-dimethyl-1,3-butadiene 109 to see if diatomic sulfur was generated and could be trapped. The reaction resulted in the successful isolation of the cyclic tetrasulfide 127 but in modest yield.

The reaction mixture was heated to completely decompose the addition complex and chromatographed in order to isolate all the products. Chromatography on silica gel yielded several components: sulfur (isolated yield 44% based on the expected conversion of 162b to 164), a small amount of triphenylmethane, a mixture of bis(triphenylmethyl)sulfides (41%), the starting thioketone 27, 4,4'dimethoxybenzophenone (isolated yield 75%, formed from the hydrolysis of 193 on silica gel chromatography), and triphenylmethanol (169) (isolated yield 31%, formed from the hydrolysis of 169 on silica gel chromatography). The yields were based on the amount of the triphenylmethyl group due to hydrolysis on chromatography and are therefore approximate as the exact sulfur content of the products is unknown. The formation of 193 is indicated by the appearance of the blue color but the color faded upon chromatography. The decomposition is summarized below (Scheme 57). The products isolated do not differ greatly from those isolated from the decomposition of 162b.

۰.-

÷

1

Two decomposition pathways are possible. One might involve a reversal of the addition reaction to give back starting materials which could decompose thermally. The addition complex may also eliminate triphenylchloromethane 164 forming the thioozonide which may not be stable, decomposing to give 193 and sulfur.



#### Scheme 57

The decomposition was repeated in the presence of diene 109 to determine if  $S_2$  was produced as a sulfur intermediate in the decomposition. From the decomposition tetrasulfide was identified. The reaction was not followed-up as work on the decomposition of disulfide 162b showed that it decomposed with the formation of products consistent with the trapping of  $S_2$ . It is impossible to determine if the products result from the formation of the thioozonide or results from the reaction of diene 109 with 162b.

From the data presented above there is clear evidence for the formation of the addition adduct. The most likely structures are those involving the addition of the S-Cl bond of 162b across the C=S bond of 193. From the data it is impossible to determine the mechanism by which the decomposition occurred.

Figure 18. <sup>19</sup>F NMR Spectra for the Addition Reaction Between 4,4'-Dimethoxythiobenzophenone (193) and Chloro(mono-4fluorotriphenylmethyl)disulfide (172b). a = Addition Adduct; d = Disulfide 172b; c = Chloromethane 174b

-----

r A



## **CHAPTER 5**

#### **BIS(TRIPHENYLMETHYL)SULFIDES**

#### 5.1 Introduction

Thermal decomposition of the chloro(triphenylmethyl)di- and trisulfides (162a and 162b) was thought to give a mixture of several bis(triphenylmethyl)sulfides 167 as some of the products. Identification of which sulfides were formed was difficult as there was no simple method available for the identification the sulfides.

The bis(triphenylmethyl)sulfides 167 containing 1-4 sulfurs were originally examined by Vorländer and Mittag<sup>119</sup> while the higher sulfides with 5-8 sulfurs were prepared by Nakabayashi, Tsurugi and Yabuta<sup>165</sup> who also compared all of the sulfides from 1-8 sulfurs (167a-167f). The sulfides from 3-6 sulfurs (167c-167f) were found to have nearly identical physical properties. The identification of the pure sulfides was confirmed by elemental analysis but this technique is not a routine process and is not feasible for mixtures. <sup>13</sup>C NMR spectroscopy was thought to be a possible method of identification of the sulfides as <sup>1</sup>H NMF. spectroscopy has been used to distinguish between alkyl sulfides with 1-8 sulfur atoms.<sup>177</sup>



167a X = 1167b X = 2167c X = 3167c X = 4167c X = 5167f X = 6167g X = 7

167h X = 8

<sup>177.</sup> T. L. Pickering, K. J. Sanders and A. V. Tobolsky in "The Chemistry of Sulfides," A. V. Tobolsky (Ed.), Interscience Publishers, N.Y. (1968).

As a relatively hindered disulfide, 167b has received little attention. Blicke<sup>178</sup> reported that 167b decomposed in air to form bis(triphenylmethyl)peroxide which was later confirmed by the experiments of Wood.<sup>179</sup> The thermal stability of 167b in comparison with bis(triphenylmethyl)tri- and tetrasulfide was determined by ESR and EPR spectroscopy. The order of stability decreased in the following manner trisulfide > tetrasulfide > disulfide.<sup>179</sup> The reaction of 167b with diborane was observed to occur with carbon-sulfur bond cleavage and the formation of hydrogen, triphenylmethane and (HBS)<sub>x</sub> polymer.<sup>180</sup> The mono-, di- and higher sulfides were prepared and the series compared by UV spectroscopy; no anomalies were observed.<sup>165</sup>

A spectrophotometric study of the oxidation of thiols to disulfide by iodine showed that the synthesis of 167b by this method was unfeasible.<sup>181</sup> Sosonovsky and Krough<sup>182</sup> reported that the disulfide could be isolated from a mixture of monosulfide (162a) and triethylamine after 24 h at room temperature. The disulfide 167b was also reported to be synthesized from triphenylmethanethiol (163a) with the following reagents:  $Fe(NO_3)_3 \cdot 9H_2O$  supported on clay,<sup>183</sup> VOCl<sub>3</sub><sup>184</sup> and FeCl<sub>3</sub> with Bu<sub>3</sub>SnOMe.<sup>185</sup>

#### 5.2 Synthesis

The sulfides were prepared to allow conclusive evidence for their formation in the decomposition of (162a-162c) and allow for a reexamination of the phenomena of the reported nearly identical melting points for 167c-f. The thermolysis of each sulfide above its melting point was also examined and compared to the decomposition of 167b. Each sulfide containing 3-7 sulfurs was synthesized by different methods than the literature procedures and are discussed separately. Several attempts at a new synthesis of 167b are described.

<sup>178.</sup> F. F. Blicke, J. Am. Chem. Soc., 45, 1965 (1923).

<sup>179.</sup> R. D. Costa, J. Tanaka, and D. E. Woods, J. Phys. Chem., 80, 213 (1976).

<sup>180.</sup> J. Tanaka and A. Risch, J. Org. Chem., 35, 1015 (1970).

<sup>181.</sup> J. P.Danchy, B. T. Doherty and C. P. Egan, J. Org. Chem., 36, 2525 (1971).

<sup>182.</sup> G. Sosonovsky and J. A. Krough, Liebigs Ann. Chem., 121 (1982).

<sup>183.</sup> A. Cornélis, N. Depaye, A. Gerstmans and P. Laszlo, Tetrahedron Lett., 24, 3103 (1983).

<sup>184.</sup> F. Pruess and H. Noichl, Z. Naturforsch, 42b, 121 (1987).

<sup>185.</sup> T. Sato, J. Otera and H. Nozaki, Tetrahedron Lett., 31, 3591 (1990).

The monosulfide (167a) was prepared according to the literature.<sup>119</sup> The solid displayed identical properties as those reported in the literature.

The disulfide (167b) has been of interest for several years as a very hindered disulfide. Although iodine oxidation was determined to be unfeasible, Robertson<sup>186</sup> examined the procedure as a possible source of the disulfide. A mixture of 163a and iodine refluxed in ethanol did not yield 167b but, instead 167a and sulfur were isolated.

To overcome the difficulty experienced with the iodine oxidation Bodzay<sup>187</sup> attempted a modified procedure. A sample of *n*-butyl triphenylmethylthiotin(IV) (202) was oxidized with either bromine or iodine. The oxidation produced an oily mixture which on addition of a 1:7 mixture of hexanes/ $r^2$  foromethane slowly crystallized. Recrystallization yielded a white solid which was identified as 167a (43%) a sample of 202 was slowly oxidized by air depositing a small amount of a white solid which was once again identified as 167b.

#### PhyC-S-Sn-( Bu )3

## (202)

The direct condensation of thiol 163a with monosulfide 162a gave no reaction.

The reaction of the anion of triphenylmethane and 162b gave a mixture consisting of three components: the starting triphenylmethane and 167b and 167c. The mixture of the sulfides could not be separated. Formation of disulfide 167b and trisulfide 167c were confirmed by comparison of the <sup>13</sup>C NMR spectra with those of the authentic compounds.

The disulfide was prepared by the method of Vorländer and Mittag.<sup>119</sup> Robertson<sup>186</sup> attempted to prepare 167b in this way but after recrystallization from acetone isolated only 167a as confirmed by the elemental analysis. The therma! instability of 167b has been reported.<sup>165</sup>

<sup>186.</sup> J. Robertson and D. N. Harpp, unpublished results.

<sup>187.</sup> S. J. Bodzay, "Organotin Reagents Toward the Preparation of Cyclic Disulfide and Related Compounds" Ph.D. Thesis, McGill University, (1986).
The trisulfide (167c) was prepared by the reaction of N,N'thiobisbenzimidazole<sup>188</sup> with triphenylmethanethiol. The solid obtained in this way was identical to a sample prepared by the literature procedure of condensing thiol with sulfur dichloride.<sup>165</sup> Careful recrystallization from a chloroform/ethanol mixture gave a white crystalline solid, m.p. 154-157°C which was 7°C higher than that previously reported.<sup>119,165</sup>

The tetrasulfide (167d) was prepared by the same procedure as 167c by using N,N'-dithiobisbenzimadazole (116)<sup>188</sup> in place of N,N'-thiobisbenzimadazole. Once again a comparison to the product obtained from the literature procedure<sup>165</sup> of the thiol and diulfur dichloride showed the two compounds to be identical. The melting point corresponded with that previously reported.<sup>119,165</sup>

The pentasulfide (167e) was prepared by the condensation of two equivalents of chloro(triphenylmethyl)disulfide (162b) and one equivalent of hexamethyldisilathiane.<sup>189</sup> The formation of 167e was obtained in the reaction of anhydrous sodium hydrosulfide with 162b.

The heptasulfide (167g) was prepared in the reaction of chloro(triphenylmethyl)trisulfide (162c) and anhydrous sodium hydrosulfide. It likely was result of a coupling reaction between hydro(triphenylmethyl)tetrasulfide formed in the reaction and 162c. The reaction of 162c and hexamethyldisilathiane also gave 167g.

The melting points of the sulfides prepared above agreed relatively well with the values reported in the literature except for 167c which was higher.

The hexasulfide (167f) and octasulfides (167h) were identified in the decomposition mixture for 167c, see below.

### 5.3 Spectroscopic Analysis

1

Ę

All the sulfides showed similar <sup>1</sup>H NMR spectra, a multiplet near 7.3 ppm as expected, but the <sup>13</sup>C NMR chemical shifts were surprisingly different. The <sup>13</sup>C NMR chemical shifts for sulfide 167a-167h are summarized in Table 18. The effect of the addition of a sulfur atom can be clearly seen to shift upfield the signal for the quaternary carbon, a similar trend is also observed for the other carbon signals. The

<sup>188.</sup> D. N. Harpp, K. Steliou and T. H. Chan, J. Am. Chem. Soc., 100, 1222 (1978).

<sup>189.</sup> D. N. Harpp and K. Steliou, Synthesis, 721 (1976).

only discrepancy in this effect can be observed for 167b. The discrepancy can be more clearly seen in a plot of chemical shift for the quaternary carbon vs the number of sulfur atoms as seen in Figure 19. A similar effect is also observed in the <sup>13</sup>C NMR spectra of the chloro(triphenylmethyl)sulfides. The <sup>13</sup>C NMR chemical shifts for the quaternary cart ons in 162a-162c are included here for comparison.

4

There are two competing influences on the  ${}^{13}C$  NMR chemical shift for the quaternary carbons which may account for the anomalous shifts observed for 167b. The addition of a sulfur atom causes an upfield shift of the  ${}^{13}C$  NMR signal. With 167b and 162b there is also a steric effect due to the interaction of the triphenylmethyl group with a second in 167b and with the chlorine atom in 162b.

Table 18. Sur bis(triphenylr	mmary of <sup>13</sup> C international straight methyl) sulfides	NMR chemica	l shifts for the		•••••
sulfide	C-S	C-2	C-3	C-4	C-5
mono (167a)	67 <b>.76</b>	143.71	127.34	130.43	128.83
di (167b)	73.53	143.84	127.47	130.58	126.97
tri (157c)	72.55	143.45	127.81	130.25	126.95
tetra (167d)	73.49	143.27	127.86	130.33	127.13
penta (167e)	73.66	143.10	127.93	130.30	127.21
hexa (167f)	73.78	1 <b>42.97</b>	*(From decomp of SSS)		
hepta (167g)	73.80	142.86	128.01	130.26	127.29
octa (167h)	73.80	142.83	•(From decor	np of SSS)	

\* The compounds were not directly synthesized but the signals could be identified in the 13C NMR spectra from the decomposition of 167c **Figure 19.** Plot of <sup>13</sup>C Chemical Shift for the Quaternary Carbon vs Number of Sulfur Atoms. "+" Chloro(triphenylmethyl)sulfide (162). " $\Delta$ " Bis(triphenylmethyl)sulfides (167).

-

Ĩ



#### 5.4 Crystallographic Analysis of 167b

こころしてきちゃく ひろうちちちちちちちちょう ちっちょうちょうちょう シティー

-----

3

The difficulty in the preparation of 167b was thought to be caused by steric problems thus an X-ray crystal structure was obtained. A sample of 167b, prepared by the procedure of Vorländer and Mittag,<sup>119</sup> was recrystallized from dichloromethane to obtain a crystal suitable for analysis. The ORTEP<sup>132</sup> diagram of 167b is shown in Figure 20 and selected bond lengths and angles are summarized in Table 19.

Bond lengths		Bond angles			
S-S C(19)-S C(38)-S C(19)-C	2.006(1) 1.939(3) 1.905(5) 1.525(4) 1.537(4)	C-S-S S-S torsional S-C(19)-C	112.5(1) 109.2(1) -111.4(1) 111.5(2) 108.4(2)		
C(38)-C	1.535(4) 1.529(4) 1.540(4) 1.532(4)	S-C(38)-C	101.3(2) 110.1(2) 101.3(2) 109.9(2)		

The angles about the sulfur atoms in 167b appear to be the largest ever reported. The large angles imply an almost tetrahedral structure about the sulfur atoms. The S-S dihedral angle  $(-111.4(1)^{\circ})$  is one of the largest ever measured with the notable exceptions of rigidly hydrogen bonded cysteine derivatives<sup>190</sup> and disulfides rigidly held in a protein.<sup>191</sup> Dipyridyl disulfide was found to have a dihedral angle of 180° in a copper complex.<sup>192</sup> Other complexed disulfides also have large dihedral angles.<sup>193</sup> The dihedral angle of 167b is close to that measured for di-*tert*-adamantyl disulfide (166)<sup>141</sup> (110.5(9)°) previously the largest free dihedral angle reported.

The carbon-sulfur bond distances appear to be the largest ever reported. Those found in 166 were only 1.84(2)Å whereas those found in 167b were 1.939(3)Å and 1.905(5)Å. The C-S bond length for normal open-chain sulfides has been measured

<sup>190.</sup> H. L. Yakel and E. W. Hughes, Acta Chrystallogr., 7, 291 (1954). R. E. Rosenfield, Jr and R. Parthasarathy, Acur Chrystallogr., Sect. B, B31, 462 (1975).

<sup>191.</sup> U. Ludenscher and R. Schwyzer, Helv. Chem. Acta, 54, 163a7 (1971).

<sup>192.</sup> For example see J. A. Bertrand and J. L. Breece, Inorg. Chim. Acta, 8, 267 (1974).

<sup>193.</sup> C. L. Simmons, M. Lundeen and K. Seff, Inorg. Chem., 18, 3444 (1979).

in the range of 1.80Å.<sup>139</sup>

-----





### 5.5 Thermal Decomposition

On heating above their melting points 167c, 167d and 167e decomposed into mixtures of four sulfides; 167c, 167d, 167e and 167f as confirmed from the <sup>13</sup>C NMR spectrum of the decomposition mixture. When the sulfides were heated to higher temperatures appreciable amount of triphenylmethane was formed. The effect of temperature on the product distribution is shown below in Table 20. The most intense signal is indicated by "+ + " while confirmation of each sulfide is indicated by a single "+". The thermolysis results confirm the earlier experiments of Wood who found that the trisulfide was the most stable. The major product of the decomposition was the trisulfide as expected. The mechanism for the decomposition is discussed below.

Sample	Temp (°C)	CH&	167a	167b	167c	167d	1 <b>67e</b>	167f	167g	167h
167c	160				++	+				
	165				+ +	+	+			
	170				++	+	÷			
	180				++	+	+	+		
	190	+			++	+	+	+	+	
167d	145				+	++	+	+	+	
	150				+	+ +	+	+	+	
	160				+	++	+	+	+	
	170				++	+	+	+	+	
	190	+			+ +	+	+	+	+	
l67e	150				+	+	++	+	+	+
	160				++	+	+	+	+	+
	170				++	+	+	÷	+	+
67b <sup>*</sup>	155	+			++	+	+	+		

Thermolysis of 167b above its melting point under a nitrogen atmosphere gave a complex mixture of products. A <sup>13</sup>C NMR spectrum of the crude decomposition mixture corresponding gave signals to triphenylmethane, and bis (triphenylmethyl)di- (167b), tri- (167c) and tetrasulfide (167d) and at least four other components which could not be identified (Scheme 59). TLC of the thermolysis mixture separated a blue spot which corresponded to thiobenzophenone. The presence of sulfur was not observed. Chromatography of the mixture on silica gel with 20% chloroform in hexanes gave four fractions from which could be identified; triphenylmethane (10%), and a mixture of 167c and 167d (50%). Two other components could not be isolated in pure form but there were signals identified in the <sup>13</sup>C NMR spectra corresponding to triphenylmethanol, thiobenzophenone and thiobenzophenone.

PhyC--S-S-CPhy ------ PhyC=S + PhyC-H + PhyC-SSS-CPHy

+ PhyC-SSSS-CPHy + PhyC==0 + PhyC-OH

#### Scheme 59

Taking an <sup>13</sup>C NMR following the thermolysis was inconvenient so the bis(mono-4-fluorotriphenylmethyl)tri- and tetrasulfides were prepared. These compounds (due to the abundance of <sup>19</sup>F) allowed for the analysis to be conducted on a much smaller scale. The NMR spectra was also obtained at a much quicker rate. As with the unsubstituted solfides the <sup>13</sup>C chemical shifts of the sulfides differ as do the <sup>19</sup>F NMR chemical shifts. The chemical shifts are summarized below in Table 21. As can be seen the shifts allow for differentiation of the species.

Table 21. 1º F and 13 C Chemical Shifts of<br/>Bis(mono-4-fluorotriphenylmethyl)sulfidesSulfide13 C shift19 F shift372.0376.78472.8877.19

From the thermolysis a mixture of tri-, tetra-, penta- and hexasulfides resulted along with the methane. The product distribution was identical to the found above for the unsubstituted compounds.

#### 5.3 <u>A Probable Mechanism for the Decompositions</u>

なるもの

.....

- 6

It is the long C-S bond which is responsible for the anomalous results observed for 167b.

The greater stability of alkyl disulfides when compared to the corresponding tri and tetrasulfides is well known. The effect can clearly be seen in a comparison of some sulfur-sulfur bond dissociation energies (BDE), Table 22.<sup>177</sup>

Table 22. Comparison of Selected Sulfur-SulfurBond Dissociation Energies					
Compound	Bond Dissociation Energy (Kcal/mol)				
MeS-SMe	69				
HS-SH	72				
MeS-S-SMe	46				
HS-S-S-SH	64				
MeSS-SSMe	37				
S <sub>8</sub> (ring)-S <sub>8</sub> (chain)	33				

From Table 22 the energy required to break the disulfide sulfur-sulfur bond is much greater than required to break the central sulfur-sulfur bond of the tetrasulfide. The corresponding trisulfide has a BDE intermediate between that of the di- and tetrasulfide. The common explanation for the difference in the BDE is that the RSS• radical is much more stable than the RS• radical.

- water

Į

Experiments of Wood<sup>179</sup> on 167b, 167c and 167d showed that the disulfide is less stable than either the tri- or tetrasulfide. Since it is clear that sulfur-sulfur bond dissociation is not the preferred decomposition mode for 167b, the only possible explanation for the difference in stability found for 167b must be the BDE of the carbon-sulfur bonds. The X-ray structure of 167b showed the C-S bond to be exceptionally large (likely the result of steric effects): the energy required to break this bond therefore must be lowered considerably. To account for the observed differences in stability the C-S BDE of 167b must be less than the S-S BDE found in either 167c or 167d. Similar large C-S bonds would not be found in 167c or 167d due to a lessening of steric hindrance by the inclusion of additional sulfur atoms (Scheme 60).



In the thermolysis of 167b, the formation of 167d would likely result from the direct coupling of two  $Ph_3CSS \cdot radicals$  or the reaction of the  $Ph_3CSS \cdot radical with$  a molecule of the disulfide 167b. The formation of 167c could then result from the reaction of a molecule of 167d with the  $Ph_3CSS \cdot radical$ . The formation of the thermolysis products in 167c, 167d and 167e are likely from sulfur radical reactions (Scheme 61).



عد ۱

#### Scheme 61

From the thermolysis of 167c, 167d and 167e these compounds decompose when heated above their melting points. The melting must therefore occur with the formation of sulfur radicals. The melting point of 167c was found to be 7°C higher than that of the other sulfide. The higher m.p. would be expected as cleavage of the trisulfide bond would be less likely than cleavage of the tetrasulfide bond (the formation of two Ph<sub>3</sub>CSS• radicals in 167d to only one Ph<sub>3</sub>CSS• radical in 167c).

The mechanism to explain the formation of the thiobenzophenone is shown below (Scheme 62). The thiobenzophenone would result from the rearrangement of the radical. Other rearrangements would yield tetraphenylethylene and phenyldisulfide but the compounds could not be identified in the reaction mixture as a result of their low concentration. There was one <sup>13</sup>C NMR signal at 137 ppm which corresponded to the carbon of the aromatic ring directly bonded to a sulfur atom indicating the presence of either phenyldisulfide or tetrasulfide. The triphenylmethane formed in the thermolysis of 167b would result from the direct abstraction of a proton from a phenyl ring.

143



# 5.7 <u>Reaction of Bis(triphenylmethyl)trisulfide 167c with Triphenylphosphine</u> <u>Dibromide (81)</u>

Triphenylphosphine dibromide (81) in the presence of triarylmetal trisulfides (82) or di(cyclopentadienyl)titanium pentasulfide (89) generated  $S_2$ . It was anticipated that bis(triphenylmethyl)trisulfide (167c) would react in an analogous fashion with triphenylphosphine dibromide (81) to generate sulfur in the form of  $S_2$  (Scheme 63).<sup>194</sup>



## Scheme 63

A similar reaction of bis(triphenylmethylthia)phenylphosphine (203) and

194. Preliminary work on the generation of S<sub>2</sub> from this reaction were conducted by M. Bernstein and S. Chan.

and the second s

dibromide (81) has yielded the thioxophosphanes (Ph-P=S) which was successfully trapped with 1,3-dienes.<sup>195</sup>

<u>م^</u>

1. Angle 1

. .



#### (203)

The reaction of trisulfide 167c and dibromide 81 in the presence of 2,3dimethyl-1,3-butadiene was conducted with dichloromethane as the solvent. The reaction after removal of the solvent, gave <sup>1</sup>H NMR signals corresponding to the trapping of S<sub>2</sub>. All attempts to isolate the adduct in pure form were unsuccessful as the yield of the adduct was low. Silica gel column chromatography gave a mixture, by <sup>1</sup>H NMR spectroscopy, of the cyclic disulfide, the tetrasulfide and a signal which corresponded to brominated diene. The brominated diene was identified by the reaction of bromine with the diene on an NMR scale. The expected side products from the reaction of trisulfide 167c and dibromide 81, triphenylphosphine sulfide (145) and the triphenylbromomethane (204) were also formed.

The reaction of trisulfide 167b and dibromide 81 appears to be much slower than that of the dicyclopentadienyltitanium pentasulfide (89) and dibromide 81 prepared using identical condition in both reactions. After 1 hr a strong TLC spot for triphenylphosphine sulfide is obtained for the reaction of 89 while the reaction of the trisulfide had only a small spot for the sulfide after 1 h and most of the trisulfide remained unreacted.

The reaction was conducted in the absence of diene to ensure that the products of the reaction were the expected sulfur, triphenylphosphine sulfide and triphenylbromomethane. These products were successfully isolated in modest yield.

<sup>195.</sup> P. L. Folkins and D. N. Harpp, unpublished results.

#### CONCLUSIONS AND CLAIMS TO ORIGINAL WORK

Ĩ

A wide variety of substrates were investigated as possible sources of diatomic sulfur. Dialkoxy disulfides when decomposed in the presence of 1,3-dienes yielded products which were consistent with the trapping of diatomic sulfur. The cyclic disulfide and tetrasulfide, 1,2-dithia-4,5-dimethyl-4-cyclohexene and 1,2,3,4tetrathia-5,6-dimethyl-6-cyclooctene respectively were isolated in good yields. Several substrates were shown to decompose *via* a diatomic sulfur intermediate. Bis(triphenylmethyl)trisulfide reacted with triphenylphosphine dibromide in the presence of a 1,3-diene to yield a product consistent with the generation of diatomic sulfur, but in modest yield.

The second sulfurated product of the reaction of 1,3-dienes with  $S_2$  precursors originally identified as a polymeric species by Harpp and MacDonald<sup>73</sup> was identified to be a cyclic tetrasulfide, 1,2,3,4-tetrathia-5,6-dimethyl-6-cyclooctene, . The tetrasulfide was desulfurized directly to the disulfide by triphenylphosphine.

The first X-ray crystal structures of chloro(triphenylmethyl)disulfide and chloro(triphenylmethyl)trisulfide were obtained. The disulfide exhibited the smallest C-S bond distance ever reported. The first chlorotrisulfide was isolated in pure form. Evidence of the first chlorotetrasulfide was obtained but could not be isolated. The reaction of the chloro(triphenylmethyl)sulfides were examined. The sulfides used synthesize series of were to а mixed sulfides. butyl(triphenylmethyl)sulfide, with 1-4 sulfurs.

A novel sulfur extrusion in the reaction of chloro(triphenylmethyl)monosulfide and thiocarbonyl was identified and examined. Indirect evidence for a thiosulfine intermediate for the extrusion was indicated from  $^{19}$ F NMR studies.

The X-ray crystal structure of bis(triphenylmethyl)disulfide was obtained and showed the largest free S-S dihedral angle known.

The mechanism of the solvent dependent sulfur extrusion from 4-tolylsulfenic 4tolylsulfonic thioanhydride was examined. HPLC analysis demonstrated that the reaction occurred by a mechanism involving a concatenation of sulfur atoms and not diatomic sulfur as anticipated.

# **CHAPTER 6**

## **EXPERIMENTAL**

## 6.1 General Procedures

د بي ا

Reagents obtained from commercial sources were tested for purity before use using proton nuclear magnetic resonance spectroscopy, thin layer chromatography or gas chromatography. When necessary reagents were purified by known methods and these procedures are indicated where appropriate.

Solvents were treated as follows: hexanes were distilled from concentrated sulfuric acid and passed through a column of deactivated aluminium oxide prior to use; dichloromethane (methylene chloride) was distilled over phosphorus pentoxide and stored over 3Å molecular sieves;<sup>196</sup> tetrahydrofuran was distilled over sodium metal using the blue ketal of thiobenzophenone as an indicator and used immediately; benzene and toluene were stored over metallic sodium; triethylamine was distilled from potassium hydroxide and stored over 3Å molecular sieves prior to use; All other solvents were stored over 3Å molecular sieves. Molecular sieves were activaled 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 diethylether.

Sulfur dichloride was distilled twice from 0.1% phosphorus pentachloride and the fraction boiling 57-61°C collected. The red liquid was used immediately. Disulfur dichloride was distilled twice from a mixture of sulfur and charcoal and the fraction boiling 136-139°C collected. The orange liquid was used immediately. Thionyl chloride and sulfuryl chloride were distilled immediately prior to use.

Melting points (m.p.) were obtained on a Gallenkamp melting point apparatus using open end capillaries and are uncorrected. Boiling points (b.p.) were measured directly and are uncorrected.

Thin layer chromatography (TLC) was performed on silica gel backed with polyester and treated with a 254 nm fluorescence indicator. Preparative TLC plates were constructed on glass coated with a 0.75 mm layer of silica gel HF-256 + 366 (EM Reagents). Column chromatography was performed using E. Merck Silica Gel

<sup>196.</sup> D. R. Burfield, G.-H. Gan and R. H. Smithers, J. Appl. Chem. Biotechnol., 28, 23 (1978).

60 (230-400  $\mu$ m) or neutral alumina using flash chromatography conditions.<sup>197</sup> All TLC and column chromatography solvent mixtures are volume/volume percentages. Gas chromatography was performed on a Varian Associates (VA) model 3700 gas chromatograph equipped with a model 4270 printing integrator and an FID detector. Separations were obtained using either a 2 m x 5 mm o.d. glass column packed with 3% silicone OV-17 on chromasorb HP 80/100 or a 15 m glass capillary column bonded with 3% silicone OV-101 or a 30 m glass capillary column bonded with phenyl methyl silica (SE-54).

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded on either a VA T-60, T-60a, XL 200-FT, or XL 300-FT spectrometer. Signals are reported as parts per million,  $\delta$  (ppm) relative to internal tetramethylsilane (TMS) or referenced to the solvent peak. The spectra are reported according to: shift, multiplicity, and integration. The following abbreviations are used to indicate multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet.

<sup>13</sup>C, <sup>19</sup>F, <sup>31</sup>P and <sup>33</sup>S NMR spectra were recorded on a VA XL 300-FT spectrometer and are reported in ppm and unless otherwise reported are proton decoupled. The <sup>13</sup>C spectra were recorded in and are referenced to the deuterated solvent and reported relative to TMS. <sup>19</sup>F spectra are reported relative to external dichlorodifluoromethane and were not proton decoupled. <sup>31</sup>P spectra are reported in ppm relative to 85% phosphoric acid as an external standard. <sup>33</sup>S spectra are reported relative to carbon disulfide as an external reference.

Infrared (IR) spectra were recorded on either a Perkin-Elmer model 297 Grating Spectrometer (referenced to the 1602 cm<sup>-1</sup> band of a polyethylene film) or on an Analect Instruments ASQ-18 FTIR Spectrometer equipped with an Analect Instruments MAP-67 Data System and an Analect Instruments RAM-56 Color Display. The spectra are reported in wavenumbers (cm<sup>-1</sup>).

Raman spectra were measured on an Instruments S. A. Ramonor Spectrometer equipped with a U-1000 double monochrometer and a Spectra-Physics Argon ion laser at 514.532 nm. The spectra are reported in wavenumbers ( $cm^{-1}$ ).

Mass spectra (MS) were recorded on a Dupont Instruments 21-492B or on a Kratos MS25RFA Mass Spectrometer. The analysis of the spectra are reported

]

<sup>197.</sup> W. C. Still, M. Kahn and A. Mitra, J. Org. Chem., 43, 2923 (1978).

according to: mass to charge ratio (m/z), assignment, relative intensity.

د ب

High performance liquid chromatography (HPLC) was performed courtesy of Dr. Ralf Steudel at the Institut für Anorganische and Analytische Chemie, Berlin Germany. Sulfur allotropes were identified by a comparison to authentic solution of each allotrope.

Sulfur analysis was determined using an Antek model 714 Sulfur Detector coupled with an Antek model 771 Pyroreactor. Sulfur percentages were determined from a calibration curve of total counts against percentage of sulfur (w/v), where counts refers to the intensity of the signal which results from the fluorescence of sulfur dioxide impinging on a photomultiplier tube.

Elemental analyses were obtained from the laboratory of Dr. Charles Larsen at Kemisk Laboratorium II, University of Copenhagen, Denmark.

Ultraviolet-Visible spectra (UV) were recorded on a Hewlett Packard 8451A Diode Array Spectrometer.

#### 6.2 Experimental Procedures

# 6.2.1 Diatomic Sulfur Precursor Preparation and Trapping Experiments

2,3-Dimethyl-1,3-butadiene was obtained from Aldrich Chemical Co. and stored at -15°C over molecular sieves. 2,3-Diphenyl-1,3-butadiene<sup>198</sup> was obtained by the dehydration of 2,3-diphenyl-1,4-butanediol.<sup>199</sup>

Unless otherwise indicated all  ${}^{1}S_{2}$  trapping experiments were conducted in the dark.

# Attempted Trapping of Diatomic Sulfur in the Reaction of 1,2-Diphenylhydrazobenzene (112) and N.N<sup>2</sup>-Dithiobisbenzimidazole (111)

To a mixture of 112 (0.90 g, 5.0 mmol) and 2,3-dimethyl-1,3-butadiene (1.23 g, 15.0 mmol) in 100 mL of dry ether was added 111 (1.49 g, 5.0 mmol) as a fine powder. The mixture was stirred at room temperature for 90 h, during which time the solution turned from colorless to orange. Filtration to remove the benzimidazole 114 gave a bright orange solution. A <sup>1</sup>H NMR spectrum of the crude filtrate showed no signals which would have corresponded to the Diels-Alder adduct of diatomic sulfur (3.20 ppm). Chromatography of the filtrate on neutral alumina with 5% ethyl acetate in hexanes gave only unreacted diene (<sup>1</sup>H NMR), transazobenzene (IR, <sup>1</sup>H NMR, MS) 113 and sulfur (TLC). No evidence for the Diels-Alder adduct was observed in the <sup>1</sup>H NMR spectra when carbon tetrachloride, dichloromethane or deuterated dichloromethane were substituted for ether as the reaction medium.

## Attempted Trapping of Diatomic Sulfur in the Reaction of 2-Mercaptobenzothiazole (118) and 111

To a solution of 118 (1.67 g, 10.0 mmol) and 2,3-dimethyl-1,3-butadiene (1.23 g, 15.0 mmol) in 50 mL of benzene was added 111 (1.49 g, 5.0 mmol) as a powder. The mixture was stirred at room temperature for 1 h under nitrogen. Filtration gave a white solid (1.18 g, 100%) identified as benzimidazole 114 (<sup>1</sup>H NMR), m.p. 150-155°C (lit. 170.5°C) and a yellow filtrate. <sup>1</sup>H NMR analysis of the filtrate showed no evidence of the formation of a Diels-Alder adduct. Chromatography of the

150

<sup>198.</sup> M. S. Newman, J. Org. Chem., 26, 582 (1961).

<sup>199.</sup> K. Alder and J. Haydn, Justus Liebigs Ann. Chem., 570, 201 (1950).

filtrate on neutral alumina with 5% ethyl acetate in hexanes gave only sulfur and benzathiazole disulfide 119, identified by comparison to the authentic compounds (m.p., <sup>1</sup>H NMR). No evidence for the Diels-Alder adduct was observed in the <sup>1</sup>H NMR spectra when carbon tetrachloride, dichloromethane or deuterated dichloromethane were substituted for ether as the reaction medium.

# Preparation of Bis(4-nitrobenzyloxy)disulfide<sup>200</sup> (124a)

The preparation was based on that of Thompson<sup>53</sup> who prepared other alkoxydisulfides. To a solution of 4nitrobenzylalcohol 125 (6.6 g, 0.043 mol) and



triethylamine (4.4 g, 0.043 mol) in 100 mL of ether maintained at 5°C was slowly added disulfur dichloride (2.91 g, 0.022 mol). The resulting mixture was stirred for 2 h at 5°C, allowed to warm slowly to ambient temperature. The solution was washed with water separated dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. The orange solid was chromatographed on silica gel with 40% ethyl acetate in chloroform and the major component isolated. Recrystallization from the same solvent system yielded an orange solid, (3.5 g, 44%), m.p. 93-95°C;  $R_f = 0.52$  (40% ethyl acetate in chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 4.84, 4.90, 4.97, 5.03 (dd, 2H); 7.45, 7.50 (d, 2H); 8.18, 8.23 (d, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 75.05 (CH<sub>2</sub>); 123.70; 128.61; 143.55; 147.77 ppm. Elemental analysis: cal'd %C = 45.64, %H = 3.29, %N = 7.60: found %C = 45.53, %H = 3.07, %N = 7.23.

## Bis(benzyloxy)disulfide (124b)

. . **.** .

This was obtained as a tan solid m.p. 54-56°C (lit<sup>53</sup> 59-60°C);  $R_f = 0.69$  (40% ethyl acetate in chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 4.78, 4.84, 4.90, 4.96 (dd, 2H); 7.36 (s, 5H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 76.58 (CH<sub>2</sub>); 128.48; 128.52; 128.64; 136.53 ppm.

<sup>200.</sup> The initial sample of the compound was obtained courtesy of S. Tardif.

# Preparation of Bis(4-methylbenzyloxy)disulfide (124c)

The procedure used was identical as that used to prepare the 4-methoxy derivative. The beige liquid was dissolved in 40% ethyl acetate in chloroform and permitted to



crystallize at -15°C. Long needle like crystals formed in solution which on attempted isolation by filtration liquified. A small amount of solid was isolated by filtration at 0°C; on warming to ambient temperature it liquified.  $R_f = 0.69$  (40% ethyl acetate in chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.38 (s, 3H); 4.76, 4.82, 4.88, 4.94 (dd, 2H); 7.18, 7.22 (d, 2H); 7.26, 7.30 (d, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.23 (CH<sub>3</sub>);76.59 (CH<sub>2</sub>); 128.77; 129.18; 133.55; 138.31 ppm.

## Preparation of Bis(4-chlorobenzyloxy)disulfide (124d)

The procedure used was identical as that used to prepare the 4-methoxy derivative. The beige solid was dissolved in 40% ethyl acetate in chloroform and permitted to



slowly crystallize at -15°C. Filtration gave a tan solid (3.2 g, 41%), m.p. 44-48°C;  $R_f = 0.69$  (40% ethyl acetate in chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 4.72, 4.78, 4.84, 4.90 (dd, 2H); 7.24-7.36 (m, 4H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 75.76 (CH<sub>2</sub>); 128.72; 129.91; 134.40; 134.93 ppm.

#### Preparation of Bis(4-methoxybenzyloxy)disulfide (124e)

To a solution of 4-methoxybenzylalcohol (6.6 g, 0.051 mol) and triethylamine (5.1 g, 0.050 mol) in 100 mL of ether maintained at 5°C was slowly added disulfur dichloride

1.191



(3.37 g, 0.025 mol). The resulting mixture was stirred for 2 h at 5°C, allowed to warm slowly to ambient temperature and the solvent removed under reduced pressure to yield a tan colored liquid. The liquid crystallized at -15°C for 24 h. Recrystallization of 1/2 the solid from 40% ethyl acetate in chloroform gave a tan solid (1.6 g, 42%) m.p. 34-36°C;  $R_f = 0.57$  (40% ethyl acetate in chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.81 (s, 3H); 4.69, 4.75, 4.82, 4.87 (dd, 2H); 6.86, 6.90 (d, 2H); 7.26, 7.30 (d, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 55.22 (CH<sub>3</sub>O); 76.42 (CH<sub>2</sub>); 113.85; 128.68; 130.43; 159.78 ppm.

#### Thermal Decomposition of Solid Samples of Bis(benzyloxy)disulfides (124)

Samples of the disulfide were placed into melting point capillaries and heated to the desired temperature using a melting point apparatus. Samples were heated to the following temperatures  $60^{\circ}$ C,  $90^{\circ}$ C,  $120^{\circ}$ C and  $150^{\circ}$ C. Each sample was dissolved into CDCl<sub>3</sub> and a <sup>1</sup>H NMR spectrum acquired. Once the initial decomposition temperature range was identified the alkoxydisulfide was heated at 5°C increments. From the <sup>1</sup>H NMR spectra the temperature of decomposition was determined. The formation of sulfur was confirmed by TLC. For 124a the decomposition was observed to occur at 135°C.

#### Thermal Decomposition of Solid 124a with 2.3-Diphenyl-1.3-butadiene

A mixture of 124a (0.080 g, 0.20 mmol) and 2,3-diphenyl-1,3-butadiene (0.40 g, 0.20 mmol) were heated neat to  $155^{\circ}$ C for 10 min. A <sup>1</sup>H NMR spectrum of the reaction mixture was acquired and gave signals corresponding to the alcohol, aldehyde, unreacted diene and trapped adduct (3.76 ppm) were identified. Chromatography with 20% chloroform in hexanes and then changing to 10% ethyl acetate hexanes gave several components. Isolated products were elemental sulfur (TLC) (5.9 mg, 42%), unreacted diene (TLC, <sup>1</sup>H NMR) (14.2 mg, 36% recovered), trapped product (6.1 mg, 12%), and a 1:1 mixture of 4-nitrobenzylalcohol and 4-nitrobenzaldehyde by <sup>1</sup>H NMR. Also isolated was a compound assigned to structure 128. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 4.10 (s,2H); 6.95 (m, 5H) ppm.

## Thermal Decomposition of 124a in Solution.

A sample of 124a was refluxed in toluene for 72 h, allowed to cool to ambient temperature and the solvent removed under reduced pressure. The resulting reddish oil was separated by chromatography on silica gel with 10% ethyl acetate in hexanes to yield sulfur (16 mg, 89%), alcohol (60 mg, 79%), aldehyde (70 mg, 92%) and unreacted 124a (11 mg, 6%).

## Thermal Decomposition of (124a) with 2.3-Dimethyl-1.3-butadiene in Benzene

A solution of 124a (0.368 g, 1.0 mmol) and 2,3-dimethyl-1,3-butadiene (0.041 g, 0.5 mmol) was prepared in 25 mL dry benzene. The mixture was heated to reflux under nitrogen and the decomposition was followed by TLC using 40% ethyl acetate in hexanes. After 72 h no starting material 124a remained and the decomposition

was deemed complete. The <sup>1</sup>H NMR spectrum of the reaction mixture showed signals corresponding to the trapped adduct. The solution was chromatographed on silica gel with 5% chloroform in hexanes to yield a product consistent with the trapping of  $S_2$ . The yield of cyclic disulfide 107 was only 5%.

# Thermal Decomposition of 124a with 2.3-Dimethyl-1.3-butadiene in Toluene

. .

ckis.

A solution of 124a (0.368 g, 0.10 mmol) and 2,3-dimethyl-1,3-butadiene (0.041 g, 0.05 mmol) was refluxed for 36 h in 50 mL of toluene. The solvent was removed under reduced pressure and the residue chromatographed with 5% chloroform in hexanes to yield three fractions, sulfur (48 mg, 75%), a product consistent with dimerized diene and cyclic disulfide (17 mg, 12%). The column was flushed with ethyl acetate to yield a 1:1 mixture of 4-nitrobenzyl alcohol and 4-nitrobenzaldehyde (0.281 g, 92%). The products were identified from the <sup>1</sup>H NMR spectra

# Thermal Decomposition of (124e) with Excess 2.3-Dimethyl-1.3-butadiene in Toluene

A sample of 124e (0.169 g, 0.50 mmol) and 2,3-dimethyl-1,3-butadiene (0.121 g, 1.5 mmol) in 50 mL of toluene were heated to reflux for 3 h. A TLC of the reaction mixture indicated the decomposition of 124e. The solvent was removed by reduced pressure in the presence of silica gel and the residue chromatographed on silica gel with 5% chloroform in hexanes. Chromatography yielded three fractions, a trace of sulfur (TLC), cyclic disulfide (13.0 mg, 17%) and cyclic tetrasulfide (17.0 mg, 17%). The column was flushed with ethyl acetate to yield a red oil which gave a <sup>1</sup>H NMR spectra consistent with a mixture of the alcohol and the aldehyde.

### Preparation of Methoxycarbonylsulfenic 4-tolylsulfonic thioanhydride (129a)

This compound was prepared by the method of Brooker, Child and Smiles.<sup>201</sup> To a solution of methoxycarbonylsulfenyl chloride<sup>93</sup> (4.0 g, 31 mmol) in 100 mL of



ether was added in one portion, potassium 4-toluenethiosulfonate<sup>202</sup> (7.2 g, 32 mmol) as a fine powder. The mixture was stirred for 3 h at room temperature,

<sup>201.</sup> L. G. S. Brooker, R. Child and S. Smiles, J. Chem. Soc., 1384 (1927).

<sup>202.</sup> B. G. Boldyrev, L. M. Grivnak, S. A. Kolesnikova, L. E. Kolmakova and G. A. Voloshin, Zh. Org. Khim., 3, 37 (1967); Chem. Abstr., 66, 94769v (1967).

during which time the yellow color of the sulfenyl chloride dissipated. Filtration of the mixture gave a white solid (2.2 g) identified as KCl (IR). Removal of the solvent under reduced pressure gave a faint yellow solid (8.82 g, 99%), m.p. 46-51°C. Repeated recrystallizations from ethanol gave an analytical sample, m.p. 52.5-54°C;  $R_f = 0.49$  (1:1 chloroform hexane). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.46 (s, 3H); 3.78 (s, 3H); 7.36 (d, 2H); 7.84 (d, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.71 (CH<sub>3</sub>); 56.34 (CH<sub>3</sub>O); 128.26 (CH); 129.78 (CH); 139.12 (C); 145.85 (C); 165.17 (C=O) ppm. IR (KBr) cm<sup>-1</sup>: 3034; 3014 (H aromatic); 2960; 2928 (H aliphatic); 1752 (C=O); 1431; 1332; 1195; 1144; 954; 811; 740; 613; 551. MS (EI, 70 eV, 45°C) m/z: 278 (M<sup>+</sup>•, 0.3); 246 ([M - S or 2O]<sup>+</sup>, 2.3); 214 ([M - S<sub>2</sub>]<sup>+</sup>•, 6); 182 (3); 170 (3); 155 ([CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>]<sup>+</sup>, 34); 139 (40); 123 (35); 91 ([C<sub>7</sub>H<sub>7</sub>]<sup>+</sup>, 100). Elemental analysis: cal'd: %C = 38.81, %H = 3.62: found %C = 38.96, %H = 3.65.

# Preparation of Methoxycarbonylsulfenic 4-chlorobenzenesulfonic thioanhydride (129b)

To a solution of methoxycarbonylsulfenyl chloride<sup>93</sup> 0.95 g (7.5 mmol) in ether was added in one portion, potassium 4-chlorobenzenethiosulfonate<sup>202</sup> (2.0 g,

رش که



8.0 mmol) as a fine powder. The mixture was stirred for 4 h filtered and the solvent removed under reduced pressure to yield a faint yellow liquid which crystallized on standing. Recrystallization from ether gave a white solid, (0.69 g, 31%), m.p. 58-61°C;  $R_f = 0.49$  (1:1 chloroform hexane). TLC of the solid showed an impurity which could not be removed be several recrystallizations. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.79 (s, 3H); 7.51-7.55 (dt, 2H); 7.85-7.90 (dt, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 56.56; 129.50; 129.65; 140.22; 141.35 ppm. MS (EI, 70 eV, 60°C) m/z: No M<sup>+</sup>; 177 ([<sup>37</sup>ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>]<sup>+</sup>•, 16); 175 ([<sup>35</sup>ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>]<sup>+</sup>•, 41) 113 ([<sup>37</sup>ClC<sub>6</sub>H<sub>4</sub>]<sup>+</sup>•, 24) 111 ([<sup>35</sup>ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>]<sup>+</sup>•, 60). IR (KBr) cm<sup>-1</sup>: 3093 (H aromatic); 2960 (H aliphatic); 1756 (C=O); 1157; 1139; 1091; 1074; 807; 751; 605.

## Preparation of Methoxycarbonylsulfenic methylsulfonic thioanhydride (129c)

To a solution of methoxycarbonylsulfenyl chloride<sup>93</sup> (6.3 g, 50 mmol) in 25 mL of ether was added in one portion, potassium methanethiosulfonate<sup>202</sup> (7.8 g, 52 mmol).



Filtration followed by removal of the solvent under reduced pressure gave a light yellow liquid (7.3 g, 72%). Attempts to purify the liquid by distillation (direct, vacuum or Kugelrhor) were unsuccessful. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.36 (s, 3H); 3.96 (s, 3H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 56.72; 49.08; 166.18 ppm. MS (EI, 70 eV, 40°C) m/z: No M<sup>+</sup>•; 171 ([M-CH<sub>3</sub>O]<sup>+</sup>, ); 138 ([M-2S]<sup>+</sup>, ); 79 ([CH<sub>3</sub>SO<sub>2</sub>]<sup>+</sup>, ); 64 (SO<sub>2</sub> or 2S, ); 59 ([CH<sub>3</sub>OC=O]<sup>+</sup>, ). IR (neat) cm<sup>-1</sup>: 2954 (H aliphatic); 1761 (C=O); 1423; 1333; 1188; 1147; 1132; 1075; 667; 521.

#### The Reaction Between 129a and Sodium Methoxide in Methanol

1

To a solution of 129a (0.6 g, 2.2 mmol) in 25 mL of methanol was added, in excess, sodium methoxide (0.2 g, 3.7 mmol) as a fine powder. The mixture was stirred at room temperature for 48 h. GC analysis of the reaction mixture showed the presence of dimethylcarbonate by a comparison of the retention time with an authentic sample. The solvent was removed under reduced pressure and the resulting yellow solid extracted with two 25 mL portions of carbon disulfide. Removal of the carbon disulfide under reduced pressure left a yellow solid, identified as elemental sulfur, (0.12 g, 87%) (TLC, MS, m.p. 110-111°C (lit<sup>203</sup> 112°C)). The residue contained a mixture of sodium 4-tolylsulfonate dihydrate and excess sodium methoxide, total mass (0.56 g, 104%).

## Attempted Trapping of Diatomic Sulfur from 129a

To a solution of 129a (0.6 g, 2.2 mmol) and 2,3-dimethyl-1,3-butadiene (0.58 g, 6.6 mmol) in 15 mL of benzene was added, in excess, sodium methoxide (0.2 g, 3.7 mmol) as a fine powder. The reaction was refluxed for 48 h with stirring, under nitrogen. The solvent was removed under reduced pressure and the resulting mixture analyzed by <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H NMR spectrum exhibited no signals which corresponded to the Diels-Alder adduct for diatomic sulfur. Chromatography of the mixture gave no trapped adduct, but sulfur was isolated, (47 mg, 67%).

## Attempted Trapping of Diatomic Sulfur in the Thermal Decomposition of 2-Methyl-2-propyltetrasulfide

Equal mixtures of 2-methyl-2-propyltetrasulfide and 2,3-dimethyl-1,3-butadiene

<sup>203. &</sup>quot;CRC Handbook Of Chemistry and Physics", R. C. Weast (Ed.), CRC Press, Boca Raton, Flordia, 60th Ed., 1979.

were heated in sealed tubes at 70°C and 160°C for three days. <sup>1</sup>H NMR analysis of the resulting mixtures exhibited no signals corresponding to the Diels-Alder adduct of singlet diatomic sulfur. The presence of sulfur and 2-methyl-2-propanethiol were confirmed by TLC and GC respectively.

# Attempted Trapping of Diatomic Sulfur in the Reaction of Morpholine Disulfide (63) and Di(ethylthiocarbonyl)disulfide (64)

Two identical samples of  $63^{204}$  (0.118 g, 0.50 mmol) and  $64^{205}$  (0.121 g, 0.50 mmol) were prepared in 2 mL of chloroform-d. To one sample was added 2,3-dimethyl-1,3-butadiene (0.121 g, 1.50 mmol). The reaction was heated to 50°C and followed by acquiring <sup>1</sup>H NMR spectra over 5 days.

# Attempted Isolation of Diatomic Sulfur in the Reaction of Tetramethylthiuram Disulfide (136) and Sulfuryl Chloride<sup>96</sup>

To a solution of 136 (0.480 g, 2.0 mmol) and 2,3-dimethyl-1,3-butadiene (0.240 g, 6.0 mmol) in 25 mL of carbon tetrachloride was added sulfuryl chloride (0.270 g, 2.0 mmol). The resulting mixture was stirred under a nitrogen atmosphere at room temperature for 3 h. A <sup>1</sup>H NMR spectrum of an aliquot of the solution showed no evidence of trapped Diels-Alder adduct indicating the presence of S<sub>2</sub>. An aliquot of the mixture stirred for a further 18 h gave the same result. Heating the solution to reflux for 0.33 h resulted in the precipitation of sulfur (TLC) but gave no evidence of trapped product in <sup>1</sup>H NMR spectrum. The product was isolated as reported and identified to be 137.

# Effect of various reagents on the Trap of S<sub>2</sub> with 2.3-Dimethyl-1.3-butadiene (109): 1.2-dithia-4.5-dimethyl-3-cyclohexene (107).

A sample of the trapped adduct 107 isolated from the decomposition of 162b in the presence of diene 109 was divided into seven samples. A standard sample was stored in the freezer at  $-15^{\circ}$ C. The remaining samples were treated as follows: heated to  $60^{\circ}$ C in the dark; heated to  $60^{\circ}$ C with sodium methoxide in the dark;, heated to  $60^{\circ}$ C in ambient light; stored at room temperature in the dark with acetic acid; stored as room temperature in ambient light: stored at room temperature in the dark with silica gel. After 48 h a <sup>1</sup>H NMR spectrum of each sample was

100

<sup>204.</sup> Prepared from S<sub>2</sub>Cl<sub>2</sub> and morpholine.

<sup>205.</sup> G. Barany, A. L. Scholl, A. W. Mott and D. A. Halsrud, J. Org. Chem., 48, 4751 (1983).

acquired and analyzed.

The sample examined in the dark were virtually unchanged. The sample heated to 60°C in ambient light displayed the development of signal in the <sup>1</sup>H NMR corresponding to aromatic protons

# Desulfurization of the 1.2.3.4-Tetrathia-6.7-dimethyl-6-cyclooctene (127) with Triphenylphosphine (143).

To a solution of 127 (48 mg, 0.23 mmol)) in  $CDCl_3$  was added 143 (85 mg, 30 mg) as a solid. A <sup>1</sup>H NMR spectra of the mixture was obtained after 3 h. Three signals were observed in the mixture, 127, 107 and triphenylphosphine sulfide (144).

To a solution of 127 (48 mg, 0.23 mmol) in  $CDCl_3$  was added 143 (170 mg, 60 mmol) as a solid. A <sup>1</sup>H NMR spectra of the mixture was obtained after 3 h. Two signals were observed in the mixture; disulfide 107 and 144. Addition of two more equivalents of triphenylphosphine had no effect on the disulfide.

### 6.2.2 Sulfenic Sulfonic Thioanhydrides

#### Preparation of 4-Tolylsulfenic 4-Tolylsulfonic Thioanhydride (146)

This compound was prepared using the procedure of Harpp, Ash and Smith.<sup>38</sup> The spectra data is included here for completeness.  $R_f = 0.54$  (50% chloroform in



hexanes). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.33 (s, 3H); 2.42 (s, 3H); 7.05-7.81 (m, 8H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 21.16 (CH<sub>3</sub>); 21.66 (CH<sub>3</sub>); 128.06; 129.68; 129.91; 130.64; 139.37; 139.96; 145.26 ppm.

#### Preparation of Bis(4-tolvl)thiosulfonate (147)

To a solution of 3-chloroperoxybenzoic acid (8.65 g, 42 mmol, 85% preparation) in 50 mL dichloromethane was slowly added 4tolyl disulfide (5.2 g, 21 mmol) in 25 mL

, and the second s



dichloromethane. Addition time was 1 h and the reaction was followed by TLC. The mi<sup> $\cdot$ </sup> ture was stirred for a further 2 h and then cooled to 0°C to precipitate 3chlorobenzoic acid, which was removed by filtration. The filtrate was washed three times with 15% sodium bicarbonate, once with water, separated and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave a light yellow solid. Chromatography on silica gel with 20% chloroform in hexanes yielded a white solid, m.p. 73.5-75°C. Recrystallization from ethanol gave white crystals, m.p. 77-77.5°C (lit.<sup>206</sup> 78.5-79.5);  $R_f = 0.54$  (50% chloroform in hexanes). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.37 (s, 3H); 2.42 (s, 3H); 7.12-7.48 (m, 8H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.36 (CH<sub>3</sub>); 21.54 (CH<sub>3</sub>); 124.35; 127.40; 129.27; 130.09; 136.32; 140.18; 141.95; 144.56 ppm.

#### Isolation of Sulfur from 146 in Ethanol.

A sample of 146 (0.16 g, 0.53 mmol) was dissolved in 25 mL of ethanol and stirred for 24 h. Over the reaction time mixture became cloudy and the formation of sulfur was confirmed by TLC. The precipitate was dissolved by the addition of 50 mL of chloroform. The solution was absorbed onto silica gel by removing the solvent under reduced pressure in the presence of about 0.5 g silica gel. The solid was chromatographed on silica gel with 20% chloroform in hexanes to yield sulfur (6.3 mg, 40%), m.p. 90-112°C and 147. The isolated sulfur was analyzed by HPLC and found to consist primarily of S<sub>8</sub> with traces of S<sub>6</sub> and S<sub>7</sub>.

### Chromatography of 146 on Silica Gel.

A sample of 146 was chromatographed on silica gel with 20% chloroform in hexanes. A single component was isolated which gave <sup>1</sup>H and <sup>13</sup>C NMR spectra consistent with 147.

#### Effect of Acid on the Rate of Sulfur Extrusion From 146

Two equal samples of 146 (0.075 g, 0.25 mmol) were prepared. One sample was dissolved in absolute ethanol and the second in 2.9 N HCl in ethanol. After 2 h and 12h equal aliquots of each sample were removed. The solvent was removed under reduced pressure and the residue dissolved in chloroform-d and analyzed by <sup>1</sup>H NMR spectroscopy. After 2 h the sample dissolved in HCl/ethanol was almost totally converted into 147. The sample in ethanol was virtually unchanged after 2 h.

#### Effect of Acid on Potassium 4-Tolylthiosulfonate (156)

A sample of 156 (0.953 g, 4.21 mmol) was dissolved in 20 mL of distilled water

206. L. Field, J. Am. Chem. Soc., 74, 394 (1952)

. ~

and 0.5 mL of concentrated HCl (12 N) added. The solution turned yellow on standing for five minutes. The reaction mixture was stirred for 24 h and filtered to yield a yellow solid identified as sulfur (13 mg, 98%) (TLC, m.p. 96-111°C).

#### Preparation of Potassium 4-Fluorobenzenethiosulfonate.

×.

Í

Prepared by the method of Boldyrev<sup>202</sup> to yield a white powder, m.p. 312°C (decomposition).

# Attempted Preparation of 4-Tolylsulfenic-4-fluorobenzenesulfonic Thioanhydride (152)

To a solution of 4-tolylsulfenyl chloride<sup>109</sup> (1.34 g, 8.45 mmol) in 25 mL of <sub>CH3</sub>ether was added potassium 4-fluoro-benzene-



thiosulfonate<sup>202</sup> (2.29 g, 9.5 mmol) as a fine powder. The mixture was stirred for 2 h over which time the orange color of the sulfenyl chloride dissipated. The KCl produced was separated by filtration and the solvent removed under reduced pressure. Recrystallization from hexanes gave a white solid (1.14 g, 43%), m.p. 98-100°C;  $R_f = 0.58 (50\%$  chloroform in hexanes). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.38 (s, 3H); 7.05-7.25 (m, 6H); 7.54-7.61 (m, 6H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.42 (CH<sub>3</sub>); 115.83, 116.13 (d); 124.14; 130.30; 130.42; 136.40; 138.99, 139.03 (d); 142.32; 163.71, 167.11 (d) ppm. MS (EI, 70 eV, 40°C) m/z: 282 (M<sup>+</sup>, 6.4); 139 (FC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub><sup>+</sup>, 100); 123 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>S<sup>+</sup>, 89); 91 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub><sup>+</sup>, 14). The solid was identified to be 4-fluorobenzene-4-tolylthiosulfonate 154 from the mass spectral data.

# Attempted Preparation of 4-Fluorobenzene-4-tolylsulfenic sulfonic thioanhydride (153).

To a solution of 4-fluorobenzenesulfenyl chloride<sup>207</sup> (20.0 mmol) in 25 mL of ether (prepared *in situ* from 4-fluorothiophenol



(2.56 g, 20.0 mmol) and N-chlorosuccinimide (2.69 g, 20.0 mmol)) was added potassium 4-tolylthiosulfonate (4.75 g, 21.0 mmol) as a fine powder. The mixture was stirred for 4 h over which time the color of the sulfenyl chloride dissipated. The KCl produced was removed by filtration and the solvent removed under reduced pressure. Crystallization of a white solid occurred slowly over 48 h.

207. Prepared using the procedure of Harpp and Mathiaparanam Ref 109.

Recrystallization from hexanes gave a white solid (1.04 g, 16%), m.p. 82-84°C;  $R_f = 0.59$  (50% chloroform in hexanes). <sup>1</sup>H NMR (CDCl<sub>3</sub>) : 3.23 (s, 3H); 6.98-7.46 (m, 6H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.63 (CH<sub>3</sub>); 116.55, 116.84 (d); 123.49; 123.53; 127.54, 129.44 (d); 138.71, 138.83 (d); 139.93; 144.92; 163.02, 166.38 (d) ppm. MS (EI, 70 eV, 40°C) m/z: 282 (M<sup>+</sup>, 7); 155 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub><sup>+</sup>, 75); 139 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sup>+</sup>, 39); 127 (FC<sub>6</sub>H<sub>4</sub>S<sup>+</sup>, 27); 91 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub><sup>+</sup>, 100). The solid was identified to be 4-tolyl-4-fluorobenzenethiosulfonate 155 from the mass spectral data.

#### Attempted Sulfur Extrusion From 152 and 153

A sample of each thioanhydride was dissolved in ethanol and stirred at ambient temperature for 48 h. The solvent of each was removed under reduced pressure and  $^{13}C$   $^{19}F$  and  $^{1}H$  NMR spectra obtained. The spectra showed only the presence of starting material after 24 h.

#### Preparation of 4-Fluoro-4-tolyl Thiosulfonate 155

To a solution of 4-tolylsulfenyl chloride (1.00 g, 6.3 mmol) in 25 mL of ether was added sodium 4-fluorobenzenesulfonate (2.0 g, 9.2 mmol). The mixture was stirred for 12 h, dried over anhydrous sodium sulfate and filtered. Removal of the solvent under reduced pressure followed by recrystallization from hexanes gave a light yellow solid (1.37 g, 76%), m.p. 75.5-78°C;  $R_f = 0.57$  (50% chloroform in hexanes). The solid gave NMR spectra corresponding to those thiosulfonate isolated above.

# Attempted Isolation of Diatomic Sulfur from the Sulfur Extrusion from Thioanhydride 146

To a solution of 146 (0.306 g, 1.0 mmol) in 25 mL of ethanol was added 2,3dimethyl-1,3-butadiene (0.024 g, 3.0 mmol). The solution was stirred for 24 h at ambient temperature under a nitrogen atmosphere. The solvent was removed under reduced pressure and the residue taken up into chloroform-d. The <sup>1</sup>H NMR spectra of the residue displayed no signals which could correspond to the trap of diatomic sulfur (a signal at 3.20 ppm). The thiosulfonate was isolated (0.22 g, 79%). Repeating the experiment in methanol-d<sub>4</sub> using one-tenth the amounts and following it by <sup>1</sup>H NMR spectroscopy gave no indication of S<sub>2</sub> trapping.

# 6.2.3 Synthesis of Chloro(triphenylmethyl)sulfides

#### Triphenylmethanethiol (163a)

A modification of the procedure of Vorländer and Mittag<sup>119</sup> was used to prepare 163a Hydrogen sulfide gas was passed through a suspension of triphenylmethanol (78 g, 0.30 mol) in 250 mL glacial acetic



acid containing 1 mL concentrated sulfuric acid. Hydrogen sulfide gas addition was halted with the disappearance of the yellow color. The resulting mixture was flushed with nitrogen and treated with 500 mL distilled water to precipitate the products, the solution was filtered and the solid washed twice with about 250 mL of water. Two recrystallizations from acetone gave a white crystalline solid (57.8 g, 74%), m.p. 105.5-106.5°C (lit.<sup>119</sup> 107°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.07 (s, 1H); 7.21-7.27 (m, 15H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 62.77 (C-SH); 126.79; 127.74; 129.25; 147.07 ppm.

## Triphenylmethyl Hydrodisulfide 163b

The disulfide 163b was prepared by Gerard Debersy<sup>208</sup> according to the literature.<sup>165</sup> m.p. 110-112°C (lit.<sup>165</sup> 114°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.76 (s, 1H); 7.35 (m, 15H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 70.32 (C-SH); 127.12; 127.99; 129.95; 143.49 ppm.

#### Preparation of Chloro(triphenvlmethyl)monosulfide (162a)

The monosulfide was prepared by the method of Vorländer and Mittag.<sup>119</sup> The spectral data is included here for completeness. Recrystallization from a petroleum ether chloroform mixture yielded a yellow solid, m.p. 135-137°C (lit 137°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.28



(m). <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm: 72.21 (C-S); 127.90; 128.19; 129.87; 141.76. IR (KBr) cm<sup>-1</sup>: 3056; 3030 (H aromatic); 1494; 1489; 1440; 1033; 1000; 754; 743; 691; 674; 626; 616; 520; 498; 487. Raman (solid) cm<sup>-1</sup>: 520; 501; 488; 365.

- 125-251 -

<sup>208.</sup> The sample of 164b was provides by Gerard Debersy. G. Debersy and D. N. Harpp, unpublished results.

## Preparation of Chloro(triphenylmethyl)disulfide (162b)

Chloro(triphenylmethyl)disulfide was prepared according to the procedure of Harpp and Ash.<sup>127</sup> To a stirred solution of sulfur dichloride (3.60 g, 35.6 mmol) in 50 mL anhydrous ether under a nitrogen atmosphere at -78°C was slowly added a solution of 163a (7.61 g, 26.1 mmol) in 80 mL of anhydrous ether.



The addition time was 1 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 separated by filtration. Crystallization from hexanes gave an orange solid (6.54 g, 73%), m.p. 91-93.5°C (lit.<sup>127</sup> 91-93°C). Once initial crystallization had occurred the solution was cooled to  $-15^{\circ}$ C. Storage of the solution at ambient temperature for more than 12 h resulted in a decomposition, as evidenced by a brown color. The products of the decomposition were not identified. Caution is required during recrystallization as excessive heating of the hexanes solution results in the formation of a yellow precipitate, identified as sulfur (TLC). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.34 (m) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 77.60 (C-S); 127.65; 128.07; 130.58; 142.17 ppm. IR (KBr) cm<sup>-1</sup>: 3048; 3032; 3019; 1486; 1438; 1000; 974; 890; 758; 728; 699; 661; 626; 616; 507; 482. Raman (solid) cm<sup>-1</sup>: 534; 483; 422; 416; 402; 341. Sulfur analysis: cal'd %S = 18.69: found %S = 18.06.

#### Preparation of Chloro(triphenylmethyl)trisulfide (162c)

The procedure used was similar to that for the preparation of 162b except disulfur dichloride was substituted for sulfur dichloride. To a stirred solution of disulfur dichloride (2.70 g, 20 mmol) in 50 mL anhydrous ether at -78°C under a nitrogen atmosphere was slowly added a solution of 163a (4.1 g, 15 mmol) in 80 mL



anhydrous ether. The reaction mixture was allowed to warm slowly to room temperature and concentrated to 30 mL under reduced pressure. Crystallization resulted on cooling at -15°C for 24 h. Filtration yielded a light orange solid (3.4 g, 61%), m.p. 76-78°C. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 74.36 (C-S); 127.48; 128.10; 130.12; 142.61 ppm. IR (KBr) cm<sup>-1</sup>: 3056; 3029; 1489; 1440; 1000; 756; 735; 694; 669; 626;

616; 488; 472; 459. Raman (solid) cm<sup>-1</sup>: 519; 487; 470; 454; 449; 357; 346. Elemental analysis: cal'd %C = 60.96, %H = 4.01: found %C = 61.02, %H = 4.01.

In a separate experiment a solution of 163a (2.60 g, 0.010 mol) in 50 mL of ether was added dropwise to disulfur dichloride (1.6 g, 0.0119 mol) in 50 mL ether at -78°C. The reaction mixture was warmed to room temperature and the ether was removed under reduced pressure leaving a gummy yellow solid, (4.4 g). The solid was triturated with hot pentane, but only 2.5 g dissolved. Crystallization of the pentane solution at -15°C yielded a light yellow solid (1.2 g), identified as 164 (<sup>13</sup>C NMR, m.p. 109-111°C (lit<sup>203</sup> 110-112°C)). The residue was extracted with ether and the remaining solid collected (0.58 g) identified as sulfur (m.p. 107.5-110°C, TLC, MS).

## Preparation of Chloro(triphenylmethyl)tetrasulfide (162d)

To a stirred solution of disulfur dichloride in 50 mL of ether at -78°C was slowly added dropwise a solution of hydrosulfide **163b** in 50 mL of ether. The solution was stirred was concentrated to 10 mL under reduced pressure and stored at -15°C. A yellow precipitate was

Sundawa .

í



removed from the solution after 24 h and was identified to be sulfur, m.p. 100-114°C (lit.<sup>203</sup> 112). All attempts to precipitate the tetrasulfide were unsuccessful.

A small aliquot of the original solution was removed and the solvent removed under reduced pressure to dryness. The gummy solid was taken up in CDCl<sub>3</sub> and a <sup>13</sup>C NMR spectra acquired. The spectra had signals corresponding to 162d but was contaminated with triphenylchloromethane. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 73.92 (C-S); 127.44; 128.12; 130.13; 142.45 ppm. The sulfide 162d decomposed in solution as the signals for 164 increased in intensity as the spectrum was acquired over time. A yellow precipitate formed in the NMR solution that was identified as sulfur (TLC).

# 6.2.4 Crystallographic Analysis of the Chloro(triphenylmethyl)sulfides

A single crystal of the sulfide was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Cu-K<sub>2</sub> radiation at 1.75kw ( $\lambda = 1.54178$ Å). The structures were obtained at either 20 or 21°C using  $\omega$ -20 scan type and a scan rate of 32.0°/min. The structures were solved

Table 23. Crystal and Data Collection Parameters							
	162a	162b					
empirical formula	$C_{19}H_{15}SCl$	$C_{19}H_{15}S_2Cl$	$C_{19}H_{15}S_{3}Cl$				
formula weight	310.84	342.90	374.96				
crystal system	triclinic	triclinic	orthorhombic				
lattice parameters							
a(Å)	10.792(2)	9.758(1)	9.224(1)				
b(Å)	15.090(2)	10.426(2)	19.196(3)				
c(Å)	10.027(2)	9.1691(6)	10.308(1)				
a(deg)	100.15(1)	97.52(1)					
$\beta(deg)$	103.12(1)	90.116(8)					
$\gamma(\text{deg})$	88.80(1)	116.750(9)					
$vol(Å^3)$	1565.1(4)	823.9(2)	1825.0(8)				
space group	P1 (#2)	P1 (#2)	Pna2 <sub>1</sub> (#33)				
Z value	4	2	4				
$D_{calc}(g \setminus cm^3)$	1.319	1.382	1.365				
Finn	648	356	776				
$\mu$ (Cuk <sub>n</sub> ) (cm <sup>-1</sup> )	33.13	43.42	50.00				
no. of observations	3020	2083	869				
no. of variables	379	259	82				
residuals: R; Rw	0.062; 0.052	0.049; 0.047	0.053; 0.074				
goodness of fit	2.30	4.30	1.38				

and a second and a second to the second second second second second second second

. . 5 ĭ i ţ by either direct methods or the Patterson method and refined using full-matrix least squares. The crystal parameters are given in Table 23.

# Thermal Decomposition of Solid Samples of 162a, 162b and 162c

A sample of each sulfide 162 was heated to its melting point and the temperature maintained for three minutes. The resulting solids were dissolved in CDCl<sub>3</sub> and analyzed by <sup>13</sup>C NMR spectroscopy. The spectrum for each sulfide showed the only decomposition product to be 164. The <sup>13</sup>C NMR spectrum of 162a showed the presence of some starting material. The NMR solutions were filtered to yield a yellow solid identified as sulfur (TLC, m.p. 116-119°C, (lit.<sup>203</sup> 112°C) m.m.p.).

## Effect of Ambient Light on the Room Temperature Decomposition of Solid 162c

Two samples of 162c were prepared; one sample was maintained in the dark and the other in ambient light. After 48 h the samples were dissolved in  $CDCl_3$  and the <sup>13</sup>C NMR spectra acquired. The sample maintained in light showed considerable amount of chloromethane 164 which was not present in the sample maintained in the dark. The sulfur formed in the decomposition (TLC) was isolated by filtration of the NMR solution.

# Column Chromatography of a Sample of Triphenylchloromethane (Trityl Chloride) (164)

A sample of 164 (0.085 g, 3.05 mmol) was chromatographed on silica gel with 10% ethyl acetate in hexanes. The column yielded two fractions both of which were eleuted quickly. Fraction A: was a white solid which showed only aromatic protons in the <sup>1</sup>H NMR spectrum identified as triphenylmethanol 169 (0.0229 g, 29%). Fraction B: which was a light yellow solid which was identified as 164 (TLC, <sup>1</sup>H NMR and <sup>13</sup>C NMR) (0.0466 g, 55%). After 48 h open to the atmosphere at ambient temperature fraction A had decomposed to 169 (<sup>1</sup>H NMR, TLC).

Chromatography of a sample of 164 (0.135 g, 0.48 mmol) on silica gel with 20% chloroform in hexanes yielded only one compound which was identified as 169 (0.108 g, 89%) (TLC, <sup>1</sup>H NMR and <sup>13</sup>C NMR).

# Isolation of the Products of the Thermal Decomposition of 162b at Ambient Temperature, Catalyzed by Silica Gel

A sample of 162b (0.329 g, 0.96 mmol) was stirred with silica gel for 12 h in chloroform at ambient temperature under a nitrogen atmosphere. The resulting mixture was chromatographed on silica gel with chloroform in hexanes (the

chloroform concentration was increased from 20% to 100% as the chromatography was conducted) to yield four fractions: sulfur (0.0264 g, 86%)), triphenylmethane **168** (0.0358 g) (TLC, <sup>1</sup>H NMR, <sup>13</sup>C NMR, G.C.), a mixture of **167c** and **167d** (0.0338 g) (TLC, <sup>1</sup>H NMR, <sup>13</sup>C NMR, G.C.), and **169** (0.1886 g, 72%) (TLC, <sup>1</sup>H NMR, <sup>13</sup>C NMR, G.C.). The carbinol **169** was formed as a result of the hydrolysis of **164** on chromatography. Calculation of the yield based on the triphenylmethyl group indicated a recovery rate of 96%.

#### Decomposition of 162b at Ambient Temperature

A sample of 162b (0.17 g, 0.50 mmol) was dissolved in chloroform and the solution stirred for 48 h in the dark. The mixture was adsorbed onto silica gel and chromatographed (silica gel) with 20% chloroform in hexanes to yield sulfur (22.7 mg), a mixture of 167c-e (76 mg, 50%), and 169 (54.1 mg, 42%). The reaction was repeated in acetone, carbon tetrachloride, dichloromethane and tetrahydrofuran using the above procedure. The same products were isolated in each case but in varying yields as shown in Table 10.

### Decomposition of 162c at Ambient Temperature

A sample of 162c (0.095 g, 0.25 mmol) was dissolved in 25 mL of chloroform. The procedure was repeated as above yielding after chromatographed on silica gel with 20% chloroform in hexanes; sulfur (24 mg, 64%), 167c-f (43.2 mg, 35%), and 169 (22.9 mg, 50%).

#### 6.2.5 <u>Preparation of Substituted Triphenylmethanes</u>

#### Mono-4-fluorotriphenvlmethanol (170b)

The methanol was prepared by the addition of thiobenzophenone (36.0 g, 0.20 mol) in 100 mL dry benzene to a solution of 4fluorobenzenemagnesium bromide (made from 4-fluorobromobenzene (35.0 g, 0.20 mol) and magnesium turnings (4.6 g, 0.20 mol)) in 200 mL



of ether. The resulting solution was neutralized with a sulfuric acid-crushed ice mixture, washed with water, 5% sodium carbonate and finally with water. Removal of the solvent under reduced pressure left a yellow liquid which was steam distilled

to remove volatile impurities. Recrystallization of the residue from methanol yielded a white solid, 37.8 g (69%), m.p. 120.5-122.0°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.84 (s, 1H); 6.94-7.03 (m, 2H); 7.21-7.34 (m, 12H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 81.57 (C-OH); 114.41, 114.678 (d); 127.29; 127.77; 127.92; 129.61, 129.72 (d); 142.66, 142.70 (d); 146.69; 160.17, 163.44 (d) ppm. IR (nujol) cm<sup>-1</sup>: 1653.9; 1558.7; 1539.5; 1506.6; 667.7; 636.9. MS (EI, 70 eV, 60°C) m/z: 278 (M<sup>+</sup>, 30); 261 ([M - OH]<sup>+</sup>, 4); 201 ([M - C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 100); 183 ([M - C<sub>6</sub>H<sub>6</sub>O]<sup>+</sup>, 28).

## 6.2.5.1 Preparation of Thiols

N.

4

# General Procedure for the Preparation of 4-Substituted Triphenylmethanethiols (171)

The procedure followed was similar to the preparation of 163a prepared above. A sample of the corresponding alcohol was dissolved in 100 mL glacial acetic acid and 10 drops of concentrated sulfuric acid were added giving an immediate color change. Hydrogen sulfide gas was bubbled into the reaction mixture through an inlet below the surface of the liquid during which time the color was observed to gradually change to light yellow. Addition of  $H_2S$  was continued for a further 0.5 h after the color change and the mixture purified as indicated.

## Tri-4-chlorophenylmethanethiol

The thiol was prepared from tri-4chlorophenylmethanol<sup>209</sup> (8.0 g, 0.022 mol). The addition of the sulfuric acid resulted in the formation of a red solution. A white precipitate formed after 1 h but the addition of  $H_2S$  was continued for an additional 0.5 h. The mixture



was poured into 500 mL water, filtered and air dried for 2 h. The resulting off-white solid was recrystallized from acetone to yield (3.5 g, 42%) as a white solid. TLC indicated the presence of two small impurities. Column chromatography of the solid on silica gel using 20% chloroform in hexanes yielded a fluffy white solid (3.00 g, 39%) m.p. 133-135°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.03 (s, 1H); 7.13-7.16 (dt, 6H); 7.24-7.28 (dt, 6H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 61.38 (C-SH); 128.56; 131.65; 134.22; 140.03 ppm. IR (nujol) cm<sup>-1</sup>: 3023 (H aromatic); 1377; 1117; 1095; 1011; 801. MS (EI, 70 eV, 100°C) m/z; 345 ([M - SH]<sup>+</sup>, 98); 347 ([M + 2 - SH]<sup>+</sup>, 100); 349 ([M +

<sup>209.</sup> N. N. Lichtin and M. J. Vignale, J. Am. Chem. Soc., 79, 579 (1957).

# 4 - SH]<sup>+</sup>, 36).

#### Mono-4-methyltriphenylmethanethiol (171a)

The thiol was prepared from mono-4methyltriphenylmethanol<sup>209</sup> (10.0 g, 0.034 mol). Addition of sulfuric acid to the acetic acid solution resulted in the formation of a dark green solution. No precipitate formed over the 1.5 h addition time. The reaction mixture was



poured into 500 mL water and the resulting cloudy solution extracted with ether. The ether layer was washed twice with 100 mL water, twice with sodium bicarbonate solution and finally once more with 100 mL water. The ether layer was separated dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure to yield a light yellow solid (8.0 g, 76%). TLC of the solid indicated the presence of several impurities. Chromatography on silica gel with hexanes gave a colorless liquid which on standing solidified to a white solid (5.5 g, 54%), m.p. 61-64°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.34 (s, 3H); 3.06 (c 1H); 7.06-7.17 (dd, 4H); 7.24-7.29 (m, 10H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 22.38 (CH<sub>3</sub>); 62.62 (C-SH); 126.74; 127.73; 128.47; 129.12; 129.27; 136.46; 144.20; 147.30 ppm. IR (KBr) cm<sup>-1</sup>: 3018 (H aromatic); 2914; 2867 (H aliphatic); 2547 (SH, weak); 1596; 1507; 1442; 1186; 1034; 743; 697. MS (EI, 70 eV, 30°C) m/z: 257.2 ([M-SH]<sup>+</sup>, 100); 179.1 ([M-SH-C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 30); 165.1 ([M-SH-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 66). Sulfur analysis: cal'd %S = 10.93: found %S = 11.03.

## Mono-4-fluorotriphenylmethanethiol (171b)

The thiol was prepared from 170b (16.3 g 58.6 mmol). Addition of sulfuric acid to the alcohol solution resulted in the formation of a red solution. Addition of water gave an off-white solid which was isolated by filtration and air dried for 2 h. Recrystallization from acetone



yielded a white solid (12.8 g, 74%), m.p. 89.0-89.5°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.08 (s, 1H); 6.92-7.00 (m, 2H); 7.20-7.27 (m, 12H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 62.29 (C-SH); 114.37, 114.65 (d); 129.96; 127.88; 129.16; 131.02, 131.12 (d); 142.97, 143.02 (d); 146.96; 159.83, 163.10 (d) ppm. IR (nujol) cm<sup>-1</sup>: no SH; 1559; 1654; 668; 637.
MS (EI, 70 eV, 30°C) m/z: No M<sup>+</sup>; 261 ([M - SH]<sup>+</sup>, 100); 183 ([M - C<sub>6</sub>H<sub>6</sub>S]<sup>+</sup>, 54). Sulfur analysis: cal'd %S = 10.88: found %S = 11.55.

## Mono-2-methyltriphenylmethanethiol (171c)

The thiol was prepared from  $170c^{209}$  (6.00 g, 0.021 mol). Addition of sulfuric acid resulted in the formation of an orange-red solution which turned pink upon addition of hydrogen sulfide gas. Addition of water to the alcohol solution gave an off-white solid which was isolated by



filtration and air dried. Recrystallization from acetone yielded a white solid (5.66 g, 89%), m.p. 116-117°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.07 (s, 3H); 3.05 (s, 1H); 6.98-7.33 (m, 14H) ppm <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 23.22 (CH<sub>3</sub>); 63.06 (C-SH); 125.14; 126.72; 127.37; 127.78; 129.35; 129.44; 132.75; 137.84; 144.83; 146.58 ppm. IR (nujol) cm<sup>-1</sup>: no SH peak; 3030; 3024; 2956; 1182; 1033; 761; 751; 738; 699; 667; 624. MS (EI, 70 eV, 30°C) m/z: No M<sup>+</sup>; 257 ([M - SH]<sup>+</sup>, 76); 179 ([M - (C<sub>6</sub>H<sub>5</sub> + SH)]<sup>+</sup>, 93); 165 ([M - (CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub> + SH)]<sup>+</sup>, 100).

## Mono-4-methoxytriphenylmethanethiol (171d)

The thiol was prepared from  $170d^{209}$  (3.00 g, 0.0104 mol). Addition of sulfuric acid to the alcol... solution resulted in the formation of a red solution. Addition of water formed a white precipitate which was separated by filtration and air dried. Recrystallization from acetone



yielded a white solid (2.47 g, 79%), m.p. 97-98°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.07 (s, 1H); 3.79 (s, 3H); 6.78, 6.82 (d, 2H); 7.14-7.26 (m, 12H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 55.19 (CH<sub>3</sub>O); 62.40 (C-SH); 113.00; 126.74; 127.74; 129.22; 130.46; 139.24; 147.42; 158.22 ppm. IR (KBr) cm<sup>-1</sup>: 3008; 2961; 2837; 2575 (SH, weak) 1443; 1255; 1188; 1031; 746; 701; 578. MS (EI, 70 eV, 30°C) m/z: no M<sup>+</sup> peak, 273 ([M - SH]<sup>+</sup>, 100).

## 6.2.5.2 Preparation of Substituted Chloro(triphenylmethyl)monosulfides

## Chloro(mono-4-methyltriphenylmethyl)monosulfide (172a)

The thiol 171a (0.76 g, 2.6 mmol) and sulfuryl chloride (0.45 g, 3.0 mmol) were mixed in 50 mL ether for 24 h under nitrogen. Removal of the solvent under reduced pressure followed by recrystallization from pentane yielded a light yellow solid (0.44 g, 51%), m.p.



89-92°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.12 (s, 3H); 6.98-7.07 (m, 2H); 7.18-7.37 (m, 12H) ppm.

#### Chloro(mono-4-fluorotrizhenylmethyl)monosulfide (172b)

The thiol 171b (1.00 g, 3.4 mmol) and sulfuryl chloride (0.52 g, 4.0 mmol) were stirred in 50 mL of ether for 24 h under a nitrogen atmosphere. Removal of the solvent under reduced pressure followed by recrystallization from pentane yielded a light yellow solid (0.81 g,



72%), m.p. 86.5-88°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.36 (s, 3H); 7.12-7.35 (m, 14H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 71.61 (C-S); 114.86, 115.15 (d); 128.08; 128.32; 129.67; 131.78, 131.89 (d); 137.61, 137.65 (d); 141.61; 160.44, 163.73 (d) ppm.

## 6.2.5.3 Preparation of Substituted Chloro(triphenylmethyl)disulfides

## Chloro(mono-4-methyltriphenylmethyl)disulfide (173a)

The disulfide was prepared in similar fashion to 162b above. To a stirred solution of sulfur dichloride (1.24 g, 12.0 mmol) in 50 mL of anhydrous ether at -78°C under a nitrogen atmosphere was slowly added a solution of 171a (2.90 g, 10.0 mmol) in 100 mL ether. After the



addition (1 h) the mixture was allowed to warm to room temperature and concentrated to 5 mL under reduced pressure. The solution stored at -15°C for 24 h yielded a bright orange crystalline solid which was separated by filtration (3.06 g,

86%), m.p. 75.5-78.0°C. A sample of the solid was recrystallized from hexanes to give fine orange crystals, m.p. 76-77°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.36 (s, 3H); 7.15 (s, 4H); 7.25-7.30 (m, 10H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.04 (CH<sub>3</sub>); 77.59 (C-S); 127.61; 128.04; 127.81; 130.49; 130.62; 137.51; 139.29; 142.37 ppm. IR (KBr) cm<sup>-1</sup>: 1506; 1442; 1192; 756; 731; 712; 696. MS (EI, 70 eV, 75°C) m/z: No M<sup>+</sup> ; 257 ([M - SSCl]<sup>+</sup>, 51); 179 ([CH<sub>3</sub>Ph<sub>2</sub>C]<sup>+</sup>, 16); 165 ([Ph<sub>2</sub>C - H]<sup>+</sup>, 25).

## Chloro(mono-4-fluorotriphenylmethyl)disulfide (173b)

The disulfide was prepared from 171b (3.00 g, 10.2 mol) in 50 mL of ether and sulfur dichloride (1.30 g, 12.5 mmol) in 50 mL of ether as above. The solution was concentrated to 10 mL under reduced pressure and on cooling at -  $15^{\circ}$ C for 24 h followed by filtration yielded a



yellow solid, (2.34 g, 64%), m.p. 81.0-83.5°C. Recrystallization from pentane gave an orange solid, m.p. 86.5-88.0°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 6.98-7.06 (m, 2H); 7.22-7.36 (m, 12H) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 77.46 (C-S); 115.11, 115.40 (d); 128.23; 128.63; 130.78; 132.98, 133.09 (d); 138.33, 138.38 (d); 142.61; 160.85, 164.14 (d) ppm. IR (nujol) cm<sup>-1</sup>: 1506; 1163; 1103; 736; 699; 636. MS (EI, 70 eV, 30°C) m/z: No M<sup>+</sup> peak; 261 ([M - SSCl]<sup>+</sup>, 100). Sulfur analysis: cal'd %S = 17.75: found %S = 17.41. The solid was unstable as <sup>13</sup>C NMR analysis over 5 h andicated decomposition to mono-4-fluorotriphenylchloromethane.

## Chloro(mono-2-methyltriphenylmethyl)disulfide (173c)

The disulfide was prepared from 171c (3.00 g, 10 mmol) and sulfur dichloride (1.40 g, 14 mmol) in 50 mL of ether. Upon addition of the sulfur dichloride no precipitate formed in the reaction mixture. The solvent volume was reduced to 10 mL under reduced pressure but no



crystallization resulted at -15°C for 24 h. The solvent was allowed to slowly evaporate at -15°C over 72 h over which time an orange solid formed in solution which was isolated by filtration. The material decomposed before a 1H NMR spectra could be obtained. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 23.22 (CH<sub>3</sub>); 79.16 (C-S); 125.66; 127.58; 127.79; 128.16; 130.49; 131.51; 132.72; 138.43; 139.77; 140.92 ppm.

#### Chloro(mono-4-methoxytriphenylmethyl)disulfide (173d)

The disulfide was prepared from (1.53 g, 5.0 mmol) in 50 mL of ether and sulfur dichloride (0.72 g, 7.0 mmol) in 50 mL or ether as above. Upon addition of the thiol to sulfur dichloride a yellow precipitate formed in the reaction mixture. The solution was concentrated to 1/2



volume and stored at -15°C for 24 h. Filtration gave a yellow solid (1.4 g, 76%), m.p. 85-87°C. Recrystallization from pentane gave a light orange solid, m.p. 60-87°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.82 (s, 3H); 6.84, 6.88 (d, 2H); 7.15, 7.19 (d, 2H); 7.254-7.309 (in, 10H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 55.21 (CH<sub>3</sub>O); 77.47 (C-S); 113.34; 127.61; 128.04; 129.62; 130.52; 131.95; 142.55; 158.92 ppm. IR (KBr) cm<sup>-1</sup>: 3006; 2959; 2836; 1506; 1490; 1440; 1251; 1030; 740; 715; 700; 582. MS (EI, 70 eV, 150°C) m/z: 273 ([M - SSCl]<sup>+</sup>, 100); 258 ([M - SSCl - CH<sub>3</sub>]<sup>+</sup>, 63).

## 6.2.5.4 Preparation of Substituted Triphenylchloromethanes

## Mono-4-methyltriphenylchloromethane (174a)

The preparation is based on the similar preparation of mono-4chlorotriphenylchloromethane.<sup>152</sup> To mono-4methyltriphenylmethanol (1.5 g, 5.6 mmol) was added 3 mL acetyl chloride and the mixture heated to reflux for 1 h. To the hot mixture was



added 10 mL petroleum ether and the mixture allowed to crystallize at -15°C for 24 h. Filtration followed by vacuum drying gave a light yellow solid (0.91 g, 57%), m.p. 90.5-92.0°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.35 (s, 3H); 7.11 (s, 4H); 7.25-7.29 (m, 10H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 20.99 (CH<sub>3</sub>); 81.45 (C-Cl); 127.65; 127.86; 128.38; 129.57; 129.64; 137.56; 142.38; 145.39 ppm. MS (EI, 70 eV, 100°C) m/z: 257 ([M -Cl]<sup>+</sup>, 28); 241 ([M - CH<sub>4</sub>Cl]<sup>+</sup>, 12); 179 ([M - C<sub>7</sub>H<sub>7</sub>Cl]<sup>+</sup>, 10); 165 ([M - C<sub>8</sub>H<sub>9</sub>Cl]<sup>+</sup>, 17).

## Mono-4-fluorotriphenylchloromethane (174b)

ţ

1

The chloromethane was prepared from the 170b (3.00 g, 10.8 mmol) and 4.0 mL of acetyl chloride, following the procedure above yielded after recrystallization from petroleum ether, a light yellow solid (2.39 g, 75%), m.p 87.0-89.5°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 6.94-7.03 (m, 2H); 7.18-7.33



(m, 12H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 80.75 (C-Cl); 114.38, 114.67 (d); 127.80; 127.90; 129.55; 131.46, 131.57 (d); 141.22, 141.26 (d); 145.07; 160.41, 163.76 (d) ppm. IR (nujol) cm<sup>-1</sup>: 1506; 1458; 1162; 1103; 743; 697; 643; 636; 615. MS (EI, 70 eV, 30°C) m/z: 261 ([M - Cl]<sup>+</sup>, 100); 183 ([M - C<sub>6</sub>H<sub>6</sub>Cl]<sup>+</sup>, 51); 165 ([M - C<sub>6</sub>H<sub>5</sub>ClF]<sup>+</sup>, 39).

## Determination of the Kinetics of the Thermal Decomposition of 173a in Solution.

The decomposition kinetics of 173a were followed by examining the decrease in the area of the <sup>1</sup>H NMR signal assigned to the aromatic protons of the tolyl group. The areas were measured relative to the methyl protons which did not exhibit a shift on conversion from disulfide to chloromethane. The kinetic experiments for the thermal decomposition of 173a were conducted as follows: exactly 1 mL of dry deuterated chloroform was added to a known mass of 173a; once dissolution was complete (1 min) a portion of the solution was transferred to a 5 mm NMR tube and the sample introduced into the spectrometer which had been previously warmed to the desired temperature. The spectra were then acquired at set time intervals. The signal of the aromatic tolyl protons for the chlorodisulfide were observed at 7.14 ppm while those of the product of the decomposition chloromethane at 7.11 ppm. Each run was an NMR experiment with an array of a pre-acquisition delays (PAD) to allow for observations of changes in the spectra.

# Effect of a Radical Inhibitor or Initiator on the Rate of Decomposition of 173a at 30°C.

A) Inhibition - p-Hydroquinone (175)

To the solid 173a (31.6 mg, 0.88 mmol) was added 175 (4.6 mg, 0.41 mmol). To this mixture was added 1 mL CDCl<sub>3</sub> and a spectra obtained immediately and at 10

minute intervals. The concentration of 175 was low due to low solubility in chloroform. The rate of the reaction was found to roughly 1/3 that of the non inhibited rate.

## B) Initiation - m-Chloroperoxybenzoic acid (176)

To the solid 173a (32.6 mg, 0.89 mmol) was added 176 (1.0 mg, 0.006 mmol). To this mixture was added the  $CDCl_3$  and a spectra obtained immediately. The rate of decomposition was greatly enhanced with an observed rate that was almost a ten fold increase. The increase was difficult to measure as a limited number of data points were obtained due to the rapid decomposition. There was no initiation period observed for the decomposition.

## Effect of Elemental Sulfur on the Rate of Decomposition of 173a.

A solution of 173a (0.0292 g, 0.0823 mmol) prepared in 1 mL deuterated chloroform, divided into two equal portions and stored at  $-10^{\circ}$ C for 20 min. To the first sample was added 0.1 mL of a sulfur suspension in CDCl<sub>3</sub>. The decomposition was then studied in the NMR at 40 °C. The rate of the decomposition was found to be 8.9  $\times$  10<sup>-6</sup>. The second sample was run with no sulfur at 40°C and the rate determined to be 1.5 X 10<sup>-5</sup>.

## 6.2.6 <u>Reactions of Chloro(triphenylmethyl)sulfides</u>

## 6.2.6.1 With Nucleophiles

## Preparation of Butyl(triphenylmethyl)sulfides (177).

## Reaction of the 162a-c with ButyImagnesium Chloride: General Procedure.

To a solution of the sulfide (1 mmol) in ether at  $0^{\circ}$ C under nitrogen was added butylmagnesium chloride 0.5 ml of a 2.0 M solution in ether. the mixture was stirred for 1 h over which time the yellow color of the sulfide solution dissipated. Column chromatography with 20% chloroform in hexanes yielded 177. The reaction with either di- or trisulfide also yielded mixtures of 167c-d. The <sup>13</sup>C NMR chemical shifts for 177a-d are summarized in Table 13.

Butyl(triphenylmethyl)disulfide (177b) (0.167 g, 46%): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.731, 0.766, 0.801 (t, 3H); 1.13-1.34 (m, 4H) 1.64, 1.68, 1.71 (t, 2H); 7.23-7.48 (m, 15H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 13.53 (CH<sub>3</sub>); 21.46 (CH<sub>2</sub>); 30.84 (CH<sub>2</sub>); 36.38 (CH<sub>2</sub>); 70.79 (C-S); 126.75; 127.68; 130.07; 143.86 ppm. MS (EI, 70 eV, 30°C) m/z: 243 (Ph<sub>3</sub>C<sup>+</sup>, 100); 165 ([Ph<sub>2</sub>C - H]<sup>+</sup>, 41); 57 ([C<sub>4</sub>H<sub>9</sub>]<sup>+</sup>, 11). A second fraction was isolated which was identified as 167d.

Butyl(triphenylmethyl)trisulfide (177c) (0.23 g, 58%): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.821, 0.858, 0.894 (t, 3H); 1.25-1.56 (m, 4H); 2.58, 2.61, 2.65 (t, 2H); 7.17-7.35 (m, 15H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 13.60(CH<sub>3</sub>); 21.53(CH<sub>2</sub>); 31.01(CH<sub>2</sub>); C9.31(CH<sub>2</sub>); 73.19(C-S); 127.11; 127.85; 130.42; 143.55 ppm. A second impure fraction was obtained which was identified to be a mixture of 177c, 167c and 167d.

#### Reaction of 162b with n-Butyl Lithium.

outer to

To a solution of 162b (0.68 g, 2.0 mmol) in 25 mL of ether at  $-78^{\circ}$ C under nitrogen was added (0.8 mL) a 2.5 M solution of *n*-butyllithium. The resulting solution was stirred at  $-78^{\circ}$ C and allowed to warm slowly to ambient temperature. The mixture was washed with water and filtered to remove a yellow precipitate (9.1 mg) identified as sulfur (TLC). The mixture was separated and the ether layer dried over anhydrous sodium sulfate and after removal of the solvent under reduced pressure chromatographed on silica gel with 20% chloroform in hexanes to yield a small amount of sulfur (TLC) 4.5 mg and two other fractions. The second fraction was identified as 177b (0.291 g, 40%) and the third fraction a mixture of the 167d and 167c which on removal of the solvent was a brittle foam.

Butyl(triphenylmethyl)sulfide (177a) (0.12 g, 36%): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.780, 0.809, 0.844 (t, 3H); 1.28-1.42 (m, 4H); 2.14, 2.18, 2.21 (t, 2H); 7.19-7.48 (m, 15H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 13.62 (CH<sub>3</sub>); 22.12 (CH<sub>2</sub>); 30.65 (CH<sub>2</sub>); 31.69 (CH<sub>2</sub>); 66.31 (C-S); 126.45; 126.75; 129.57; 145.06 ppm.

#### Reaction 162a-c with 1-Butanethiol: General Procedure.

To a solution of the sulfide (0.10 mmol) in 25 mL ether was added 1-butanethiol (0.80 g, 0.10 mmol). The resulting mixture was stirred in the dark for 48 h under nitrogen. TLC showed a mixture of four components identified as sulfur, 1-butanethiol, and a mixture of 167 and 177. Chromatography of the resulting mixture on silica gel with 20% chloroform in hexanes yielded the sulfide.

Tetrasulfide (177d): (0.245 g, 62%) <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 13.62 (CH<sub>3</sub>); 21.49 (CH<sub>2</sub>); 30.98 (CH<sub>2</sub>); 38.86 (CH<sub>2</sub>); 73.50 (C-S); 127.19; 127.93; 130.28; 143.08 ppm.

Trisulfide (177c): (0.284 g, 72%) spectra identical to that obtained in the reaction of 162c and butylmagnesium chloride.

Disulfide (177b): (0.184 g, 52%) spectra identical to that obtained in the reaction of 162b and butylmagnesium chloride.

## Preparation of Butyl(triphenylmethyl)monosulfide (177a)

In 50 mL of toluene was mixed 164 (2.78 g, 1.0 mol) and 1-butanethiol (0.080 g, 1.0 mol). The solution was refluxed for 24 h under a nitrogen atmosphere. The solution was allowed to cool to ambient temperature and the solvent removed under reduced pressure. Recrystallization from ethanol gave a brown crystalline solid m.p.  $62-64^{\circ}C$ .

## Reaction of 162a-c with triphenylmethanethiol 163a

A mixture of the sulfide (0.10 mmol) and 163a (0.276 g, 0.10 mmol) in 25 mL of ether was stirred for 24 h in the dark under nitrogen. The resulting mixtures were analyzed by <sup>13</sup>C NMR. The sulfides were isolated by removal of the solvent followed by drying under vacuum to give brittle foams. The sulfides were identified by comparison of the <sup>13</sup>C NMR spectra with those of the authentic compounds. Reaction of 162c yielded 167d, (0.56 g, 88%) while the reaction of 162b yielded 167c (0.49 g, 80%). The monosulfide did not react.

## Reaction of 162a-c with Anhydrous Sodium Hydrosulfide (NaSH).

To each sulfide in 25 ml of ether at 0°C was added NaSH (2 equivalents) as a fine powder. The mixture was stirred under nitrogen for 24 h at ambient temperature. The mixture was filtered and the solvent removed under reduced pressure to yield a brittle foam. Chromatography on silica gel with 20% chloroform in hexanes gave the bis(triphenylmethyl)sulfide. Reaction of 162a (0.310 g, 1 mmol) gave 167c (0.11 g, 38%). Reaction of 162b (0.342 g, 1 mmol) gave 167d (0.19 g, 58%). Reaction of 162c (0.187 g, 0.5 mmol) gave 167e (0.082 g, 46%).

## Reaction of 162b with Potassium Phthalimide: Preparation of Phthalimido(triphenylmethyl)disulfide (179a)

The preparation of 179a is a modification of the procedure of McClaskey, Kohn and Moore<sup>210</sup> who prepared other phthalimido disulfides. To a solution of potassium phthalimide (0.93 g, 5 mmol) in 10 mL water was



added 10 g of crushed ice and a solution of chloro(triphenylmethyl)disulfide (1.71 g, 5 mmol) in 20 mL of hexanes. The reaction mixture was stirred vigorously for 2 h. Within 10 min of mixing, the color of the chlorodisulfide dissipated and a white precipitated was formed. The precipitate was isolated by filtration, washed with water and air dried to yield a white solid, (1.93 g) m.p. 145-159°C. Recrystallization from ethanol gave an analytical sample m.p. 187-193 °C d;  $R_f = 0.51$  (chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.14-7.18 (m, 9H); 7.32-7.37 (m. 6H); 7.79 (s, 4H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 72.46 (C-S); 123.73; 127.26; 127.84; 130.11; 132.04; 134.47; 143.00; 166.35 (C=O) ppm. MS (EI, 70 eV, 205°C) m/z: No M<sup>+</sup>·244 (82.2); 243 (Ph<sub>3</sub>C<sup>+</sup>, 74.7); 166 (Ph<sub>2</sub>C<sup>+</sup>, 71.7); 165 ([Ph<sub>2</sub>C-H]<sup>+</sup>, 100); 104 (56.2). Elemental analysis: cal'd %C = 71.52, %H = 4.19, %N = 3.09: found %C = 71.57, %H = 3.93, %N = 3.00.

## Reaction of 162c with Potassium Phthalimide: Preparation of Phthalimido(triphenylmethyl)trisulfide (179b)

To a solution of 162c (0.187 g, 0.5 mmol) in 25 mL ether was added 2 equivalents of potassium phthalimide (0.186 g, 1.0 mmol) as a fine powder. The heterogeneous mixture was stirred for 4 h under nitrogen, over which time the



yellow color of the trisulfide dissipated. The reaction was filtered to remove excess potassium phthalimide and KCl. TLC with 20% chloroform in hexanes shows a product and a small amount of a mixture of 167. Removal of the solvent under reduced pressure followed by recrystallization gave a white solid, (0.11 g, 47%), m.p. 128-134°C d;  $R_f = 0.64$  (chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.22-7.41 (m, 15H);

<sup>210.</sup> B. L. Mccaskey, G. K. Kohn and J. E. Moore, U. S. Patent 3,356,572, (1968); Chem. Abstr., 68, 29441j (1968).

## <u>Reaction of 162b with Xanthic Acid Potassium Salt: Preparation of O-</u> <u>Ethylthiocarbonyl(triphenylmethyl)trisulfide</u>

A mixture of 162b (1.71 g, 5.0 mmol) and xanthic acid potassium salt (0.160 g, 10.0 mmol) as a fine powder was stirred in 50 mL ether under nitrogen for 24 h. The mixture was filtered to remove any unreacted xanthic acid potassium salt and potassium chloride. Removal of the solvent under reduced pressure followed by recrystallization from ether yielded a light yellow solid (0.80 g, 40%), m.p. 107-108.5°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.35, 1.39, 1.42 (t, 3H); 4.49, 4.52, 4.56, 4.593 (q, 2H); 7.25-7.34 (m, 15H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 13.58 (CH<sub>3</sub>); 71.36 (CH<sub>2</sub>); 73.43 (C-S); 127.42; 128.06; 130.21; 142.87; 210.65 (C=S) ppm. MS (EI, 70 eV, 150°C) m/z: 243 (Ph<sub>3</sub>C<sup>+</sup>, 63); 165 ([Ph<sub>2</sub>C - H]<sup>++</sup>, 100); 150; 76 (CS<sub>2</sub><sup>+</sup>, 49); 60 (COS<sup>+</sup>, 90); 45 (EtO<sup>+</sup>, 42).

## Reaction of 162b with Lithium Aluminium Hydride

To a stirred solution of 162b (0.17 g, 0.50 mmol) in 25 mL ether was added lithium aluminium hydride (0.019 g, 0.50 mmol). The evolution of a gas with a foul odor was detected, H<sub>2</sub>S. The mixture was stirred for 0.12 h and then filtered to yield a colorless solution. Removal of the solvent under reduced pressure yielded a foam which was chromatographed on silica gel with 5% chloroform in hexanes. Two fractions were identified as, 163a (45.6 mg, 31%) (<sup>13</sup>C and <sup>1</sup>H NMR) and 167d (64.7 mg, 42%) (<sup>13</sup>C NMR and comparison to the actual compound).

#### Reaction of 162b with Triphenylphosphine (143)

A sample of 162b (0.345 g, 0.0010 mol) and 143 (0.262 g, 0.0010 mol) were stirred in 15 mL chloroform at room temperature under a nitrogen atmosphere. The reaction was monitored by GC and after 12 h all of 143 was consumed and formation of triphenylphosphine sulfide was indicated. Chromatography of the mixture on silica gel with 20% chloroform in hexanes gave four fractions: sulfur (4.8 mg) (TLC), 167c (0.165 g); 144 (0.271 g) (GC, TLC, m.p., <sup>1</sup>H NMR); and triphenylphosphine oxide (0.056 g) (GC, TLC, m.p., <sup>1</sup>H NMR).

#### Reaction of 162b with Ethanol

-

Ţ

A sample of 162b (0.342 g, 0.001 mol) was stirred in 10 mL absolute ethanol under a nitrogen atmosphere. After 1 h the yellow color of the chlorodisulfide had dissipated. After 24 h a white precipitate has formed in solution which was isolated by filtration (0.082 g). TLC indicated that it was one component, <sup>1</sup>H NMR indicated only aromatic protons. Both TLC and GC revealed that the solid was not ethyl triphenylmethyl ether (183). After 24 h in a chloroform solution the solid has decomposed to sulfur (TLC), and ethyl triphenylmethyl ether. The solid obtained from the filtrate contained 183, sulfur and two slower moving components (TLC).

## Reaction of 162b with Sodium Ethoxide

A sample of 162b (0.342 g, 0.001 mol) and potassium methoxide were stirred in 10 mL absolute ethanol under a nitrogen atmosphere. The active species was therefore potassium ethoxide. After 0.5 h the yellow color of the chlorodisulfide had dissipated. After 24 h a light yellow precipitate has formed in the reaction mixture. Filtration gave (0.182 g) of a light yellow solid which was indicated by TLC to consist of only one component. The ethanol solution consisted of several components identified as sulfur and 183 (TLC, GC). The solid was also identified as 183 by a comparison of the spectra of the authentic compound.

In a separate experiment, the ethanol solution was washed with ether and water and then separated by TLC plates with hexanes as the eluent to yield four components, sulfur (TLC), 183 (TLC, <sup>1</sup>H NMR, <sup>13</sup>C NMR, m.p. 79.5-80°C (lit<sup>211</sup> 82-83°C), m.m.p. 77.5-79.5°C)), bis(triphenylmethyl)trisulfide (<sup>1</sup>H NMR, <sup>13</sup>C NMR, GC) and triphenylchloromethane.

## 6.2.6.2 Reaction Of 162a, 162b and 162c With 1,3-Dienes

## Trapping of S<sub>2</sub> from the Decomposition of 162b; Representative Experiments

To a solution of 162b (0.51 g, 1.5 mmol) in 25 mL of dichloromethane was added 2,3-dimethyl-1,3-butadiene (0.041 g, 0.5 mmol). The solution was heated to reflux under nitrogen for 2 h, cooled to ambient temperature and the mixture adsorbed on silica gel. Chromatography on silica gel with 20% chloroform in hexanes yielded two isolated components identified as sulfur (TLC) and a pungent

<sup>211.</sup> H. A. Smith and R. J. Smith J. Am. Chem. Soc., 70, 2400 (1948).

yellow oil (44 mg, 61%). The oil gave a  ${}^{1}H$  NMR spectrum with signals corresponding to a 1:2.5 mixture of tetrasulfide and disulfide.

The reaction was conducted by varying solvent, reaction time, temperature and ratio of the reactants. The results of these experiments and the condition are summarized in the main text (Table 14).

The reaction above was repeated and chromatography with alumina as the solid support with 20% chloroform in hexanes. No separation of the disulfide from the tetrasulfide was obtained.

The above reaction was repeated and the chromatography conducted on silica gel using 5% chloroform in hexanes as the eluent. The chromatography fractions collected were one-third normal size. Three components were isolated and identified as: sulfur, the cyclic disulfide and cyclic tetrasulfide. Disulfide (21.6 mg, 29%) <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.75 (s, 3H); 3.20 (s, 2H) ppm, <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 20.80 (CH<sub>3</sub>); 34.15 (CH<sub>2</sub>); 125.13 (C=C) ppm. Tetrasulfide (25.4 mg, 35%), <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.79 (s, 3H); 3.66 (s, 2H) ppm, <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 18.13 (CH<sub>3</sub>); 42.78 (CH<sub>2</sub>); 130.29 (C=C) ppm.

# <u>Trapping of S<sub>2</sub> from the Decomposition of 162b in the Presence of *p*-Hydroquinone (175)</u>

To a solution of 162b (0.51 g, 1.5 mmol) and 175 (10 mg, 0.01 mmol) in 25 mL of chloroform was added 2,3-dimethyl-1,3-butadiene (0.041 g, 0.5 mmol). The solution was refluxed for 1 h under nitrogen and allowed to cool to ambient temperature. Chromatography on silica gel with 20% chloroform in hexanes gave a 1:6 mixture of trapped adducts (32 mg, 44%).

Changing the solvent system from chloroform to benzene gave a 40% yield of a 1:6 disulfide to tetrasulfide mixture

## Attempted Trapping of Diatomic Sulfur from the Thermal Decomposition of 162b in the Presence of Inhibitor 175, Separation with TLC Plates.

A mixture of 162b (0.102 g, 0.300 mmol), 2,3-dimethyl-1,3-butadiene (0.100 g, 1.20 mmol) and 175 (0.005 g, 0.045 mmol) was heated at  $40^{\circ}$ C in 10 mL of chloroform, under nitrogen for 12 h. The solvent was removed under reduced pressure and the mixture chromatographed on silica gel TLC plates. The plates were developed twice with hexanes to yield a band below sulfur which corresponded

to a trapped adduct. Extraction of the silica gel with chloroform and filtration followed by removal of the solvent under reduced pressure gave a yellow oil (10.0 mg, 22.8%). The <sup>1</sup>H NMR spectrum indicated the oil to be a 1:3 mixture of disulfide to tetrasulfide.

A mixture of 162b (0.102 g, 0.300 mmol), 2,3-diphenyl-1,3-butadiene (0.124 g, 0.600 mmol) and 175 (0.005 g, 0.045 mmol) was heated at 40°C in 10 mL of chloroform, under nitrogen for 12 h. The solvent was removed under reduced pressure and the mixture chromatographed on silica gel TLC plates with hexanes. The fraction from  $R_f$  0.1-0.3 was collected, extracted with chloroform and chromatographed for a second time using the same conditions. The chromatography yielded two fractions, the disulfide (3.0 mg, 4%), <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.67 (s, 2H); 7.20 (m, 5H) and the tetrasulfide (9.0 mg, 11%).

## Attempted Trapping of Diatomic Sulfur from the Decomposition of 173a

## a) 2,3-Dimethyl-1,3-butadiene 109

To a solution of 173a (0.0494 g, 0.139 mmol) in 5 mL of chloroform was added three equivalents of 2,3-dimethyl-1,3-butadiene (0.0340 g, 0.417 mmol). The mixture was heated to 50°C for 2 h, cooled to ambient temperature and the solvent removed under reduced pressure to near dryness. Chromatography of the residue on TLC plates with 2% chloroform in hexanes yielded a band corresponding to tetrasulfide (4.6 mg, 22.7%). <sup>1</sup>H NMk (CDCl<sub>3</sub>)  $\delta$ : 3.64 (s, 2H); 1.79 (s, 3H).

#### b) 2,3-Diphenyl-1,3-butadiene 110

The above reaction repeated using 110 (0.086 g, 0.43 mmol) for 109 gave a complex mixture which could not be separated by TLC. The <sup>1</sup>H NMR spectrum of the crude reaction mixture exhibited a small signal which corresponded to the trapped adduct, 3.67 ppm. The material could not be isolated.

## Attempted Trapping of Diatomic Sulfur from the Thermal Decomposition of 173a in the Presence of 175

A mixture of 173a (0.070 g, 0.200 mmol), 2,3-dimethyl-1,3-butadiene (0.050 g, 0.600 mmol) and 175 (0.010 g, 0.090 mmol) in 10 mL of chloroform was heated at  $50^{\circ}$ C, under nitrogen for 12 h. The solvent was removed under reduced pressure and the residue chromatographed on silica gel TLC plates using hexanes as the eluent. A band below sulfur was isolated which corresponded trapped adduct, 6.6

mg (23.1%). <sup>1</sup>H NMR indicated a 1:1 mixture of disulfide and tetrasulfide.

## Reaction of 162a with 2.3-Dimethyl-1.3-butadiene.

To a solution of 162a (0.620 g, 2 mmol) in 25 mL of dry dichloromethane was added 2,3-dimethyl-1,3-butadiene (0.242 g, 3.0 mmol). The mixture was heated to reflux in the dark for 72 h and then chromatographed on silica gel with 5% chloroform in hexanes; small amount of sulfur was obtained. No 107 or 127 were indicated.

## Reaction of 162c with 2.3-Dimethyl-1.3-butadiene.

To a solution of 162c (0.187 g, 0.50 mmol) in dry dichloromethane was added 2,3-dimethyl-1,3-butadiene (0.121 g, 1.50 mmol). The mixture was heated to reflux in the dark for 2 h and then chromatographed on silica gel with 5% chloroform in hexanes to yield a 1:3 mixture of 107 and 127 (12.6 mg, 17%)

## 6.2.6.3 <u>Reaction of Chloro(triphenylmethyl)monosulfide with Thiocarbonyl</u> <u>Compounds.</u>

## Purification of 4.4'-Dimethoxythiobenzophenone (193)

Technical grade 193, obtained from Aldrich Chemical Company, was purified using the procedure of Steliou and Mrani.<sup>88</sup> To the thioketone-ketone mixture (<sup>1</sup>H NMR) (3.68 g) in 25 mL of dry toluene was added hexamethyldisilathiane (3.53 mL, 0.015 mol). To this mixture was added 9 mL of a 1 M boron



trichloride solution in dichloromethane and the resulting mixture was refluxed for 4 h. The solution was extracted with water and toluene and separated. The organic layer was dried with anhydrous sodium sulfate and the solvent removed under reduced pressure. Two recrystallizations from absolute ethanol gave 2.71 g (74%) of blue needle like crystals, m.p. 119-119.5°C (lit.<sup>212</sup> 115°C);  $R_f = 0.04$  (20% chloroform in hexanes, 0.64 (chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.87 (s, 6H); 6.87 (dt, 4H) 7.72 (dt, 4H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 55.47 (CH<sub>3</sub>O); 113.10 (CH);

<sup>212.</sup> L. Gattermann, Chem. Ber., 28, 2869 (1895).

## 132.07 (CH); 140.71 (C-O); 163.06; 233.27 (C=S) ppm.

## Test of Photosensitivity of 193

Two identical samples of 193 in chloroform-d were prepared in 5 mm NMR tubes. One sample was maintained in ambient light while the second sample was kept in the dark by wrapping foil. After 2 days the intense blue color of the light sample had decreased but no change was observed in sample maintained in the dark. After 5 days the <sup>1</sup>H NMR spectrum of the light sample showed signals corresponding to the formation of 4,4'-dimethoxybenzophenone, whereas the dark sample exhibited no decomposition either visually or in the <sup>1</sup>H NMR spectrum. After 8 d the sample maintained in ambient light was almost totally converted into the ketone as determined from the <sup>1</sup>H NMR spectrum.

## Preparation of Bis(4-tolyl)trithiocarbonate (194)

To a mixture of 4-methylthiophenol (3.72 g, 0.030 mol) and triethylamine (4.04 mL, 0.030 mol) in 100 mL of ether at 0°C was slowly added thiophosgene (1.73 g, 0.015 mol). Immediately upon the addition of the thiophosgene a white



precipitate formed in the reaction flask. The addition time was 0.5 h and the reaction was stirred for a further 24 h at ambient temperature. The reaction mixture was filtered and the isolated solid washed with ethe<sup>-</sup>. The ether extracts were combined and the solvent removed under reduced pressure. Two recrystallization from hexanes gave a bright yellow solid (2.1 g, 46%), m.p. 114-114.5°C (lit.<sup>213</sup> 115°C);  $R_f = 0.22$  (20% chloroform in hexanes, 0.79 (chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.43 (s, 6H); 7.28, 7.32 (d, 4H); 7.42, 7.46 (d, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.44 (CH<sub>3</sub>); 127.12; 130.26; 135.30; 141.08; 226.21 (C=S) ppm.

## Preparation of Bis(4-methoxyphenyl)thiocarbonate

The preparation was analogous for the trithiocarbonate above except the 4methoxyphenol (3.72 g 0.030 mol) replaced 4-methylthiophenol. Recrystallization from methanol yielded a flaky off white solid m.p. 151-156°C, (1.6 g, 36%);  $R_f =$ 0.04 (20% chloroform in hexanes, 0.57 (chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.81 (s,

213. W. Autenrieth, and H. Hefner, Chem. Ber., 58, 2151 (1925).

6H); 6.92, 6.97 (d, 4H); 7.11, 7.15 (d, 4H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 44.50 (CH<sub>3</sub>O); 114.47; 122.49; 147.16; 157.80; 195.92 (C=S) ppm.

#### Reaction of 193 and 162a

×.

ž

To a flask containing 193 (0.183 g, 0.71 mmol) in 25 mL chloroform was added 162a (0.210 g, 0.71 mmol) as a solid. The solution was stirred for 1 h over which time a precipitate formed in solution. The solution was filtered to leave a yellow solid which was washed with acetone and identified as sulfur (TLC), (0.207 g, 92%). Chromatography of the filtrate with 10% ethyl acetate in hexanes on silica gel yielded four components; trace amounts of sulfur, and 163a (an impurity in the sulfenyl chloride), starting material 193 (0.161 g, 89%) and 169 (0.155 g, 87%) (formed from the hydrolysis of 164). <sup>13</sup>C analysis of the crude reaction mixture showed the presence of 164 and 193.

### Reaction of 193 and 172b for NMR Analysis

A solution of 193 (0.0258 g, 0.01 mmol) and 172b (0.0310 g, 0.01 mmol) were prepared in dichloromethane- $d_2$  and cooled to -78°C. The two solution were mixed in a 5 mm NMR tube at -78°C. The resulting solution was analyzed by <sup>19</sup>F NMR, as described above.

## Reaction of 162a and 194

To a flask containing 194 (0.145 g, 0.50 mmol) in 20 mL chloroform was added 162a (0.155 g, 0.50 mmol) as a solid. The reaction mixture was stirred for 1 h over which time a yellow precipitate formed. Filtration yielded a yellow solid identified as sulfur (TLC) (17.0 mg, 106%). On melting the yellow solid expands 60-70°C, and finally melts 100-110°C. Chromatography on the filtrate with 20% chloroform in hexanes on silica gel yielded two components; starting material 194 (0.120 g, 83%) and 169 (0.097 g, 75%) (formed in the hydrolysis of 164).

## Reaction of 194 and 172b for NMR Analysis

A solution of 194 (0.029 g, 0.01 mmol) and 172b (0.0310 g, 0.01 mmol) were prepared in dichloromethane- $d_2$  and cooled to -78°C. The two solution were mixed in a 5 mm NMR tube at -78°C. The resulting solution was analyzed by <sup>19</sup>F NMR, as described above.

## Reaction of 162a and 193 for Catalytic Determination

To a solution of 193 (1.55 g, 50 mmol) in 50 mL of dry dichloromethane was added 162a (0.017 g, 0.067 mmol). The blue color of the thioketone remained and the formation of a precipitate was observed. The mixture was stirred for 8 h. Filtration yielded a yellow solid identified as sulfur, (0.157 g, 98%). Chromatography of the filtrate with 20% chloroform in hexanes on silica gel yielded three components; a trace of sulfur (TLC), the starting thioketone 193 (0.011 g, 65%) and triphenylmethanol 169 (1.102 g, 87%).

## 6.2.6.4 <u>Reaction of 162b with Thiocarbonyl Compounds: Attempted Preparation of a Thioozonide.</u>

To a stirred solution of 162b (0.172 g, 0.500 mmol) in 10 mL Jry dichloromethane at  $-78^{\circ}$ C under a nitrogen atmosphere was added dropwise a solution of 193 (0.129 g, 0.500 mmol) in 5 mL of dry dichloromethane. Upon addition, the blue color of the thione immediately dissipated forming a yellow solution on further addition solution slowly darkened to orange. As the reaction mixture warmed to room temperature the orange solution changed to cherry-red between (-25°C to -15°C). No other change was observed on warming to ambient temperature.

A sample of the red solution shaken in air converts to the blue of the thicketone over a period of five minutes. To determine the cause of the color change two experiments were conducted. A sample of the red solution was flushed with dry oxygen (over phosphorus pentoxide) and no change was observed. A small sample of the red solution was shaken with deaerated water (boiled, cooled under nitrogen) under a nitrogen atmosphere reverts to the blue of the thione. The original change is thus attributable to moisture in the air.

## Reaction of 162b and 193 for NMR Analysis.

The above reaction was repeated at -40°C using one-tenth the reagent in deuterated chloroform. The solution was analyzed by  $^{13}$ C and  $^{1}$ H NMR spectroscopy.  $^{1}$ H NMR (CDCl<sub>3</sub>) d: 3.82 (s, 6H); 6.81, 6.85 (d, 4H); 7.31 (m, 19H) ppm.  $^{13}$ C NMR (CDCl<sub>3</sub>) d: 55.31 (CH<sub>3</sub>); 72.51 (C-S); 113.00; 127.03; 127.58; 129.97; 130.36; 133.12; 142.73; 159.27 ppm.

## Preparation of bis(4-methoxyphenyl)methanethiol (200)

To a stirred suspension of lithium aluminium hydride (0.046 g, 1.20 mmol) in 10 mL of anhydrous ether was added dropwise 193 0.310 g (1.20 mmol) in 10 mL of anhydrous ether. Upon addition the blue color of the thiobenzophenone



dissipated. The mixture was stirred at room temperature for 3 h, poured onto ice water and neutralized with 10% sulfuric acid. The mixture was separated and the aqueous layer washed twice with 50 mL ether. The ether extracts were combined and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the resulting light blue solid chromatographed on silica gel with 20% chloroform in hexanes to yield a white solid, (0.135 g, 43%) m.p. 77.0-78.0°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.20, 2.23 (d, 1H); 3.76 (s, 6H); 5.37, 5.39 (d, 1H); 6.80-6.84 (dt, 4H); 7.26-7.32 (dt, 4H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 46.50 (CH-SH); 55.21 (CH<sub>3</sub>O); 113.78; 128.73; 135.82; 158.53 ppm. IR (KBr) cm<sup>-1</sup>: 3006; 2961; 2931; 2902; 2836; 1511; 1457; 1258; 1234; 1174; 1024; 808. MS (EI, 70eV, 80°C) m/z: No M<sup>++</sup>; 227 ([M - SH]<sup>+</sup>, 100); 211 ([M - (H<sub>2</sub>S + CH<sub>3</sub>]<sup>+</sup>, 39); 170 (45); 169 (12); 152 (19); 141 (18); 121 (33).

## Reaction of 193 and 173b for <sup>19</sup>F NMR Analysis.

Solutions of 193 (0.029 g, 0.01 mmol) and 173b (0.0310 g, 0.01 mmol) were prepared in dichloromethane- $d_2$  and cooled to -78°C. The two solution were mixed in a 5 mm NMR tube at -78°C. The resulting solution was analyzed by <sup>19</sup>F NMR, as described previously.

## UV analysis of reaction of 162b and 193.

Stock solutions of 162b and 193 were prepared in chloroform. The reagents were mixed in the desired ratio and the solution analyzed in the UV spectrometer with or with-out a delay period. The results are presented in the main text.

## Purification of the Decomposition Products of the Adduct of 162b and 193.

The adduct was prepared at -40  $^{\circ}$ C in chloroform from 193 0.129 g (0.50 mmol) and 162b (0.171 g, 0.50 mmol). The solution was allowed to warm to room temperature and then heated to 50 $^{\circ}$ C for 48 h in the absence of light. The resulting blue solution was chromatographed on silica gel with 20% chloroform in hexanes

and then the eluent was changed to 10% ethyl acetate in hexanes. At the start of the column a blue band which corresponded to 193 was observed but quickly faded. The initial elution with 20% chloroform in hexanes gave three fractions. The first was a yellow solid, identified to be sulfur (0.0140 g) (TLC, m.p. 116-116.5°C). The second fraction was a white solid (0.0251 g), identified to be triphenylmethane (<sup>1</sup>H NMR, <sup>13</sup>C NMR, TLC, m.p. 90-93°C). The third fraction was identified to be a mixture of bis(triphenylmethyl)sulfides (<sup>13</sup>C NMR). Changing the solvent to 10% ethyl acetate in hexanes yielded two further components. The first was 169 and the final product was a white solid, (0.0913 g), identified to be 4,4-dimethoxybenzophenone (<sup>1</sup>H NMR, <sup>13</sup>C NMR, TLC).

# Attempted Trapping of Diatomic Sulfur from the 1:1 Addition Adduct of 162b and 193: NMR Scale.

A sample of the 1:1 addition product of addition adduct of 162b and 193 and 2,3-dimethyl-1,3-butadiene in 5 mL of chloroform-d was heated to 50°C for 3 days. The colorless solution turned blue during the heating period. <sup>1</sup>H NMR analysis of the mixture showed signals corresponding to the tetrasulfide.

# Attempted Trapping of Diatomic Sulfur from the Crude 1:1 Addition Adduct of 162b and 193 in the Presence of an Inhibitor.

The adduct was prepared as above from 162b (0.061 g, 0.178 mmol) and 193 (0.044 g, 0.171 mmol). To the initiate at room temperature was added 175 (0.020 g, 0.02 mmol) and 2,3-dimethyl-1,3-butadiene (0.075 g, 0.915 mmol) in 20 mL of dichloromethane. The mixture was heated to  $50^{\circ}$ C for 12 h under nitrogen. The solvent was removed under reduced pressure and the blue mixture chromatographed on silica gel TLC plates using hexanes. Each plate was developed twice to yield a band below that of sulfur. The fraction was removed and extracted with chloroform to yield the tetrasulfide (5.0 mg, 19.2%).

## 6.2.7 Preparation and Reaction of Bis(triphenylmethyl)sulfides

## Preparation of Bis(triphenylmethyl)monosulfide (167a)

To a stirred solution of triphenylmethane (1.22 g, 5.0 mmol) in 50 mL THF at  $0^{\circ}$ C under nitrogen was added (2.0 mL, 5.0 mmol) of a 2.5M n-butyl lithium solution in ether. The resulting red solution was stirred for 0.25 h and 162a added as a solid. The red color dissipated and the light brown solution stirred for 1 h. The solvent

was removed under reduced pressure to leave a gummy yellow solid. Analysis of the crude mixture by <sup>13</sup>C NMR indicated the presence of the monosulfide, trisulfide, tetrasulfide and the starting methane. Recrystallization from acetone gave a light yellow solid (0.13 g, 5%), m.p. 161-163°C (lit<sup>165,119</sup> 165°C, 182°C d). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 67.76, 126.83, 127.34, 130.43, 143.71 ppm.

## Preparation of Bis(triphenylmethyl)disulfide (167b)

The disulfide was prepared by the procedure of Vorländer and Mittag.<sup>119</sup>  $^{13}$ C NMR (CDCl<sub>3</sub>)  $\delta$ : 73.53; 126.97; 127.47; 130.58; 143.84 ppm.

## Attempted Preparations of 167b from 162a and the Anion of 168

To a solution of 164 at  $-20^{\circ}$ C was slowly added a solution of n-butyllithium in hexanes. The resulting mixture was stirred for 10 min and a solution of 162a was slowly added dropwise and the solution allowed to stir for 1 h at ambient temperature. <sup>13</sup>C analysis of the crude mixture showed the presence of three components, 167b, 167c and 164 and the starting chloromethane.

## X-ray Analysis of 167b.

A colorless parallelpied crystal of  $C_{38}H_{30}S_2$  recrystallized from dichloromethane having approximate dimensions of 0.40 X 0.40 X 0.50 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Cu Ka at 1.75 Kw. The monoclinic cell parameters and calculated volume are a = 14.006(2), b = 12.173(1) and c =17.415(2)Å,  $\beta = 103.808^{\circ}$ , V = 2883.4(5)Å<sup>3</sup>. For Z = 4 and F.W. = 550.78 the calculated density is 1.269 g/cm<sup>3</sup>. The space group was determined to be  $P_{21}/c$ (#14). The data was collected at a temperature of 20  $\pm$  1° using the  $\omega$ -2 $\theta$  scan technique to a maximum 20 value of 110.0°. A total of 4019 reflections were collected of which 3836 were unique. The structure was solved by direct methods The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2855 observed reflections  $(I > 3.00\sigma(I))$  and 482 variable parameters and converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of  $R = \Sigma ||F_0| - |F_c|| / \Sigma$ |Fo| = 0.041,  $R_w = [(\Sigma w (|Fo| - |Fc|) / \Sigma wFo^2)]^{1/2} = 0.036$ . The standard deviation of an observation unit weight was 2.42. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure

## Corporation.

## Thermolysis of 167b.

A sample of 167b (0.203 g, 0.37 mmol) was heated slowly (5°C/min) to a temperature of 165°C under nitrogen. The mixture was then allov ed to slowly cool to ambient temperature. The residue was dissolved in CDCl<sub>3</sub> and analyzed by <sup>13</sup>C NMR. TLC of the mixture indicated the presence of thiobenzophenone and no sulfur. Chromatography on silica gel with 20% chloroform in hexanes yielded three compounds. Changing the solvent to 1:1 chloroform/hexanes yielded one further fraction. Fraction 1 was identified as triphenylmethane (19 mg, 9%); fraction 2 was identified as a mixture of 167c and 167d (106 mg, 50% (of the isolated material by weight)), 167d was the predominant component of the mixture; Fraction 3 was a mixture of several components that could not be identified as a mixture of 169, thiobenzophenone and thiobenzophenone (17 mg, 8% (of the isolated material by weight)). The identifications were made on the basis of the <sup>13</sup>C NMR spectra.

## Preparation of Bis(triphenylmethyl)trisulfide (167c).

To a stirred suspension of N,N'-thiobisbenzimidazole<sup>26</sup> (2.66 g, 10 mmol) in 50 mL benzene was slowly added 163a (5.52 g, 20 mmol) in 50 mL benzene. Addition time was 0.5 h and the mixture stirred for a further 24 h. The benzimidazole was removed by filtration and the solvent removed under reduced pressure to give a brittle foam. Recrystallization from benzene-petroleum ether gave a white solid (1.87 g, 32%), m.p. 154-156°C (lit<sup>165</sup> 146-148°C).<sup>214</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.238-7.359 (m) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 72.55; 126.95; 127.81; 130.25; 143.45 ppm.

## Preparation of Bis(triphenylmethyl)tetrasulfide (167d).

The tetrasulfide was the 167c except prepared as for N.N'dithiobisbenzimidazole<sup>26</sup> (2.99 g, 10 mmol) was replaced N.N'for thiobisbenzimidazole. Recrystallization of the brittle foam from chloroform-ethanol

<sup>214.</sup> Nabakayshi, ref. 165, synthesized the sulfides from 3-7 sulfurs and found that they all had nearly identical melting points. Careful recrystallization of 167c gave a solid which had a higher melting point. A mixed melting with the solid prepared by the method of Nabakayshi and the sample of 167c showed no depression of the melting point. This indicated that the melting point reported was incorrect. The difference in melting point is reasonable in consideration of the bond dissociation energies of di-, tri- and tetrasulfides.

yielded a white solid (0.55 g, 18%) m.p. 141-143°C (lit<sup>165</sup> 146-147°C). Mixed melting point with 167c 132-142°C <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.238-7.359 (m) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 73.49; 127.13; 127.86; 130.33; 143.27 ppm.

## Preparation of Bis(Triphenylmethyl)pentasulfide (167e).

To a solution of 162b (1.75 g, 5.0 mmol) in 50 mL ether was added hexamethyldisilathiane<sup>215</sup> (0.45 g, 2.5 mmol). The mixture was stirred under nitrogen for 18 h and extracted with a chloroform water mixture and separated. The organic layer was dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. Recrystallization from chloroform-ethanol gave a light yellow solid (0.41 g, 25%) m.p. 141-143°C (lit<sup>165</sup> 146-147°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.238-7.359 (m) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 73.66; 127.12; 127.93; 130.30; 143.10 ppm.

## Preparation of Bis(Triphenylmethyl)heptasulfide (167g).

To a solution of 162c (0.376 g, 1.0 mmol) in 50 mL ether was added hexamethyldisilathiane<sup>215</sup> (0.090 mL, 0.50 mmol). The mixture was stirred under nitrogen for 18 h and extracted with a chloroform water mixture. The organic layer was separated, dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. Chromatography on silica gel with 20% chloroform in hexanes gave a light yellow solid (0.156 g, 51%) m.p. 146-148°C (lit<sup>165</sup> 146-147°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.238-7.359 (m) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 73.80; 127.29; 128.01; 130.26; 142.86 ppm.

## Preparation of bis(mono-4-fluorotriphenylmethyl)trisulfide

To a suspension of N,N'-thiobisbenzimadizole (0.904 g, 0.0034 mol) in 50 mL benzene under nitrogen was slowly added mono-4-fluorotriphenylmethanethiol (2.0 g, 0.0068 mol) in 50 mL of benzene. Addition time was 0.5 h and the mixture stirred for a further 24 h. The reaction was filtered to remove benzimidazole and the solvent removed under reduced pressure to leave a brittle foam. Recrystallization from a mixture of petroleum ether chloroform yielded a white solid 0.15 g, (66%), m.p. 145-148°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 6.90, 6.95, 6.99 (t, 2H); 7.16-7.26 (m, 12H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 72.03 (C-S); 114.48, 114.77 (d); 127.15; 128.00; 130.03;

<sup>215.</sup> D. N. Harpp, and K. Steliou, Synthesis, 721 (1976).

## Preparation of bis(mono-4-fluorotriphenylmethyl)tetrasulfide

trisulfide except The tetrasulfide prepared the N.N'was as 0.0034 mol) was dithiobisbenzimadizole (0.99 g, replaced for N.N'thiobisbenzimadizole. The foam was recrystallized from a mixture of ethanol and chloroform to vield a white solid, m.p 126-128°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 6.89, 6.93, 6.97 (t, 2H); 7.14-7.29 (m, 12H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 72.88 (C-S); 114.55, 114.82 (d); 127.31; 128.01; 130.08; 132.15, 132.25 (d); 138.86, 138.90 (d); 143.18; 160.06, 163.34 (d) ppm.

## Thermolysis of 167c-e

A sample of the each sulfide was heated in open-end capillary melting point tube. The resulting mixtures were analyzed by <sup>13</sup>C NMR for the unsubstituted sulfides and by <sup>19</sup>F NMR for the substituted sulfides. The results are reported in the main text.

## Preparation of Triphenylphosphine dibromide (81)

The following procedure was conducted employing vigorously dry conditions. To a solution of triphenylphosphine (0.270 g, 1.05 mmol) in 5 mL of dichloromethane at  $0^{\circ}$ C under nitrogen was



slowly added bromine (0.160 g, 1 mmol). The solution was stirred and over 5 min a precipitate was formed in the reaction mixture. The mixture was used immediately.

## Isolation of the products from the reaction of bis(triphenylmethyl)trisulfide

To a solution of 167c (0.582 g, 1.0 mmol)in 25 mL of dry dichloromethane was slowly added a slurry of triphenylphosphine dibromide (1.0 mmol) in 1 mL of dichloromethane. The reaction mixture was stirred and the progress followed by TLC. After 2 h the solvent was removed under reduced pressure and the mixture chromatographed on silica gel with 10% ethyl acetate in hexanes and then flushed with methylene chloride. Isolated components included sulfur (19 mg, 30%), triphenylphosphine sulfide (213 mg, 72%) triphenylbromomethane (395 mg, 61%) and unreacted starting material (175 mg, 30%). The total recovery of material was

92 %.

# Attempted Trapping of $S_2$ from the Reaction of Bis(triphenylmethyl)trisulfide (167c) and Triphenylphosphine dibromide (81).

To a solution of 167c (0.582 g, 1.0 mmol) and 2,3-dimethyl-1,3-butadiene (0.041 g, 0.50 mmol) in 25 mL of dichloromethane was slowly added a slurry of triphenylphosphine dibromide (1.0 mmol) in 1 mL of dichloromethane. The reaction mixture was stirred and the progress followed by TLC. The reaction was stirred for 72 h and then chromatographed on silica gel with 5% chloroform in hexanes. The fraction below sulfur was collected and a <sup>1</sup>H NMR spectrum acquired. The spectrum gave signals indicating a mixture of three components, disulfide, tetrasulfide and brominated diene. The brominated diene was identified by the reaction of a sample of the diene with bromine.

## APPENDIX

atom	x	У	z	B(eq)
C1 (A)	0.1803(2)	0.5687(1)	0,4639(2)	5,6(1)
S (1A)	0.2243(2)	0.5201(1)	0.6435(2)	4.00(8)
C (1A)	0.4133(6)	0.7218(4)	0.9404 (6)	3.2(3)
C (2A)	0.5271(6)	0.7722(4)	0.9684(7)	3.9(3)
C (3A)	0.5932(6)	0.7727 (5)	0.8664(8)	4.1(3)
C (4A)	0.5461(6)	0.7242(5)	0.7360(7)	4.3(3)
C (5A)	0.4327(6)	0.6726(4)	0.7064(6)	3.7(3)
$C(\mathbf{D}\mathbf{A})$	0.3043(6)	0.6/21(4)	0.8091(6)	2.7(2)
$C(8\lambda)$	-0.1056(6)	0.6429(4)	0.0331(7) 0.6702(7)	J. D ( J )
C (9A)	-0.0920(7)	0.7872(5)	0.6943(7)	4.5(3)
C (10A)	0.0277(7)	0.8275(4)	0.7446(7)	4.0(3)
C (11A)	0.1351(6)	0.7737(4)	0.7708(6)	3.4(3)
C (12A)	0.1242(6)	0.6817(4)	0.7504(6)	2.7(2)
C (13A)	0.3294(6)	0.5059(4)	0.9326(7)	3.4(3)
C(14A)	0.3298(6)	0.4583(4)	1.0369(7)	4.1(3)
C (15A)	0.2391(7)	0.4734(5)	1.1153(7)	4.2(3)
C(15A)	0.1506(6)	0.5394(5)	1.0909(7)	4.0(3)
C(1/A)	0.1403(0)	0.50/3(4) 0.5710(4)	0.9853(6)	3.3(3)
C(10A)	0.2378(8)	0.5/10(4) 0.6206(4)	0.3020(0)	2.0(2)
H(1A)	0.3676	0.7230	1.0128	7.1
H (2A)	0.5580	0.8067	1.0604	17.3
H ( 3A)	0.6699	0.8064	0.8853	10.2
H (4A)	0.5914	0.7223	0.6627	8.7
H (5A)	0.4010	0.6385	0.6151	4.8
H(6A)	-0.0078	0.5772	0.6816	6.6
H(/A)	-0.1653	U.0004 0 9237	0.6351	0.1 7 7
H (OA)	-0.1055	0.0237	0.0/4/	11 A
$H(10\lambda)$	0.0371	0.0910	0.7009	45
H(11A)	0.3935	0.4950	0.8772	3.5
H(12A)	0.3936	0.4131	1.0554	6.1
H(13A)	0.2396	0.4405	1.1885	10.1
H(14A)	0.0854	0.5497	1.1433	3.2
H(15A)	0.0853	0.6317	0.9652	2.1
C1 (B)	0.3280(2)	0.9407(1)	0.1029(2)	5.7(1)
S(18) C(18)	0.2848(2) 0.0857(6)	0.9832(1) 0.7917(4)	0.2885(2)	4.02(8)
C(2B)	-0.0292(7)	0.7324(4)	0.3702(8) 0.3132(8)	4 3 (3)
C (3B)	-0.0913(7)	0.7328(5)	0.3132(0)	4.8(3)
C (4B)	-0.0416(7)	0.7822(5)	0.0995(7)	5.0(4)
C (5B)	0.0740(6)	0.8318(5)	0.1560(7)	3.8(3)
C (6B)	0.1377(6)	0.8312(4)	0.2927(6)	2.8(2)
C (7B)	0.5028(6)	0.8529(4)	0.3820(6)	3.4(3)
C(8B)	0.6064(6)	0.7968(5)	0.3795(7)	3.9(3)
C (9B)	0.5880(7)	0.7051(5)	0.3450(7)	4.2(3)
C(IUB)	0.4655(7)	U.5682(4)	0.3122(7)	4.1(J) 3 4(2)
(110)	(0) 619(0)	U. 1233(4)	0.2120(0)	3.4(3)

Atomic Coordinates (x,y,z) and Temperature Factors ( $B_{eq}$ ,  $A^2$ ) for 162a.

1

Ł

1.00

atom	×	У	Z	B(eq)
C(12B)	0.3780(6)	0.8173(4)	0.3483(6)	2.7(2)
C(13B)	0.1709(6)	0,9897(4)	0.5290(6)	3.4(3)
C(14B)	0.1692(6)	1,0355(4)	0.6586(7)	3.9(3)
C(15B)	0.2608(7)	1,0203(5)	0.7732 (7)	4.2(3)
C(15D)	0.3530(6)	0 9567 (5)	0.7551 (6)	3.7 (3)
C(10B)	0.3560(6)	0.9117(4)	0.6232(6)	3.1(3)
C(1/B)	0.2658(6)	0.9270(4)	0.5068(6)	2.6(2)
C(10B)	0.2660(6)	0 8800 (4)	0.3595(6)	2.6(2)
	0.2000(0)	0 7794	0.4657	5.3
H(2B)	-0.0626	0 6975	0.3693	5.8
n(2D)	-0.0020	0.00/0	0.1385	11.5
	-0.1000	0.7846	0.0041	15.6
П(ЧD) Ц(Бр)	1074	0 8664	0.1004	4.5
H(5B)	0 5161	0.0004	0.4066	6.5
п (ор) ч (7р)	0.5101	0.9175	0 4031	6.4
П(/D) П(9р)	0.0907	0.6227	0.3435	6.0
R(0D)	0.0000	0.0002	0.2873	10 1
H(9B)	0.451/	0.0044	0.2075	5 6
H(10B)	0.2771	0.0992	0.2908	3.0
H(11B)	0.1065	1.0002	0.4402	5.2
H(12B)	0.1031	1.0782	0.0/13	5.7
H(13B)	0.2591	1.0510	U.0041 0.0227	0.U E 3
H(14B)	0.4184	0.9469	0.0337	5.5
H(15B)	0.4218	0.8688	0.0100	4.2

Atomic Coordinates (x,y,z) and Temperature Factors ( $B_{eq}$ ,  $A^2$ ) for 162b.

atom	x	У	z	B(eq)
Cl S(1) S(2) C(2) C(2) C(2) C(2) C(2) C(2) C(2) C	0.7196(2) 0.7928(1) 0.8616(2) 0.3800(6) 0.2286(6) 0.1975(7) 0.3194(7) 0.4702(6) 0.5026(5) 0.8956(6) 0.9526(7) 0.8577(6) 0.7014(6) 0.7014(6) 0.7367(5) 0.6412(6) 0.7406(5) 0.6595(6) 0.7154(6) 0.7552(6) 0.7406(5) 0.6858(5) 0.6858(5) 0.6858(5) 0.6858(5) 0.399(4) 0.142(6) 0.312(5) 0.550(5) 0.965(4) 1.041(5) 0.532(5) 0.591(4) 0.619(5) 0.708(6) 0.708(6)	y         0.0362(1)         0.2395(1)         0.2364(1)         0.2104(5)         0.1263(6)         0.0672(6)         0.0944(6)         0.1790(6)         0.2376(4)         0.5644(6)         0.6941(6)         0.7413(6)         0.5644(6)         0.6571(6)         0.5266(5)         0.2525(5)         0.2525(5)         0.2525(5)         0.2525(5)         0.2525(4)         0.3689(5)         0.3689(5)         0.3689(5)         0.3689(5)         0.3385(4)         0.255(4)         0.107(5)         0.312(6)         0.3385(4)         0.255(4)         0.3385(4)         0.255(4)         0.3385(4)         0.255(4)         0.364(4)         0.107(5)         0.691(5)         0.840(4)         0.691(5)         0.471(5)         0.423(5)	$1 \cdot 3471(2)$ $1 \cdot 0843(1)$ $1 \cdot 0843(1)$ $1 \cdot 0179(5)$ $1 \cdot 0502(6)$ $1 \cdot 1605(6)$ $1 \cdot 2457(6)$ $1 \cdot 2226(6)$ $1 \cdot 3192(7)$ $1 \cdot 3914(6)$ $1 \cdot 3658(6)$ $1 \cdot 3914(6)$ $1 \cdot 3984(5)$ $0 \cdot 6653(6)$ $0 \cdot 9262(5)$ $1 \cdot 208(6)$ $1 \cdot 208(6)$ $1 \cdot 352(4)$ $1 \cdot 316(4)$ $1 \cdot 323(5)$ $1 \cdot 452(4)$ $1 \cdot 323(5)$ $1 \cdot 452(4)$ $1 \cdot 323(5)$ $1 \cdot 452(4)$ $1 \cdot 408(5)$ $1 \cdot 259(5)$ $0 \cdot 537(5)$ $0 \cdot 537(5)$	5.54(6) 3.53(5) 4.27(5) 3.5(2) 4.5(2) 4.5(2) 4.5(2) 3.8(2) 2.7(2) 3.7(2) 4.6(2) 4.3(2) 3.3(2) 3.3(2) 3.5(2) 4.1(2) 3.5(2) 4.1(2) 3.5(2) 4.1(2) 3.5(2) 4.1(2) 3.5(2) 4.1(2) 3.5(2) 4.1(2) 3.5(2) 3.5(2) 4.1(2) 3.5(2) 3.5(2) 4.1(2) 3.5(2) 3.5(2) 4.1(2) 3.5(2) 3.5(2) 3.1(2) 3.5(2) 3.1(2) 3.1(2) 3(1) 4(1) 3(1) 4(1) 5(1) 5
H(15)	0.760(4)	0.582(4)	0.965(4)	$\frac{1}{2(1)}$

~ *r* 

Atomic Coordinates (x,y,z) and Temperature Factors ( $B_{eq}$ ,  $A^2$ ) for 162c.

٢.

atom	x	У	Z	B (eq)
Cl S(1) S(2)	1.0536(3) 0.8698(3) 0.9623(3)	0.1829(2) 0.3236(1) 0.3402(1)	0.4255 0.1890(5) 0.3655(5)	6.7(2) 4.2(1) 4.8(1)
S(3)	1.1360(3)	0.2773(1)	0.3781(5) 0.080(1)	4.8(1)
C(19) C(18)	0.8828(7)	0.3667 (3)	-0.0527(7)	3.6(2)
C(17)	0.9838(6) 0.9435(8)	0.3597(3) 0.3288(4)	-0.1525(8) -0.2695(7)	4.7(2)
C(15)	0.8020(9)	0.3048(4)	-0.2867(7)	7.7(4)
C(14)	0.7009(6) 0.7413(6)	0.3118(4) 0.3427(4)	-0.1869(9) -0.0699(8)	6.6(3) 5.4(3)
H(15)	1.0802(6)	0.3761 (5)	-0.141(1)	6.8
H(14) H(13)	1.012(1) 0.775(1)	0.3240(6) 0.2837(6)	-0.3375(8) -0.3664(9)	6.8 6.8
H(12)	0.6046(7)	0.2954 (6)	-0.199(1)	6.8
H(11)	0.6724(8)	0.3474 (6) 0.4133 (3)	-0.002(1) 0.0947(8)	6.8 3.5(2)
C(7)	1.1832(6)	0.3582(2)	0.0880(8)	3.8(2)
C(8) C(9)	1.3313(6) 1.3809(5)	0.3708(3) 0.4385(3)	0.1024(9) 0.123(1)	5.0(2) 6.0(3)
C(10)	1.2825(7)	0.4936(3)	0.130(1)	5.8(3)
C(11) H(6)	1.1345(6) 1.1494(8)	0.4810(2) 0.3121(3)	0.1157(9) 0.074(1)	4.5(2) 5.1
H(7)	1.3983(7)	0.3333(4)	0.098(1)	5.1
H(8) H(9)	1.4818(5) 1 316(1)	0.4472(5) 0.5397(3)	0.133(1) 0.144(1)	5.1 5.1
H(10)	1.0674(8)	0.5185(3)	0.120(1)	5.1
C(6)	0.8260(6)	0.4620(3) 0.5052(4)	0.1057(8) 0.0012(7)	4.2(2) 5.0(2)
C(2)	0.7114(8)	0.5656(3)	0.0211(8)	6.3(3)
C(3)	0.6642(8)	0.5829(3) 0.5397(4)	0.1457(9) 0.2502(7)	6.0(3) 5.7(3)
C(5)	0.7789(7)	0.4792 (3)	0.2302(7)	4.6(2)
H(1)	0.824(1)	0.4934(5)	-0.0836(7) -0.0500(9)	5.9
H(3)	0.609(1)	0.6240(4)	0.159(1)	5.9
H(4)	0.666(1)	0.5514(5) 0.4498(A)	0.3350(8)	5.9
H(9)	0.002(1)	V. 4470 (4)	0.0014(0)	J . J

atom	x	У	z	B (eq)
atom S(1) S(2) C(1) C(2) C(3) C(4) C(5) C(6) C(7) C(8) C(9) C(10) C(11) C(12) C(12) C(13) C(14) C(15) C(16) C(17) C(16) C(17) C(16) C(17) C(20) C(21) C(22) C(22) C(23) C(24) C(25) C(25) C(26) C(27) C(28) C(25) C(27) C(28) C(30) C(31) C(35) C(36) C(37) C(38) C(37) C(38) C(37) C(38) C(37) C(38) C(37) C(38) C(37) C(38) C(37) C(38) C(37) C(38) C(37) C(38) C(37) C(38) C(37) C(38) C(37) C(38) C(37) C(38) C(38) C(37) C(38)	x 0.76908(6) 0.62789(6) 0.7433(3) 0.6928(3) 0.6972(3) 0.7520(3) 0.7520(3) 0.7984(2) 0.9591(3) 1.0310(3) 1.0727(3) 1.0435(3) 0.9715(3) 0.9276(2) 1.0128(3) 1.0623(3) 1.0107(3) 0.9099(4) 0.8607(3) 0.9114(2) 0.8560(2) 0.6101(3) 0.9099(4) 0.8607(3) 0.9114(2) 0.8560(2) 0.6101(3) 0.6681(4) 0.7633(4) 0.7994(3) 0.7417(3) 0.6459(2) 0.4474(3) 0.3492(3) 0.3080(3) 0.3080(3) 0.502(3) 0.5994(3) 0.5926(2) 0.5860(2)	y 0.20102(7) 0.15521(7) -0.0502(3) -0.1262(3) -0.1218(3) -0.0418(4) 0.0356(3) -0.0540(3) -0.0540(3) -0.0540(3) -0.0484(4) 0.0575(4) 0.1070(4) 0.2778(3) 0.2778(3) 0.2778(3) 0.2778(3) 0.3578(4) 0.2806(3) 0.1994(3) 0.1118(2) -0.1151(3) -0.2082(4) -0.1953(4) -0.2082(4) -0.1953(4) -0.0025(4) 0.0213(3) -0.0025(4) 0.0178(3) 0.0629(3) 0.0888(3) 0.0683(3) 0.1458(3) 0.2223(4) 0.3635(3) 0.2883(3) 0.1783(3) 0.0925(3) -0.0025(3) -0.0025(3) -0.0025(3) -0.0025(3) 0.0925(3) -0.0025(3)	z 0.29014(5) 0.27232(5) 0.3644(2) 0.3982(3) 0.4777(3) 0.5226(3) 0.4777(3) 0.5226(3) 0.4887(2) 0.4089(2) 0.3503(2) 0.3187(2) 0.2671(2) 0.2671(2) 0.2671(2) 0.2671(2) 0.3296(2) 0.4510(2) 0.5034(2) 0.5034(2) 0.5090(2) 0.4568(2) 0.4261(2) 0.3693(2) 0.1695(2) 0.1672(3) 0.1558(3) 0.1558(3) 0.1558(3) 0.2294(2) 0.2243(3) 0.1558(3) 0.0926(2) 0.1658(2) 0.0274(2) -0.0274(2) -0.0274(2) -0.0166(3) 0.1696(2) 0.1696(2) 0.2243(3)	B(eq) 3.42(4) 3.07(4) 3.5(2) 4.4(2) 4.3(2) 3.3(2) 2.5(1) 3.4(2) 4.3(2) 5.1(2) 5.4(2) 4.3(2) 5.4(2) 4.3(2) 2.8(1) 3.4(2) 4.3(2) 2.8(1) 3.4(2) 4.3(2) 2.6(1) 2.6(1) 4.3(2) 5.9(2) 6.2(3) 4.9(2) 3.1(2) 3.1(2) 4.3(2) 3.1(2) 3.1(2) 3.1(2) 3.5(2) 4.5(2) 4.5(2) 3.1(2) 3.5(2) 4.5(2) 3.1(2) 3.5(2) 4.5(2) 3.1(2) 3.5(2) 4.5(2) 3.1(2) 3.5(2) 4.5(2) 3.1(2) 3.5(2) 4.5(2) 3.1(2) 3.5(2) 3.1(2) 3.5(2) 3.1(2) 3.5(2) 4.5(2) 3.1(2) 3.5(2) 4.5(2) 3.1(2) 3.5(2) 3.1(2) 3.5(2) 4.5(2) 3.1(2) 3.5(2) 4.5(2) 3.1(2) 3.5(2) 3.5
C(37) C(38) H(1)	0.5926(2) 0.5860(2) 0.742(2)	0.1783(3) 0.0925(3) -0.060(2)	0.1696(2) 0.314(2)	2.7(1) 2.7(1) 3.1(8)
H(2)	0.650(2)	-0.183(3)	0.363(2)	6(1)
H(3)	0.663(2)	-0.177(3)	0.498(2)	4.4(9)
H(4)	0.760(2)	-0.035(3)	0.578(2)	4.3(9)
H(5)	0.840(2)	0.089(2)	0.518(2)	2.7(8)
H(6)	0.930(2)	-0.093(2)	0.380(2)	3.1(8)
H(7)	1.051(2)	-0.174(3)	0.333(2)	4(1)
H(8)	1.126(3)	-0.081(3)	0.242(2)	7(1)
H(9)	1.076(3)	0.099(3)	0.217(2)	7(1)
H(10)	0.958(3)	0.180(3)	0.266(2)	5(1)

Atomic Coordinates (x,y,z) and Temperature Factors ( $B_{eq}$ ,  $A^2$ ) for 167b.

، الاس<sup>ر</sup>

,

,

.

atom	x	У	Z	B(eq)
H(11)	1.049 (2)	0.146(3)	0.434(2)	4(1)
H(12)	1.132 (3)	0.271(3) 0.413(3)	0.520(2)	7(1) 5(1)
H(13)	0.874 (2)	0.406(3)	0.524(2)	5(1)
H(15) H(16)	0.792(2) 0.548(3)	0.280(2)	0.442(2) 0.183(2)	3.6(8) 6(1)
H(17)	0.639(3)	-0.277(3)	0.178(2)	7(1)
H(18) H(19)	0.800(3) 0.868(2)	-0.257(3) -0.084(3)	0.155(2) 0.146(2)	7(1) 4.2(9)
H(20)	0.769 (2)	0.072(2)	0.148(2)	3.3(8)
H(21) H(22)	0.335 (3)	-0.029(3)	0.281(2)	4.5(8) 6(1)
H(23)	0.215 (2)	0.001(3)	0.153(2)	3.7(8)
H (24) H (25)	0.423 (2)	0.119(2)	0.054(2)	3.3(8)
H(26) H(27)	0.615(2)	0.072(3)	0.026(2)	4(1)
H(28)	0.576 (3)	0.384(3)	-0.057(2)	8(1)
H(29) H(30)	0.553(3) 0.564(2)	0. <b>44</b> 0(3) 0.310(3)	0.065(2) 0.166(2)	6(1) 4.5(9)