SULFUR ALLOTROPE CHEMISTRY

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

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ABSTRACT

The synthesis of the sulfur homocycles S_6, S_9, S_{10}, S_{12} and S_{20}, which belong to the group of sulfur allotropes, has been achieved based on existing procedures. Polymeric sulfur S_μ was also prepared.

The parameters of a small scale model reaction between 2,3-diphenyl-1,3-butadiene and S_{10} were optimized. Products were identified and ^{1}H-NMR yields were calculated by comparison with an internal standard. The experimental parameters of this model served as a base for further reactions of S_{10} with a variety of simple or conjugated olefins. The products of these reactions were fully isolated and characterized using standard spectroscopic techniques. The structures of a new *bis*-sulfurated compound having a norbornane framework and of the product obtained from the dimerization of norborn-5-ene-2,3-dithiol were also confirmed by single crystal X-ray crystallography.

The sulfur homocycles S_9, S_{12} and S_{20} were also found to react with norbornene and two different 1,3-dienes. Products were identified and ^{1}H-NMR yields for these small scale reactions were calculated by internal standard comparison. Differences and similarities with the products obtained with S_{10} are discussed. Sulfuration efficiencies of the different allotropes towards selected substrates are also compared.

A mechanistic study was carried out. The implication of sulfur radicals in the thermal decomposition of S_{10} has been suggested. Reaction mechanisms accounting for the formation of the different products observed are proposed.

RÉSUMÉ

La synthèse des homocycles soufrés S_6, S_9, S_{10}, S_{12} et S_{20} appartenant au groupe des allotropes du soufre a été effectuée à partir de procédures déjà existantes. Du soufre polymérique S_μ a également été préparé.

Les paramètres d'une réaction modèle entre le 2,3-diphényl-1,3-butadiène et S_{10} ont étés optimisés sur de petites quantités. Les produits ont étés identifiés et les rendements par RMN du proton calculés par comparaison avec un standard interne. Les paramètres expérimentaux de ce modèle ont ensuite servi de base à des réactions entre S_{10} et d'autres oléfines simples ou conjuguées. Les produits de ces réactions ont été entièrement isolés et caractérisés à l'aide des méthodes spectroscopiques classiques. Les structures d'un nouveau composé *bis*-sulfuré possédant un groupement norbornane et le produit issu de la dimérization du norborn-5-ène-2,3-dithiol ont aussi été déterminées par analyse crystallographique.

Il a également été démontré que les homocycles soufrés S_9, S_{12} et S_{20} réagissent avec norbornène et deux 1,3-diènes différentes. Des produits ont été identifiés et les rendements par RMN du proton de ces réactions à petite échelle ont été calculés par comparaison avec un standard interne. Des différences et des similarités avec les produits obtenus avec S_{10} sont exposées. Le pouvoir de sulfuration de ces différents allotropes de soufre envers certains substrats sont comparés.

Une étude des mécanismes de ces réactions a été menée. La participation de radicaux soufrés lors de la décomposition thermique de S_{10} a été suggérée. Des mécanismes prenant en compte la formation des différents produits de réaction observés ont été proposés.

ACKNOWLEDGEMENTS

I would first like to thank my supervisor, Professor David N. Harpp, for his support, guidance and constant encouragement throughout this work. I have never met anybody else with this ability to communicate his energy and enthusiasm.

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I would like to thank all those from McGill University who have helped me in some way with the completion of this work; all my friends from Montreal; Joan and Bob Haris and their children for giving me a home away from home in North America.

Finally, thank you Ron for organizing some memorable or unmemorable parties!

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σ	standard deviation
Å	angstrom
Bp.	boiling point
°C	degrees Celsius
ca.	circa
CI	chemical ionization
EI	electron impact
eq.	equivalent
FAB	fast atom bombardment
g	gram
hr	hour
K	degrees Kelvin
lit.	literature
min	minute
mg	milligram
MHz	megahertz
ml	milliliter
mmol	millimole
mol	mole
Mp.	melting point
MS	mass spectrometry
n	normal
NMR	nuclear magnetic resonance
ppm	parts per million
ppb	parts per billion
s	second
tert	tertiary

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CHAPTER 1. INTRODUCTION

1.1. Background

1.1.1. Introduction

It is somehow quite difficult to be original when introducing an element that has been known for so long. Indeed, as long as history has been recorded, sulfur has been present. It can easily be argued that along with carbon, sulfur is the only non-metal that was known to ancients. The Bible contains 15 references to sulfur.

In ancient history, sulfur suffered from a bad reputation and was often referred to as a tool of destruction. The legendary devastation of Sodom and Gomorrah by brimstone,[1] the archaic name given to sulfur and derived from the phrase "fiery stone," attests to its image problem. The fact that the only known sources of sulfur were the deposits near volcanoes can probably easily explain this. The ancients often used sulfur as a bleaching and purification agent[2] as well as a constituent of pyrotechnics. The Greeks and the Romans both attributed to sulfur a divine power and its ability to cleanse evil. Interestingly, the Greek word θειον (qeion) was used to describe both "sulfur" and "having the quality of the divine". As a consequence, the *thio* in thiol and *theo* in theology have the same root.[3]

Sulfur has also been very closely bound to one of the most important discoveries of the Middle Ages and certainly one of the inventions that most changed the course of human history, the discovery of gunpowder. Its composition is a mixture of saltpeter (KNO_3), powdered charcoal and sulfur in a ratio of about 75:15:10 by weight.

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[1] Genesis 19, verse 24: "The Lord rained upon Sodom and Gomorrah brimstone and fire from the Lord out of Heaven."

[2] Homer, Odyssey, Book 22, 481: "Bring me sulfur, old nurse, that cleanses all pollution and bring me fire, that I may purify the house with sulfur."

[3] Kelly, P. *Chem. In Britain*, **April 1997**, 25.

Gunpowder appeared in Europe in the 14th century but had been discovered by Chinese Daoist alchemists three centuries before.[4]

It was only much later in 1809 that Gay-Lussac and Thenard proved with certainty the elemental nature of sulfur, which had first been postulated by Lavoisier. The composition of sulfur was indeed subject to controversy, as some still thought that oxygen and hydrogen were part of its composition. This confusion could have arisen from the fact that the manufacturing of sulfuric acid (H_2SO_4) had already started more than two centuries before that in Europe.[5] Industrial processes such as the lead chamber method introduced by Roebuck[6] (*ca.* 1755) as a modification of earlier processes, were able to produce tons of sulfuric acid. As it will be described later in this introduction, sulfuric acid nowadays is still the main product derived from sulfur.

In 1912, Beckmann showed by cryoscopy in molten iodine that sulfur was made up of S_8 molecules.[7] Later in 1935, the structure of sulfur below 95°C was fully assigned by Warren and Burwell using X-ray crystallography[8] and has been refined since then.[9] In its most stable form, sulfur is composed of 8 sulfur atoms arranged in a very characteristic crown shaped cycle as shown in Figure 1.

The molecules in the crystal lattice have an orthorhombic arrangement (α-S_8) with a density of 2.067 $g{\cdot}cm^{-3}$. The mean bond distance is 2.046 Å, the average bond angle is 108.2° and the average dihedral angle is 98.5°. Above 95°C and up to its melting point at around 119°C, *cyclo*-octasulfur S_8 exists in another less dense (1.94 $g{\cdot}cm^{-3}$) crystal

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[4] a) Butler, A. R. *Chem. In Britain*, **November 1988**, 1119. b) Seel, F. *Sulfur, its Significance for Chemistry, for the Geo-, Bio-, and Cosmosphere and Technology*, Müller, A. and Krebs, B. (Eds.), *Studies in Inorganic Chemistry*, **1984**, *5*, 55.

[5] a) Derry, T. K. and Williams, T. I. *A Short History of Technology from the Earliest Times to AD 1900*, Oxford University Press, Oxford, **1960**, 268 & 534. b) Haber, L. F. *The Chemical Industry 1900-1930*, Oxford University Press, Oxford, **1971**.

[6] Roebuck, P. *Chem. In Britain*, **July 1996**, 38.

[7] Beckmann, E. and Hanslian, R. *Z. Anorg. Chem.*, **1913**, *80*, 221.

[8] Warren, B. E. and Burwell, J. T. *J. Chem. Phys.*, **1935**, *3*, 6.

[9] a) Abrahams, S. C. *Acta Cryst.*, **1955**, *8*, 661. b) Caron, A. and Donohue, J. *Acta Cryst.*, **1965**, *18*, 562. c) Pawley, G. S. and Rinaldi, R. P. *Acta Cryst.*, **1972**, *B28*, 3605. d) Rettig, S. J. and Trotter, J. *Acta Cryst.*, **1987**, *C43*, 2260.

structure, monoclinic β-S_8.[10] A third less stable crystalline arrangement, monoclinic γ-S_8, was also discovered in 1890 by Muthmann.[11] This form of S_8 can be extracted from sulfur solutions or melts, but γ-S_8 needles can be more conveniently synthesized independently.[12] The parameters of this crystal structure have been determined.[12,13] γ-S_8 is more dense than α- and β-S_8 with a density of 2.19 g·cm^{-3}.

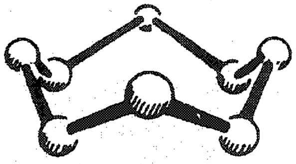

Figure 1. Structure of α-S_8

Other *cyclo*-octasulfur modifications have also appeared in the literature through the years but were constituted of either doubtful, unstable crystalline forms or probably of mixtures of α-, β- or γ-S_8.[14]

1.1.2. Sources of Sulfur

1.1.2.1. Natural Abundance

The abundance of sulfur in the Earth's crust is about 340 ppm,[15] which places it in 16th position of the elements of the earth. For comparison, sulfur is twice as abundant as the next element, carbon (180 ppm). Until 1880, the most important source of sulfur was the volcanic soil of Sicily. With the appearance of industrial processes, other sources of

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[10] a) Sands, D. E. *J. Am. Chem. Soc.*, **1965**, *87*, 1395. b) Templeton, L. K.; Templeton, D. H. and Zalkin, A. *Inorg. Chem.*, **1976**, *15*, 1999. c) Goldsmith, L. M. and Strouse, C. E. *J. Am. Chem. Soc.*, **1977**, *99*, 7580.

[11] Muthmann, I. W. *Z. Kristallogr.*, **1890**, *17*, 336.

[12] Watanabe, Y. *Acta. Cryst.*, **1974**, *B30*, 1396.

[13] Gallacher, A. C. and Pinkerton, A. A. *Acta. Cryst.*, **1993**, *C49*, 125.

[14] For a review on elemental sulfur: Meyer, B. *Chem. Rev.*, **1976**, *76*, 367 and references cited therein.

[15] Greenwood, N. N. and Earnshaw, A. *The Chemistry of the Elements*, 2nd Ed., University of Leeds, U.K., **1997**.

sulfur have been made available. This is in part due to the development of either new mining techniques or processes allowing the transformation of sulfur-containing compounds and the subsequent recovery of elemental sulfur. Some of these techniques will be discussed in the next Section.

In 2000, the world sulfur production in all forms was estimated to be around 57 megatons.[16] The contribution from the main producers is summarized in Table 1.

United States	Canada	Russia	China	Japan	Saudi Arabia	Other countries
10.4	10.3	5.5	5.2	3.5	2.4	19.7

Table 1. Estimated Sulfur Production by Country in 2000 (in megatons)

Traditionally, the sources of sulfur produced commercially can be classified in three main categories. The first includes native sulfur found in the caprock of salt domes and in sedimentary deposits mainly in the USA, in the Gulf of Mexico, and in Poland. These sulfur deposits are formed from the anaerobic bacterial decomposition of sulfate sediments over time. In 1999, this source of sulfur accounted for about 6.5% of the world commercial sulfur production.[16]

The second category includes mainly sour natural gas, which contains about 15-20% of hydrogen sulfide (H_2S) and crude oil, comprised of a wide variety of organosulfur compounds. The contribution of chemically derived sulfur from these sources has been increasing in the recent years. For the first time in 1971, chemical sulfur production exceeded that of mined sulfur. In 1999, sulfur produced from sour natural gas and petroleum accounted for about 58% of the world total sulfur production.[16] Sour gas producers are mainly Canada, USA, Russia and France.

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[16] http://minerals.usgs.gov/minerals/pubs/commodity/sulfur/, U.S. Geological Survey, Mineral Commodity Summaries, January **2001**.

Pyrites (FeS_2) and other metal sulfide minerals constitute the third main category of sulfur, but they have had a decreasing role. Pyrite is the most abundant of all metal sulfides. The largest deposits are found in China, which produced 72% of all pyritic sulfur in 1999. Pyritic sulfur accounted for about 9% of the world production in 1999.[16] Other metal sulfides are those of Cu, Ni, Zn, Pb and As. Sulfur is also derived from the metallurgy industry and in 1999, this source of commercial sulfur accounted for 18% of the world production.[16]

A less known and indirect source of elemental sulfur, comes from marine plankton. These microorganisms produce dimethylsulfide[17] and although its concentration in the oceans seems quite low at 0.01 ppb, it is estimated that about $40x10^9$ kg of sulfur is produced annually in this way.[3]

It is also difficult to neglect the sulfur released into the atmosphere in the form of sulfur dioxide (SO_2) gas from the combustion of hydrocarbons containing organosulfur impurities. In 1990, the estimated amount of anthropogenic sulfur in the atmosphere was close to 80 megatons.[18] A third of all sulfur and 99% of all sulfur dioxide entering the atmosphere comes from anthropogenic sources. Pollution problems obviously arise from this and constant efforts are devoted in order to limit this production. Finally, an average person contains about 150 g of the element in combined form, mainly in cysteine and cystine proteins.

1.1.2.2. Industrial Processes

In 1891, Frasch patented a process[15,19] that revolutionized sulfur mining that had been limited until then to the direct mining of volcanic deposits. His process allowed the

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[17] Keller, M. D.; Bellows, W. K. and Guillard, R. R. L. *Biogenic Sulfur in the Environment*, Saltzman, E. S. and Cooper, W. J. (Eds.), A.C.S. Symposium Series, **1989**, *393*, 167.

[18] http://www.asl-associates.com/sulfur.htm, A.S.L. & Associates, Helena, Montana, U.S.A., **1994**.

[19] a) Frasch, H. U.S. Patent 461 429/31, **1891**. b) For a review on Frasch's process: Haynes, W. *Brimstone: The Stone that Burns*, **1959**.

recovery of sulfur from the caprock of salt domes by injection of superheated water into the ground and then further recovery of the liquid sulfur pushed out by compressed air.

In the second half of the 20th century, the extraction of sulfur from sour gas (H_2S), also called acid gas, was developed in the USA and has become the number one source of sulfur in the world. The process[20] first patented[21] by Claus in 1882 is described in Figure 2.

$$\begin{array}{lllll} H_2S & + & 3/2\ O_2 & \longrightarrow & SO_2 + H_2O \quad \text{Eq. 1} \\ 2\ H_2S & + & SO_2 & \longrightarrow & 3/8\ S_8 + 2\ H_2O \quad \text{Eq. 2} \\ H_2S & + & 1/2\ O_2 & \longrightarrow & 1/8\ S_8 + H_2O \quad \text{Eq. 3 (overall)} \end{array}$$

Figure 2. Claus Process

The Claus process is very well suited for large acid gas streams of consistent composition. Indeed, the first part of the process, as shown in equation 1, requires a very precise control of the ratio O_2/H_2S. Some limitations include the fact that the Claus units have difficulties operating with gas streams of less than 15% H_2S. Some advantages include its low operating cost and the fact that it is capable of producing high purity sulfur (>99.9%). This process routinely recovers about 96% of the sulfur from acid gas. However, improvements, which now allow 98% to 99% conversion, have been developed by various companies.[22]

Over the past few years, many efforts have been devoted in order to limit H_2S emissions in the atmosphere.[23] Other processes adapted to various (in quantity and origin) sources of H_2S gas have thus been developed.[22]

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[20] a) Grancher, P. *Hydrocarbon Process.*, **1978**, *57*, 155. b) Grancher, P. *Hydrocarbon Process.*, **1978**, *57*, 257. c) George, Z. M. and Tower, R. W. *Can. J. Chem. Eng.*, **1985**, *63*, 618 and references cited therein.

[21] Claus, C. F. British Patent 3608, **1882**.

[22] Bourdon, J. C. *Hydrocarbon Process., Int. Ed.*, **1997**, *76(4)*, 57.

[23] Nagl, G. J. *Chem. Eng.(N.Y.)*, **1997**, *104(3)*, 125.

These pollution regulations have also generated new research on the Claus process itself. Milder and homogeneous catalytic routes for transforming H_2S into sulfur have been investigated. Platinum-based catalysts[24] and very recently, ruthenium-based catalysts[25] have been developed. Even if these homogeneously catalyzed systems have a small chance to be applied industrially,[26] they constitute very good models that will allow a better understanding of this important reaction.

The process used to extract sulfur from crude oil is called hydrodesulfurization. Crude oils, the sulfur content of which varies from 0.2 to 4 weight % depending on their origin, are first catalytically treated with hydrogen.[27] The organosulfur compounds present in the oil are thus transformed into H_2S that can further be converted into elemental sulfur, for example, by a Claus unit.

Finally, as far as sulfur production from pyrite or other metal sulfides is concerned, the mineral is usually roasted to produce SO_2, which is then directly converted into H_2SO_4.

1.1.3. Old and New Uses of Sulfur

1.1.3.1. Introduction

It is beyond the scope of this work to provide an exhaustive list of all the different applications of elemental sulfur. Instead, an emphasis will be put on the process of the vulcanization of rubber, which is quite relevant to this study as it involves the understanding of reactions between elemental sulfur and simple olefins or polyenes.

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[24] a) Shaver, A.; El-khateeb, M. and Lebuis, A.-M. *Angew. Chem., Int. Ed. Engl.*, **1996**, *35(20)*, 2362. b) Shaver, A.; Boily, H. and Lebuis, A.-M. *Inorg. Chem.*, **1996**, *35(22)*, 6356.

[25] Kovacs, I.; Pearson, C. and Shaver, A. *J. Organomet. Chem.*, **2000**, *596*, 193.

[26] *Chem. Eng. News*, October 28, **1996**.

[27] a) Gates, B. C.; Katzer, J. R. and Schuit, G. C. A. *Chemistry of Catalytic Processes*, McGraw Hill: New York, **1979**, 390. b) Angelici, R. J. *Acc. Chem. Res.*, **1988**, *21*, 387. c) Friend, C. M. and Roberts, J. T. *Acc. Chem. Res.*, **1988**, *21*, 994. d) Satterfield, C. N. *Heterogeneous Catalysis in Industrial Processes*, 2nd Ed., McGraw Hill, New York, **1991**, 378.

As an introduction, attention will be placed on a few selected uses or new properties of sulfur that have appeared in the past decade. These have drawn the attention of not only the scientific community but also the public in general.

However, if one wanted to get an overall picture of the different uses of sulfur, they can be summarized by Figure 3[15] and some common industrial applications have been reviewed in the literature.[28]

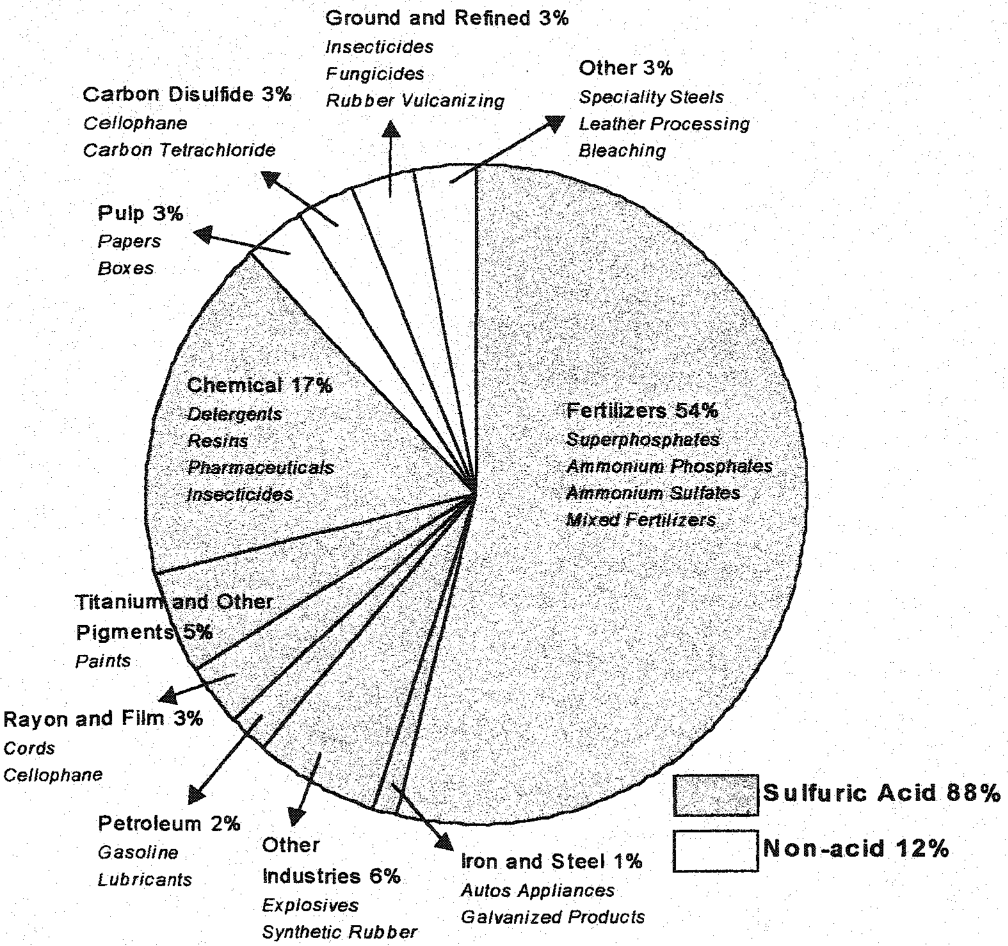

Figure 3. Principle Sulfur Uses as an Acid and a Non-acid.

This snapshot of the uses of sulfur shows how versatile this element can be and how it has impact in almost any given industry.

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[28] *New Uses of Sulfur*, West, J. R. (Ed.), Advances in Chemistry Series 140, A.C.S., Washington, D.C., **1975**.

It is appropriate to mention the tremendous amounts of sulfuric acid that are produced every year. The World's annual production is estimated to be of about 140 million tons, 40 million tons of which are produced in the United States.[6] In this country, in 2000, about 90% of sulfur was consumed in the form of sulfuric acid and agricultural chemicals (primarily fertilizers) represented 70% of the sulfur demand.[16]

The lead chamber process has been slowly replaced by the newer contact process,[6,29] which affords purer sulfuric acid (98% acid) as well as the formation of oleum ($H_2S_2O_7$). Oleum manufacture was not possible with the lead chamber process and was increasingly required in the production of dyes, drugs and explosives. The contact process involves the catalytic transformation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3) which is then converted into sulfuric acid upon dissolution in water. This process initially employed platinum as a catalyst but has now switched to vanadium pentoxide (V_2O_5) based catalysts. The conversion varies from 98% to 99.5% with the double contact process.[6]

Not all sulfur-containing compounds are being produced in such gigantic quantities as sulfuric acid. A few examples in the area of fine chemicals or pharmaceuticals are worth mentioning.

Sulfur atoms are present in drugs, some of which have been known for some years, such as Sulfathiazole (**1**), or more recently discovered, such as Calicheamicin γ^{I}_{1} (**2**).[30] Sulfathiazole belongs to the group of sulfa-drugs and was widely used against infection during World War II before being replaced by antibiotics.[31] Calicheamicin γ^{I}_{1} belongs to

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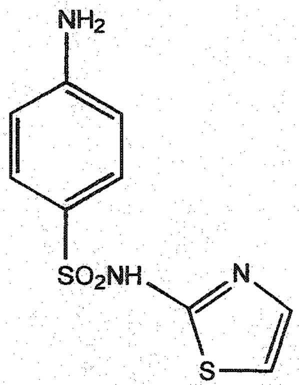
[29] a) Williams, T. I. *A Short History of Twentieth-Century Technology c.1900-c.1950*, Oxford University Press, New-York, **1982**, 133. b) For a review on industrial sulfuric acid production processes: Brändle, K., *Sulfur, its Significance for Chemistry, for the Geo-, Bio-, and Cosmosphere and Technology*, Müller, A. and Krebs, B. (Eds.), *Studies in Inorganic Chemistry*, **1984**, *5*, 237.

[30] a) Lee, M. D.; Dunne, T. S.; Siegel, M. M.; Chang, C. C.; Morton, G. O. and Borders, D. B. *J. Am. Chem. Soc.*, **1987**, *109*, 3464. b) Lee, M. D.; Dunne, T. S.; Chang, C. C.; Ellestad, G. A.; Siegel, M. M.; Morton, G. O.; Mcgahren, W. J. and Borders, D. B. *J. Am. Chem. Soc.*, **1987**, *115*, 3464.

[31] Goodman, L. S. and Gilman, A. *The Pharmacological Basis of Therapeutics*, 7th Ed. New-York: Macmillan, Weinstein, L. *The Sulfonamides*, **1985**, Chap. 56.

the enediyne[32] class of compounds and is known for its powerful anti-cancer activity. Its total synthesis has been published.[33]



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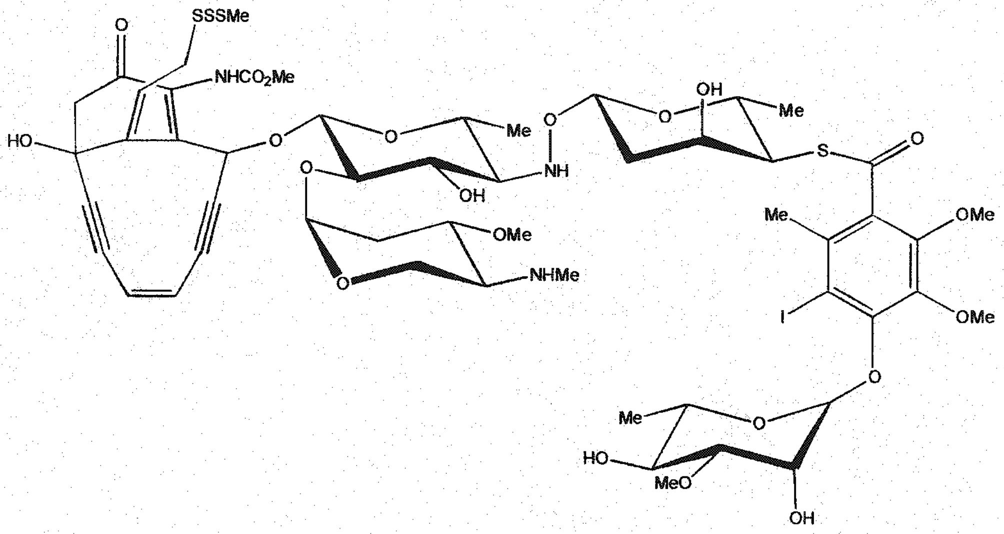

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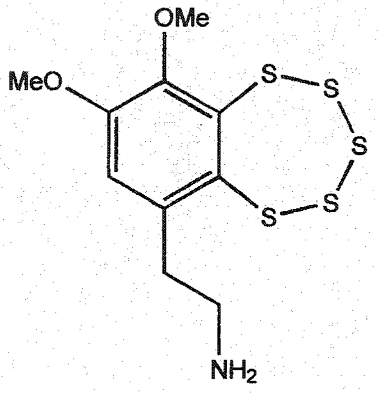
[32] Nicolaou, K. C. and Dai, W.-M. *Angew. Chem., Int. Ed. Engl.*, **1991**, *30*, 1387.

[33] a) Groneberg, R. D.; Miyasaki, T.; Stylianides, N. A.; Schulze, T. J.; Stahl, W.; Screiner, E. P.; Suzuki T.; Iawabushi, Y.; Smith, A. L. and Nicolaou, K. C. *J. Am. Chem. Soc.*, **1993**, *115*, 7593. b) Smith, A. L.; Pitsinos, E. N.; Hwang, C.-K.; Mizumo, Y.; Saimoto, H.; Scarlato, G. R.; Suzuki, T. and Nicolaou, K. C. *J. Am. Chem. Soc.*, **1993**, *115*, 7612. c) Nicolaou, K. C.; Hummel, C. W.; Nakada, M; Shibayama, K; Pitsinos, E. N.; Saimoto, H.; Mizumo, Y; Baldenius, K. U. and Smith, A. L. *J. Am. Chem. Soc.*, **1993**, *115*, 7625.

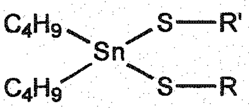
Other polysulfides such as Varacin (**3**),[34] which falls into the category of the benzopentathiepin compounds, show potent anti-fungal activity and cytotoxicity towards human colon cancer.[35] The synthesis of a series of Varacin-like compounds has been described.[36]



3

Other sulfur containing compounds include di-*n*-butyl tin-mercaptides (**4**). They find their application as thermostabilizers for PVC. Although they have been used for *ca.* three decades, they are still the topic of new research and development.[37]

Organosulfur compounds are also used in lubricating compositions for their extreme pressure and anti-wear properties. The oxidative stability in oil of some dialkylpolysulfides (**5**) has thus been investigated.[38]



R=R'=Alkyl

4

$R{-}S_n{-}R$ n=1-3

R=*n*-butyl, *tert*-butyl, *n*-dodecyl, *tert*-dodecyl, cyclohexyl

5

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[34] Davidson, B. S.; Molinski, T. F.; Barrows, L. R. and Ireland, C. M. *J. Am. Chem. Soc.*, **1991**, *113*, 4709.

[35] Ford, P. W. and Davidson, B. S. *J. Org. Chem.*, **1993**, *58*, 4523.

[36] Behar, V. and Danishefsky, S. J. *J. Am. Chem. Soc.*, **1993**, *115*, 7017.

[37] a) Lesté-Lasserre, P. *Ligand Effect on the Thermal and UV Stability of Organotin Stabilizers*, Elf-Atochem N.A. internal report, King of Prussia, PA, **1993**. b) Burchill, M. T. and Lesté-Lasserre, P. *J. Vinyl Addit. Technol.*, **1995**, *1(4)*, 250.

Considerable efforts have also been devoted for some time[28] towards the development of construction materials that make direct use of sulfur, in its elemental form, in their composition. These materials are usually classified under the generic name of "sulfur concrete." Their preparation typically involves blending S_8, polyolefins, a mineral filler and well graded aggregates at temperatures of around 140°C. Sulfur concrete finds its application mainly as a construction material in the fertilizer and metal-refining industry thanks to its very good resistance to acids and corrosive materials.[39]

Finally, in order to close on selected industrial applications of sulfur, the sulfur lamp requires inclusion.[40]

Elemental sulfur has also recently joined the group of superconductor materials. The superconducting properties of polythiazyl (SN_x)[41] had been known for a few years but evidence for the superconducting properties of sulfur are still ambiguous, contrary to those of selenium or tellurium.[42] However, it has now been demonstrated that under high pressure, sulfur, thus transformed into metallic sulfur, also acquires superconducting properties.[43]

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[38] a) Bala, V.; Hartley, R. J. and Hughes, L. J. *Lubr. Eng.*, **1996**, *52(12)*, 868. b) Chaka, A. M. *Prepr.-Am. Chem. Soc., Div. Pet. Chem.*, **1999**, *44(3)*, 297.

[39] a) Okumura, H. A. *Concr. Int.*, **1998**, *20(1)*, 72. b) Vroom, A. H. *Concr. Int.*, **1998**, *20(1)*, 68. c) Crick, S. M. and Whitmore, D. W. *Concr. Int.*, **1998**, *20(2)*, 83. d) Poulin, R. and Zmigrodzki, S. *Trois Jours Dev. Durable Ind. Cim. Beton, Recl. Commun.*, **1998**, 531. e) Gendreau, M.; Pigeon, M. and Zmigrodzki, S *Trois Jours Dev. Durable Ind. Cim. Beton, Recl. Commun.*, **1998**, 543.

[40] a) http://www.sulfurlamp.com/ b) Turner, B. P.; Ury, M. G.; Leng, Y. and Love, W. G. *J. Illum. Eng. Soc.*, **1997**, *26(1)*, 10.

[41] Labes, M. M.; Love, P. and Nichols, L. F. *Chem. Rev.*, **1979**, *79*, 1.

[42] a) Moodenbaugh, A. R.; Wu, C. T. and Viswanathan, R. *Solid State Commun.*, **1973**, *13(9)*, 1413. b) Bundy, F. P. and Dunn, K. J. *Phys. Rev. B: Condens. Matter.*, **1980**, *22(7)*, 3157. c) Bundy, F. P. and Dunn, K. J. *Phys. Rev. Lett.*, **1980**, *44(24)*, 1623. d) Akahama, Y.; Kobayashi, M. and Kawamura, H. *Solid State Commun.*, **1992**, *84(8)*, 803.

[43] a) *Chem. Eng. News*, December 1st, **1997**, 19. b) *Nature*, **1997**, *390*, 382.

Finally, sulfur has also been in the news with the discovery of the world's largest bacterium off the coasts of Namibia.[44] *Thiomargarita namibiensis*, the "Sulfur pearl of Namibia", is a giant sulfur-eating bacterium that is 100 times larger than the average bacterium with a diameter of ¾ millimeter.

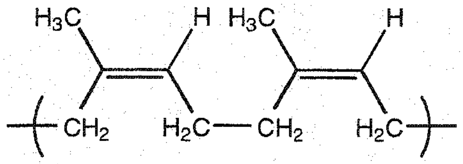
1.1.3.2. The Vulcanization of Rubber

Natural rubber, extracted as a resin from trees, has been known for more than 1400 years. The first record of rubber being used was in Central America as balls for sport. Later in the mid-16th century, Spanish explorers reported that the Aztecs had also developed a ball-game played with a rubber ball. Early in the 17th century, reports were made that Mexicans were able to make shoes and clothing from the gum issued from a tree.

Rubber was first introduced in Europe by de Condamine under the name of "caoutchouc" in 1745. Its ability to "erase the marks made by a plumbago pencil" (rub-out) gave to "rubber" its name as Priestley introduced it in England in 1770.

Natural rubber can be extracted from the *Hevea Braziliensis*, commonly known as the rubber tree. It is mainly constituted of *cis*-1,4-polyisoprene (**6**) and possesses good elastic properties. Gutta-percha, an isomer of rubber, mainly composed of *trans*-1,4-polyisoprene (**7**), can also be extracted from tropical trees but rather exhibits plastic properties and was the material used in early golf balls.

Unfortunately, natural rubber has very limited applications because it is not particularly strong and does not maintain its shape after large deformations.



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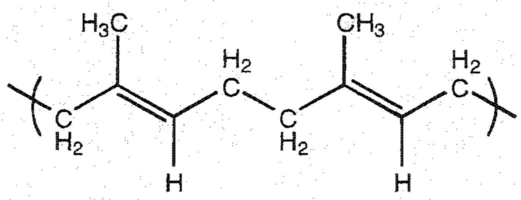

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[44] Wuethrich, B. *Science*, April 16th, **1999**, *284*, 415.

The discovery of the vulcanization process of rubber has been attributed to both Charles Goodyear and Thomas Hancock. They discovered that by heating mixtures of sulfur and natural rubber, its mechanical properties were improved. Goodyear was the first to develop this process in 1841 in Massachusetts and Hancock patented a somewhat similar process in England two years later in 1843.[45]

The vulcanization process essentially creates cross-links or bridges of sulfur chains between the long alkyl chains (saturated as well as unsaturated) of the natural rubber network (Figure 4). This process changes rubber into a material that retracts completely to its original form when deformation forces applied to it are removed. It is the only material capable of reversible extensions up to 8 times its length.[46]

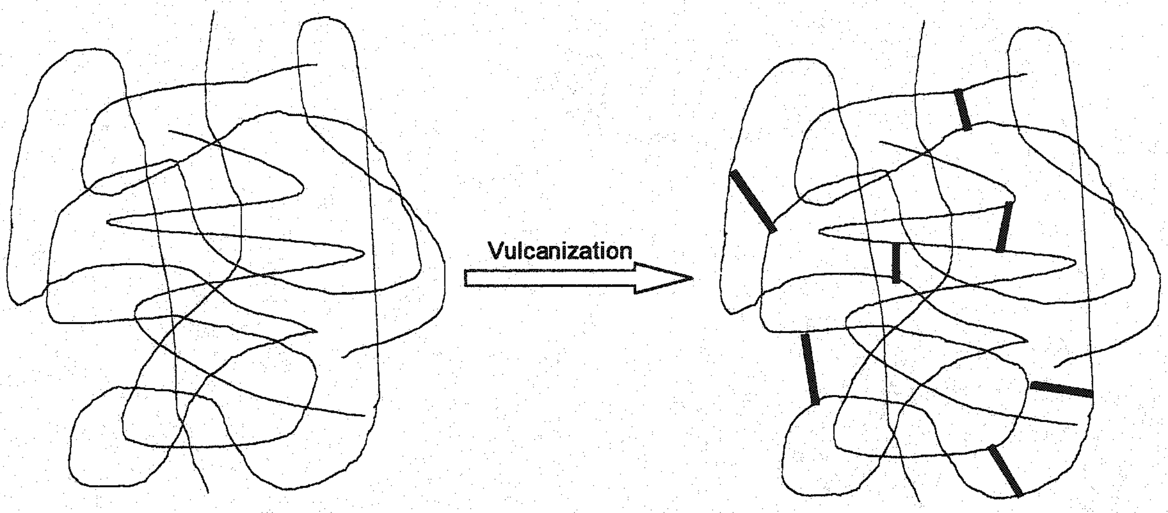

Figure 4. Cross-linking of a Rubber Network

The different types of cross-links found in a vulcanized rubber network are summarized in Figure 5 and Figure 6.

There are two types of rubber vulcanization. The first process, which is also the oldest one, is called unaccelerated sulfur vulcanization, where sulfur is the only vulcanizing agent that is added. "Sulfur-only" vulcanization is a slow process. The nature

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[45] Hancock, T. British Patent 9952, **1843**.

[46] Koenig, J. L. *Acc. Chem. Res.*, **1999**, *32(1)*, 1.

of its mechanism has been the subject of much debate but it seems now widely accepted that it is an ionic process as opposed to a radical one.[46]

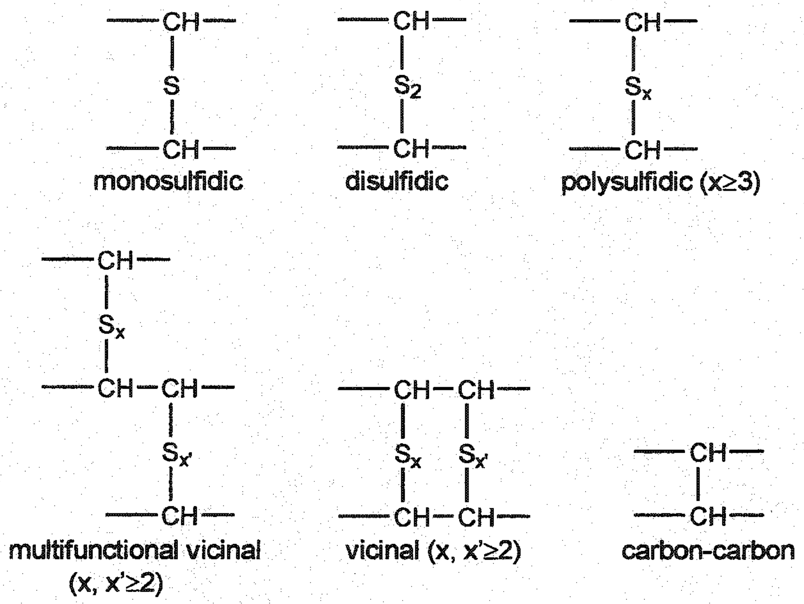

Figure 5. Different Types of Cross-links in Vulcanized Rubber

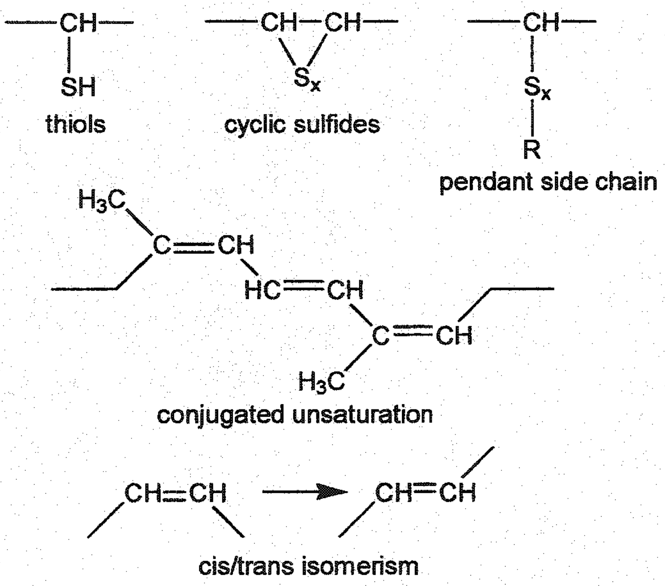

Figure 6. Other Modifications in Vulcanized Rubber

Because of the slow rate of the "sulfur-only" vulcanization, industry much prefers to use chemical accelerators and activators in addition to rubber and sulfur. This second type of vulcanization is called accelerated vulcanization. In this process, an activator, zinc oxide in most cases, interacts with an accelerator to form an active accelerator complex. This complex then reacts with sulfur in order to yield the active sulfurating agent. Sulfur chains of different lengths are then transferred to the rubber network and, upon modification of these crosslinks, the final vulcanized rubber network will be formed. A general scheme for accelerated vulcanization is presented in Figure 7.[47]

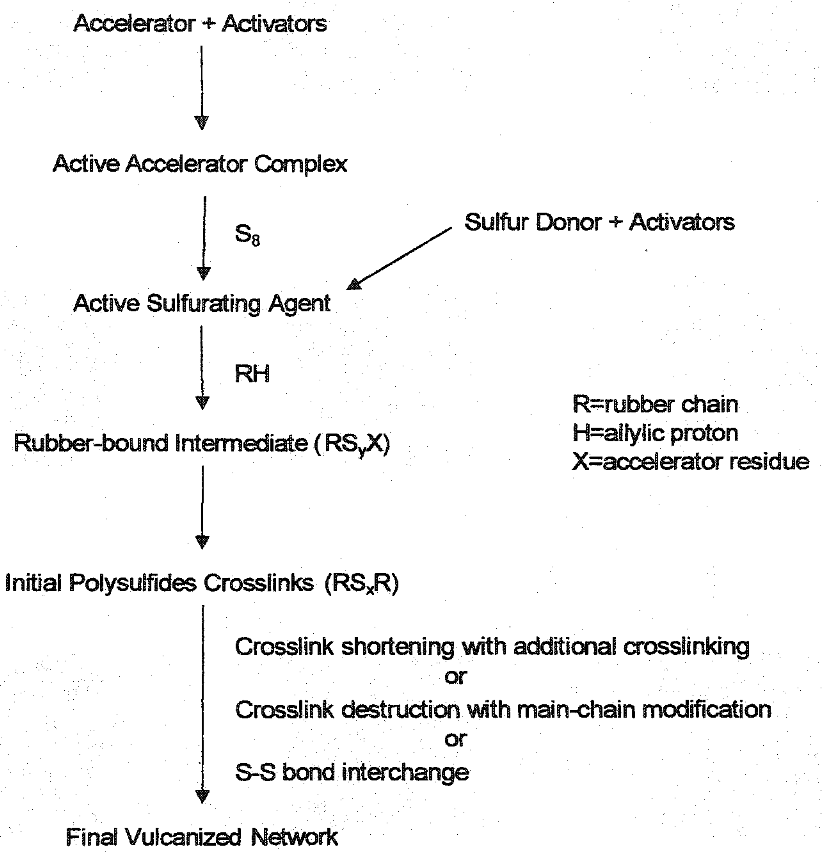

Figure 7. A General Scheme for Rubber Vulcanization

Various types of accelerators have been used through the years.[47] Among them, the following should be mentioned: benzothiazoles such as 2,2'-dithiobisbenzothiazole (**8**), dithiocarbamates such as tetramethylthiuram disulfide (**9**), benzothiazolesulfenamides

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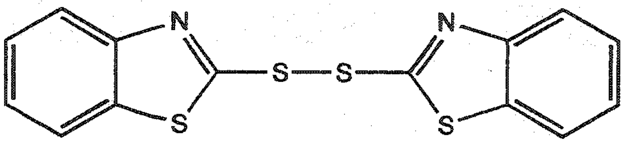
[47] Krejsa, M. R. and Koenig, J. L. *Rubber Chem. Technol.*, **1993**, 376.

such as *N*-cyclohexylbenzothiazole-2-sulfenamide (**10**) and amines such as diphenylguanidine (**11**).



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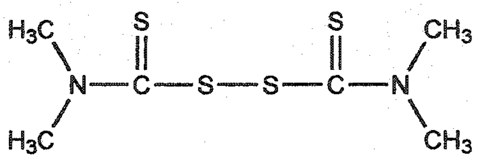
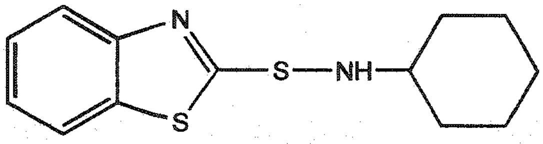


9



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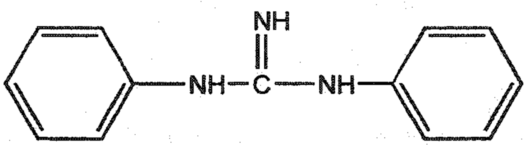

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A general consensus on the structure of the key active accelerator complex exits but the role of this complex is obscure as it is still not known whether or not this species is the actual sulfurating agent (Figure 8).[47]

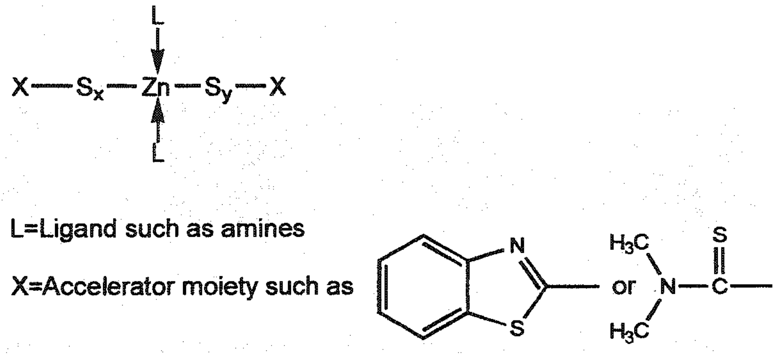

Figure 8. Active Accelerator Complex in Accelerated Vulcanization

1.2. Sulfur Allotropes

1.2.1. Definition of Allotropy

Before starting this Section, it is appropriate to define precisely the nature of a sulfur allotrope. As it was described in earlier paragraphs, elemental sulfur S_8 exists in different crystal packing arrangements such as orthorombic (α-S_8) or monoclinic (β-S_8). α-S_8 and β-S_8 are said to be polymorphs and a definition is as follows:

> *Different crystal forms of the same element in which the identical unit of the same compound, or the identical ionic formulae or identical repeating units are packed differently.*[48]

A comparative definition for allotropes is:

> *Different forms of the same element in which the chemical bonding between atoms of the same element is different and which may have different discrete molecular units, irrespective of the state.*[48]

Elemental sulfur S_8 possesses true allotropes as other sized cyclic homosulfur species exist. The next Sections will address this topic by giving an overview of the detection of sulfur allotropes, their preparation as well as what is known of their chemistry.

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[48] Rayner-Canham, G. and Kettle, J. *Educ. Chem.*, **1991**, *28(2)*, 49.

1.2.2. Detection of Sulfur Allotropes

1.2.2.1. In Sulfur Vapors

It was probably through the analysis of the vapors produced upon heating of sulfur that the first traces of elemental sulfur allotropes were detected. In 1832, Dumas, who was trying to measure the weight of known volumes of gases, came to the conclusion that sulfur vapors, at low temperatures, were composed of molecules having six atoms of sulfur.[49] Similar studies carried out in 1860 proved that at higher temperatures (above 700°C), the vapors were mainly composed of S_2 molecules.[49]

During the first part of the 20th century, other studies based on the density determination of sulfur vapors allowed two more species, namely S_4 and S_8, to be added to the two species found previously.[49]

In 1963, Berkowitz and Marquart made a significant contribution to the determination of the composition of sulfur vapors.[50] They completed some preliminary studies, which had been initiated by other groups, where they used mass-spectrometry as their detection tool. Their results concluded that all sulfur species S_n, from $n=2$ to $n=8$, were constituents of the saturated sulfur vapors they examined between 350°C and 1000°C. They also detected very small concentrations of S_9 and S_{10}, although this result is questionable because it cannot be ruled out that these species were formed in the ion source of the spectrometer.[51]

In 1973, Rau and co-workers[52] designed a thermodynamic model to determine the composition of sulfur vapors. Their model was based on the following set of equations (Figure 9).

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[49] Berkowitz, J. *Elemental Sulfur*, Meyer, B. (Ed.), Interscience Publ., New York, **1965**, 125.

[50] Berkowitz, J. and Marquart, J. R. *J. Chem. Phys.*, **1963**, *39(2)*, 275 and references cited therein.

[51] Lenain, P.; Picquenard, E.; Corset, J.; Jensen, D. and Steudel, R. *Ber. Bunsenges. Phys. Chem.*, **1988**, *92*, 859.

[52] Rau, H.; Kutty, T. R. N. and Guedes de Carvalho, J. R. F. *J. Chem. Thermodyn.*, **1973**, *5*, 833.

$$S_i \rightleftharpoons i/2\ S_2 \qquad i=3 \text{ to } 8$$

Figure 9. Equilibrium of Sulfur Vapors

The results obtained from this study are summarized by Figure 10. Up to about 800 K (527°C) saturated sulfur vapors are mainly constituted of S_8, S_7 and S_6 molecules. Between 800 K and 1000 K (727°C), smaller species such as S_5, S_4, S_3 and S_2 start to play a significant role. Finally, at temperatures above 1000 K, S_2 is the main constituent of sulfur vapors. At 1000°C, S_2 constitutes about 45% of the vapors.[52]

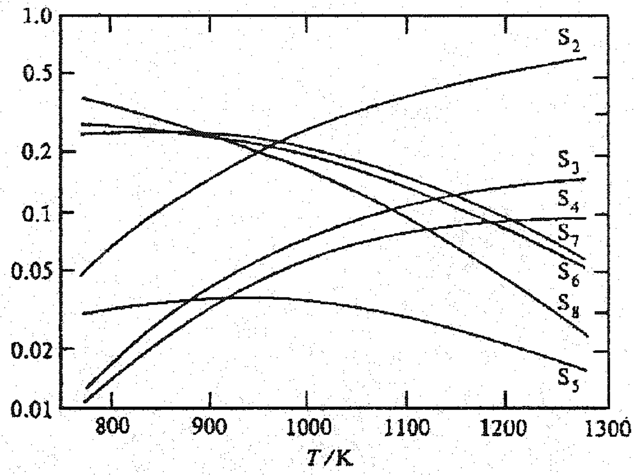

Figure 10. Rau's Sulfur Vapors Composition Diagram

More recently, Steudel and co-workers have reinvestigated Rau's model as they have looked at the composition of saturated as well as overheated sulfur vapors in a wide range of temperature and pressure.[51] The originality of their study comes from the use of a non-invasive, non-destructive analytical technique to examine the different constituents of the vapors. They have indeed made extensive use of resonance Raman spectroscopy. The latter is far more sensitive than ordinary Raman, which had been previously used,[53] and thus allows for the detection of trace quantities.

A slight modification to Rau's law has been added as they found that the concentration of S_7 in sulfur vapors had previously been underestimated, presumably because of its decomposition under electron impact in the mass-spectrometer. They concluded that S_7 is actually the main constituent in saturated sulfur vapors between 600 K (327°C) and 1000 K.

Their studies did not permit the detection of any traces of S_5, S_9 or S_{10}. Furthermore, no traces of either conformational isomers of cyclic species such as boat-like S_7 or S_6, or isomers having *exo*-cyclic sulfur-sulfur bonds (S_n=S), were found.

The structures of S_2 or S_3 have been well discussed in the literature and they have been the topic of numerous theoretical calculations.[54] These two species can be trapped at low temperature by rare gas matrices absorption techniques[55] and spectroscopic evidence is well-documented.[56]

The debate over the structure[57] of S_4 has been a "long-standing problem".[57a] The first spectroscopic evidence of S_4 was the publication of its visible spectrum by Meyer and co-workers.[56d] Since this work, further experiments have suggested that S_4 in sulfur

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[53] Schinazi, M.; Corset, J.; Delhaye, M. and Lesne, J. L. *Raman Spectrosc., Proc. Int. Conf.*, 8th, **1982**, 659.

[54] a) Suontamo, R. J.; Laitinen, R. S. and Pakkanen, T. A. *THEOCHEM*, **1994**, *119(2)*, 189. b) Bicai, P.; Changkui, D.; Shangda, X. and Chuanyun, X. *Phys. Rev. B: Condens. Matter*, **1994**, *50(23)*, 17556. c) Koch, W.; Natterer, J. and Heinemann, C. *J. Chem. Phys.*, **1995**, *102(15)*, 6159. d) Heinemann, C.; Koch, W.; Lindner, G.-G. and Reinen, D. *Phys. Rev. A: At., Mol., Opt. Phys.*, **1995**, *52(2)*, 1024.

[55] a) Meyer, B. and Stroyer-Hansen, T. *J. Phys. Chem.*, **1972**, *76*, 3968. b) For a review on these techniques see: Meyer, B. *Low Temperature Spectroscopy, Optical Properties of Molecules in Matrices, Mixed Crystals and Glasses*, American Elsevier, New York, **1971**.

[56] For S_2: a) Barletta, R. E.; Claassen, H. H. and MacBeth, R. L. *J. Chem. Phys.*, **1971**, *55(11)*, 5409. b) Yee, K. K.; Barrow, R. F. and Rogstad, A. *J. Chem. Soc. Faraday Trans. 2*, **1972**, *268*, 1808. c) Hopkins, A. G. and Brown, C. W. *J. Chem. Phys.*, **1975**, *62(4)*, 1598. For S_3: d) Meyer, B.; Stroyer-Hansen, T. and Oommen, T. V. *J. Mol. Spectrosc.*, **1972**, *42*, 335. e) Hopkins, A. G.; Tang, S.-Y. and Brown, C. W. *J. Am. Chem. Soc.*, **1973**, *95*, 3486. f) Tang, S.-Y. and Brown, C. W. *Inorg. Chem.*, **1975**, *14*, 2856. g) Lenain, P.; Picquenard, E.; Lesne, J. L. and Corset, J. *J. Mol. Struct.*, **1986**, *142*, 355. h) Picquenard, E.; El Jaroudi, O. and Corset, J. *J. Raman Spectrosc.*, **1993**, *24*, 11.

vapor could exist as two different isomers.[58] Recently, Picquenard and co-workers have probably closed the debate by finishing some work started earlier.[59] It seems that their vibrational study and calculations[60] have unequivocally determined that S_4 consists of two isomers in the vapor phase. A green absorbing chain-like S_4 molecule and a red absorbing branched-ring S_3-S isomer have been detected and identified. It is noteworthy that the chain-like isomer was concluded to have a *trans* planar conformation, in clear contradiction with previous calculations.[57a] Much less is known about the structure of S_5, which was identified for the first time by Steudel.[61]

Finally, the structure of S_6 and S_7 has been determined by X-ray crystallography as these sulfur rings exist as isolatable compounds. The parallel synthesis of elemental sulfur allotropes and their structure determination will be detailed later in this work. *Cyclo*-hexasulfur (S_6) and *cyclo*-heptasulfur (S_7) have been among the first solid allotropes to be synthesized.

1.2.2.2. In Sulfur Melts

When pure orthorhombic α-S_8 is gradually heated, it goes through a phase transition at about 95°C and is transformed into monoclinic β-S_8. β-S_8 then melts around 119°C.[62] In 1876, Gernez reported[63] a difference of about 5°C between the melting point of sulfur and the freezing point of the melt, which was observed at 115°C. This phenomenon was

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[57] a) Quelch, G. E.; Schaefer, H. F. and Marsden, C. J. *J. Am. Chem. Soc.*, **1990**, *112(24)*, 8719. b) Salahub, D. R.; Foti, A. E. and Smith, V. H. *J. Am. Chem. Soc.*, **1978**, *100(25)*, 7847.

[58] a) Billmers, R. I. and Smith, A. L. *J. Phys. Chem.*, **1991**, *95*, 4242. b) Brabson, G. D.; Mielke, Z. and Andrews, L. *Phys. Chem.*, **1991**, *95*, 79. c) Hassanzadeh, P. and Andrews, L. *Phys. Chem.*, **1992**, *96*, 6579.

[59] Picquenard, E.; Boumedien, M. S. and Corset, J. *J. Mol. Struct.*, **1993**, *293*, 63.

[60] Boumedien, M. S.; Corset, J. and Picquenard, E. *J. Raman Spectrosc.*, **1999**, *30*, 463.

[61] Strauss, E.-M. and Steudel, R Z. *Naturforsch.*, **1987**, *42b*, 682.

[62] a) Pacor, P. *Anal. Chim. Acta.*, **1967**, *37*, 200. b) Feher, F.; Goerler, G. P. and Lutz, H. D. Z. *Anorg. Allg. Chem.*, **1971**, *382*, 135. c) Steudel, R. Z. *Anorg. Allg. Chem.*, **1981**, *478*, 139.

[63] Gernez, M. D. *C. R. Acad. Sci. Fr.*, **1876**, *82*, 115.

believed to be caused by the formation in the sulfur melt of other sulfur species than S_8. These species were collectively given the name of π-sulfur by Aten in 1913.[64] Using IR and Raman spectroscopy[65] as well as for the first time reverse phase High Pressure Liquid Chromatography (HPLC),[66] Steudel and his co-workers identified small sulfur rings such as S_6 and S_7 as components of π-sulfur. Further quantitative HPLC analysis[67] or IR and Raman studies[68] on quenched sulfur melts allowed obtaining a more complete picture of the composition of sulfur melts in a 116°C to 350°C range. *All* sulfur rings S_n n=6-23 have been detected and quantified.[67] Apart from S_8, which between 116°C and 159°C represents about 90% by weight of the sulfur melts, S_6 (*ca.* 1%), S_7 (*ca.* 4%), S_9 (*ca.* 0.5%) and S_{12} (*ca.* 0.5%) constitute the allotropes that are found in the largest amounts.[67] Traces of sulfur cycles as large as S_{26}[66] and even larger rings have been detected.[69] Theoretical models have been developed in order to predict large sulfur rings (S_n $n>8$) concentrations in melts and compared with the experimental data.[70]

When the melt reaches the temperature of 159°C,[71] the viscosity increases as polymerization occurs. This phenomenon of the gelling of liquid sulfur was observed as early as 1886 by Eötvös.[72] This polymerization process of elemental sulfur was first fully described by Tobolsky and Eisenberg[73] and has also been studied by others.[74] Steudel showed that the amount of polymer in the melt increases gradually from 160°C to reach a maximum of roughly 40% by weight at about 250°C.[67] Polymeric sulfur, also called S_μ or S_∞, consists of long sulfur chains of helical conformation as well, as probably, very

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[64] Aten, A. H. W. *Z. Phys. Chem.*, **1913**, *83*, 442.

[65] Steudel, R. and Mäusle, H.-J. *Angew. Chem., Int. Ed. Engl.*, **1977**, *16(2)*, 112.

[66] Steudel, R.; Mäusle, H.-J.; Rosenbauer, D.; Möckel, H. and Freyholdt, T. *Angew. Chem., Int. Ed. Engl.*, **1981**, *20(4)*, 394.

[67] Steudel, R.; Strauss, R. and Koch, L. *Angew. Chem., Int. Ed. Engl.*, **1985**, *24(1)*, 59.

[68] Mäusle, H.-J. and Steudel, R. *Z. Anorg. Allg. Chem.*, **1981**, *478*, 177.

[69] Strauss, R. and Steudel, R. *Fresenius' Z. Anal. Chem.*, **1987**, *326*, 543.

[70] Dodgson, K.; Heath, R. E. and Semlyen, J. A. *Polymer*, **1999**, *40*, 3995.

[71] Kuballa, M. and Schneider, G. M. *Ber. Bunsenges. Phys. Chem.*, **1971**, *75*, 513.

[72] Eötvös, E. *Ann. Phys. Chem.*, **1886**, *27*, 452.

[73] a) Tobolsky, A. V. and Eisenberg, A. *J. Am. Chem. Soc.*, **1959**, *81*, 780. b) Tobolsky, A. V. and Eisenberg, A. *J. Am. Chem. Soc.*, **1959**, *81*, 2302. c) Tobolsky, A. V. and Eisenberg, A. *J. Am. Chem. Soc.*, **1960**, *82*, 289.

[74] Koningsberger, D. C. and De Neef, T. *Chem. Phys. Lett.*, **1972**, *14*, 453.

large sulfur rings. With increasing temperatures, the melt slowly becomes less viscous as depolymerization of S_μ occurs. The boiling point of sulfur has been determined at *ca.* 445°C.[75] Small sulfur species such as S_3 and S_4 have also been detected in sulfur melts.[76] It is suggested that these species are responsible for the change in color of liquid sulfur from bright yellow at its melting point to dark red at its boiling point temperature.

Some sulfur allotropes have been extracted from sulfur melts. The method employed for their extraction will be described later in Chapter 1.

1.2.2.3. In Commercial Sulfur

Different samples of commercial sulfur produced by industrial methods such as the Frasch or the Claus processes have been analyzed by quantitative HPLC methods by Steudel.[77] All commercial samples showed the presence of traces of S_7 (up to 0.56% by weight) as well as, in some cases, traces of S_6 and S_9. Polymeric sulfur, which is not soluble in any solvent, was found in some samples at a maximum concentration of 10% by weight. Mineral sulfur was also proven to contain traces of S_7 (up to 0.3% by weight).

It is also important to note that pure S_8 samples dissolved in carbon disulfide (CS_2) and heated at 130-155°C equilibrate to mixtures in which S_6 (*ca.* 2%) and S_7 (6-7%) have been quantified by HPLC.[78] At room temperature, S_8 has also been shown to produce small amounts of S_6 and S_7 when dissolved in polar solvents such as methanol or acetonitrile.[79] Finally, the photolysis of S_8 and other sulfur allotropes has been examined at ambient temperature.[61] A similar equilibrium situation, in which S_8, S_7 and S_6 were found as the main components, formed in all cases. Traces of other sulfur rings were also

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[75] Rossini, F. D. *J. Chem. Thermodyn.*, **1970**, *2*, 447.

[76] a) Meyer, B.; Stroyer-Hansen, T.; Jensen, D. and Oommen, T. V. *J. Am. Chem. Soc.*, **1971**, *93*, 1034. b) Meyer, B.; Oommen, T. V. and Jensen, D. *J. Phys. Chem.*, **1971**, *75*, 912.

[77] Steudel, R. and Holz, B. *Z. Naturforsch.*, **1988**, *43b*, 581.

[78] Steudel, R. and Strauss, R. *Z. Naturforsch.*, **1982**, *37b*, 1219.

[79] Tebbe, F. N.; Wasserman, E.; Peet, W. G.; Vatvars, A. and Hayman, A. C. *J. Am. Chem. Soc.*, **1982**, *104*, 4971.

detected. All these processes of sulfur rings interconversion will be discussed in more detail in Chapter 4.

1.2.3. Synthesis

1.2.3.1. S_2 and S_3 Generation

As it was discussed earlier, S_2 and S_3 have both been detected in sulfur vapors and S_3 has been detected in sulfur melts. However, the temperatures at which these species have been detected are not really suitable for organic reactions. Organic chemists have thus tried to develop reagents that could, under much milder conditions, generate these elusive species; S_2 and S_3 have now become more available for chemists to study their reactivity and their reaction with different substrates. Many efforts have been advanced for the generation of S_2 whereas accounts for the generation of S_3 are more rare.

The generation of diatomic sulfur in its singlet state ($^1S_2$) has been the topic of much research since the first attempts almost 25 years ago[80] and has been well reviewed.[81] In 1984, Steliou and co-workers developed what is now widely recognized as the first successful generation of diatomic sulfur.[82] The method used was similar to the phosphine ozonide technique used for the generation of singlet oxygen (Figure 11).

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[80] a) Smith, D. L. Ph.D. Thesis, University of Arizona, **1976**. b) Jahn, R. and Schmidt, U. *Chem. Ber.*, **1975**, *108*, 630.

[81] a) Steliou, K. *Acc. Chem. Res.*, **1991**, *24*, 341 and references cited therein. b) Harpp, D. N. *Phosphorus, Sulfur Silicon Relat. Elem.*, **1997**, *120 & 121*, 41 and references cited therein. c) Tardif, S. L.; Rys, A. Z.; Abrams, C. B.; Abu-Yousef, I. A.; Lesté-Lasserre, P. B. F.; Schultz, E. K. V. and Harpp, D. N. *Tetrahedron*, **1997**, *53*, 12225 and references cited therein.

[82] Steliou, K.; Gareau, Y. and Harpp, D. N. *J. Am. Chem. Soc.*, **1984**, *106*, 799.

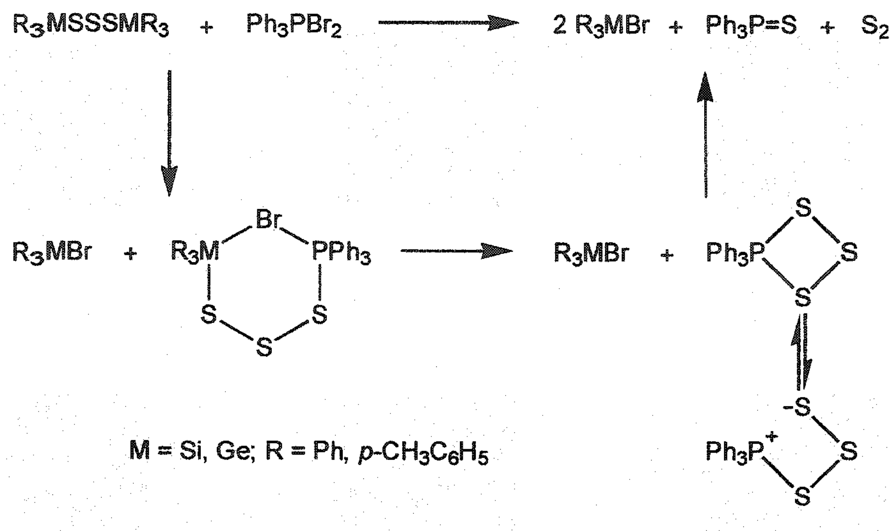
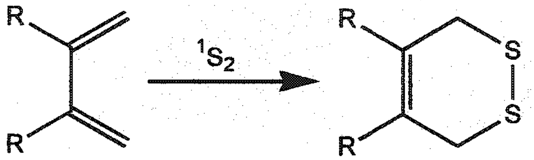


Figure 11. First Method for Diatomic Sulfur Generation

Steliou showed that diatomic sulfur can act as a dienophile and be advantageously "trapped" in a Diels-Alder fashion by various 1,3-dienes[82] (Figure 12).



12

a) R=Ph
b) R=Me

13

a) R=Ph
b) R=Me

Figure 12. Diels-Alder Trapping Reaction of $^1S_2$ with 1,3-Dienes

Moreover, it was demonstrated that such additions are governed by Woodward-Hoffmann rules[83] and that all addition products are in good agreement with parallel singlet oxygen chemistry.[81a,84] It was also demonstrated that diatomic sulfur reacts as a

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[83] a) Woodward, R. B. and Hoffmann, R. *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, **1970**. b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*, John Wiley & Sons, **1996**.

[84] Steliou, K.; Gareau, Y.; Milot, G. and Salama, P. *J. Am. Chem. Soc.*, **1990**, *112*, 7819.

free species.[85] Steliou and co-workers were also the first to show that the reaction between diatomic sulfur and strained olefins[84,86] is also possible when 2,2'-bis(thiobenzoyl)biphenyl (**14**), used as a diatomic sulfur precursor, is decomposed at 110°C in the presence of norbornene (**16**), for example. A mechanism was postulated[84] in order to rationalize the formation of *exo*-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane (**19**) commonly referred to as trithiolane **19**, which was obtained as the only reaction product. For the first time, the 1,2-dithietane **17** and the *exo*-sulfur compound **18** were envisaged as possible reaction intermediates (Figure 13).

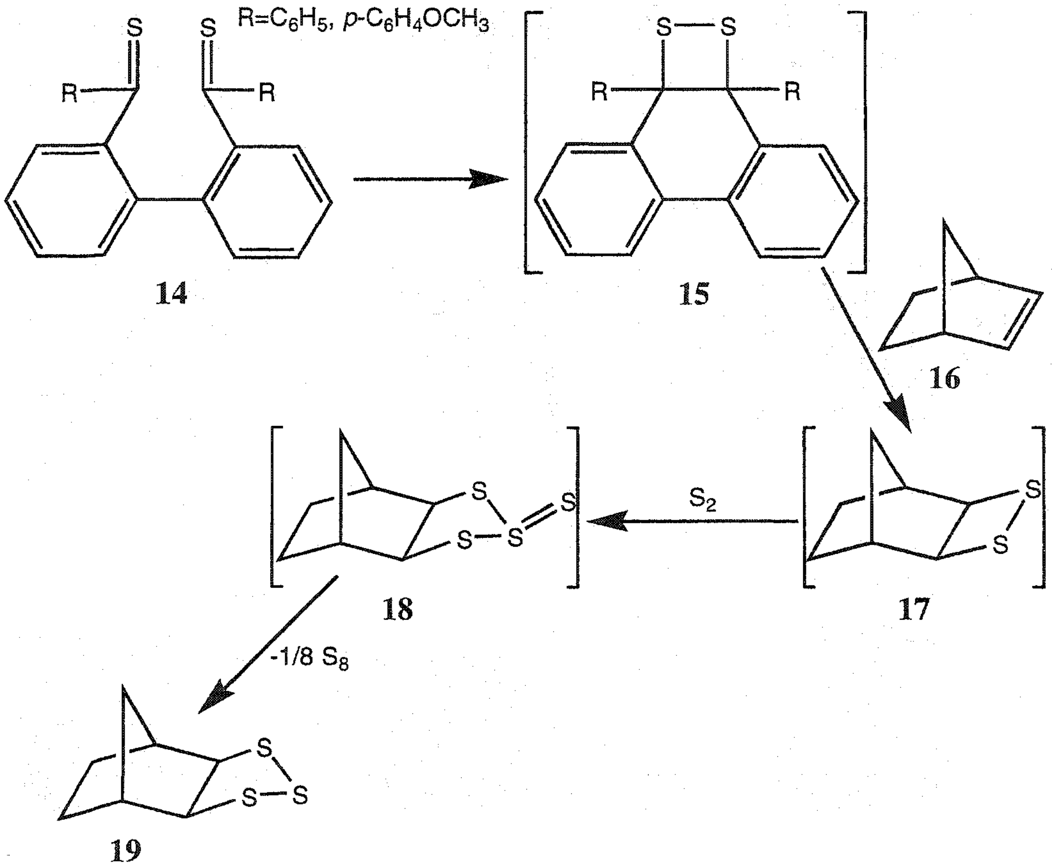

Figure 13. First Trapping Reaction of Diatomic Sulfur with Norbornene

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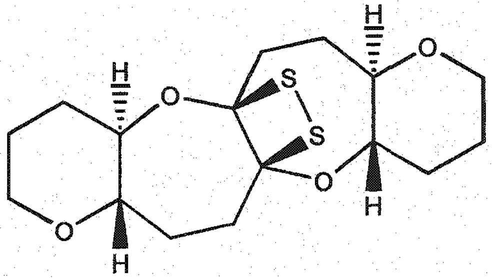
[85] Steliou, K.; Salama, P. and Yu, X. *J. Am. Chem. Soc.*, **1992**, *114*, 1456.

[86] Steliou, K.; Salama, P; Brodeur, D. and Gareau, Y. *J. Am. Chem. Soc.*, **1987**, *109*, 926.

The decomposition mechanism of **18** into trithiolane **19** is rationally supported by the decomposition study of N_2S.[87]

1,2-Dithietane **15** was also postulated as an intermediate in the decomposition process of this diatomic sulfur precursor, **14**. It is interesting to note that during the same year, Nicolaou synthesized the only known stable 1,2-dithietane, dithiatopazine (**20**),[88] that is an intermediate in the total synthesis of Brevotoxin B.[89] It was then found that dithiatopazine can also deliver diatomic sulfur as evidenced by appropriate trapping experiments.[90]



20

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[87] Bender, H.; Carnovale, F.; Peel, J. B. and Wentrup, C. *J. Am. Chem. Soc.*, **1988**, *110*, 3458.

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

[89] a) Nicolaou, K. C.; Tiebes, J.; Theodorakis, E. A.; Rutjes, F. P. J. T.; Koide, K.; Sato, M. and Untersteller, E *J. Am. Chem. Soc.*, **1994**, *116(20)*, 9371. b) Nicolaou, K. C.; Theodorakis, E. A.; Rutjes, F. P. J. T.; Tiebes, J.; Sato, M.; Untersteller, E. and Xiao, X.-Y *J. Am. Chem. Soc.*, **1995**, *117(3)*, 1171. c) Nicolaou, K. C.; Rutjes, F. P. J. T.; Theodorakis, E. A.; Tiebes, J.; Sato, M. and Untersteller, E *J. Am. Chem. Soc.*, **1995**, *117(3)*, 1173. d) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Nugiel, D. A.; Abe, Y.; Reddy, K. Bal; DeFrees, S. A.; Reddy, D. R. and Awartani, R. A. *J. Am. Chem. Soc.*, **1995**, *117(41)*, 10227. e) Nicolaou, K. C.; Theodorakis, E. A.; Rutjes, F. P. J. T.; Sato, M.; Tiebes, J.; Xiao, X.-Y.; Hwang, C.-K.; Duggan, M. E. and Yang, Z *J. Am. Chem. Soc.*, **1995**, *117(41)*, 10239. f) Nicolaou, K. C.; Rutjes, F. P. J. T.; Theodorakis, E. A.; Tiebes, J.; Sato, M. and Untersteller, E *J. Am. Chem. Soc.*, **1995**, *117(41)*, 10252. g) Nicolaou, K. C *Angew. Chem., Int. Ed. Engl.*, **1996**, *35(6)*, 589.

[90] a) Nicolaou, K. C.; Hwang, C.-K.; DeFrees, S. A. and Stylianides, N. *J. Am. Chem. Soc.*, **1988**, *110*, 4868. b) Nicolaou, K. C.; DeFrees, S. A.; Hwang, C.-K.; Stylianides, N.; Carroll, P. J. and Snyder, J. P. *J. Am. Chem. Soc.*, **1990**, *112*, 3029.

The first success of Steliou greatly stimulated research in the area of singlet diatomic sulfur ($^1S_2$) generation. A number of reports have since appeared in the literature and all diatomic sulfur precursors, that are supported by successful trapping experiments, will be compiled in a Table in the discussion Section of Chapter 2. A few selected methods will be mentioned in the following pages.

One of the most efficient methods for the generation of diatomic sulfur is probably the one reported by Harpp, Tardif and Williams.[91] This method involves the thermal decomposition of *bis*-alkoxydisulfides (**21**) as shown in Figure 14. Very good yields of trapping products, all consistent with diatomic sulfur chemistry, have been obtained with a variety of substrates.

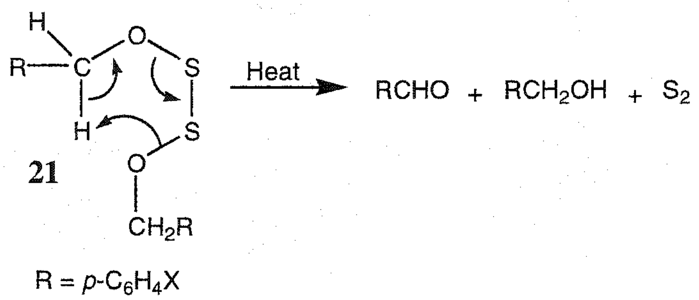

Figure 14. Generation of Diatomic Sulfur with *bis*-Alkoxydisulfides

More recently, new S_2 precursors have appeared in the literature including two developed in our lab.[92] The latter involves a reaction between hydrazine (**22**) and a sulfur transfer reagent, benzimidazole disulfide (**23**).[92b] Two pathways are proposed for the formation of diatomic sulfur *via* this method (Figure 15).

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[91] Tardif, S. L.; Williams, C. R. and Harpp, D. N. *J. Am. Chem. Soc.*, **1995**, *117*, 9067.

[92] a) Abu-Yousef, I. A. and Harpp, D. N. *J. Org. Chem.*, **1998**, *63*, 8654. b) Sawayama, A. M.; Lesté-Lasserre, P. and Harpp, D. N. *Sulfur Letters*, **2000**, *23(4)*, 163.

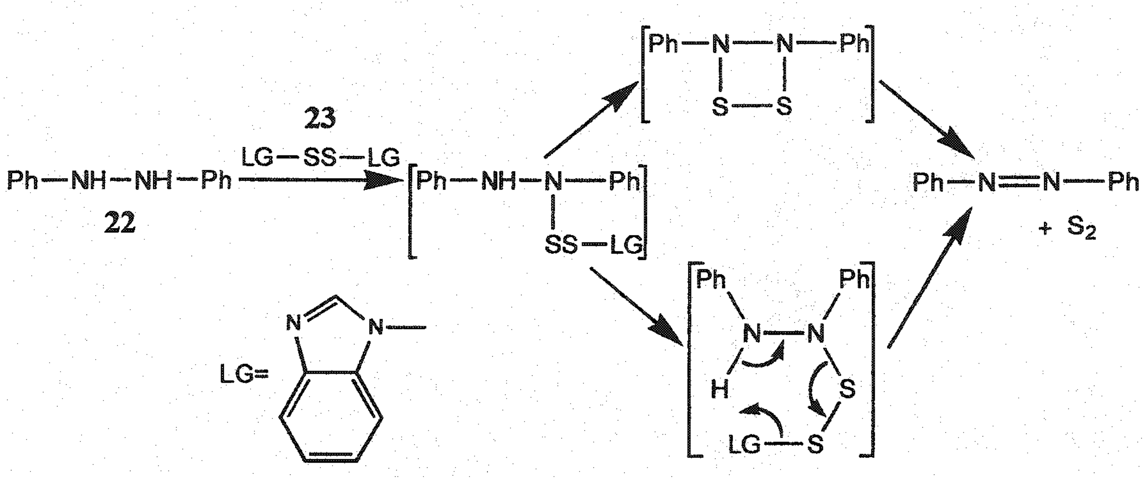

Figure 15. Diatomic Sulfur Generation from Hydrazine and Benzimidazole Disulfide

In the meantime, others have shown concern about the trapping methods used to evidence the generation of S_2 in solution.[93] Evidence for the generation of "true" singlet state diatomic sulfur has always been subject to debate and of the dozen of self-claimed diatomic sulfur precursors, some seem doubtful. Gilchrist's precursor is indisputably one that produces diatomic sulfur in its singlet state $^1S_2$ as it involves the clean retro Diels-Alder reaction of 2,3-dithiabicyclo[2.2.1]hept-5-ene (**24**) (Figure 16).[94]

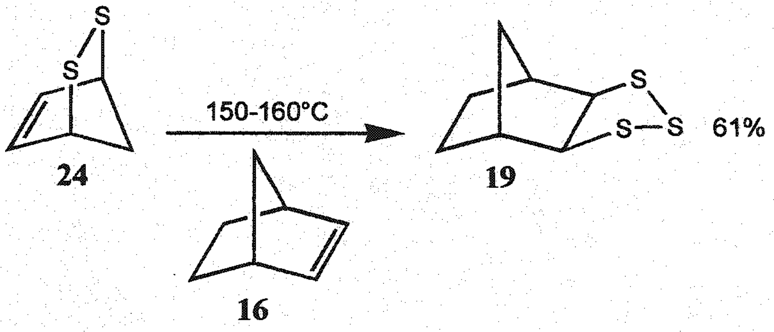

Figure 16. Diatomic Sulfur Generation *via* a Retro Diels-Alder Reaction

Reactions that show a clean transfer of an S_3 unit from a donor to an acceptor molecule are very rare. In 1988, Ghosh and Bartlett showed for the first time that *endo*-2-phenyl-*exo*-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane (**25**) could quantitatively transfer an S_3

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[93] Micallef, A. S. and Bottle, S. E. *Tetrahedron Lett.*, **1997**, *38(13)*, 2303.

molecule to norbornene (**16**) or norbornadiene (**26**) under quite mild conditions (100°C) in order to form trithiolane **19** and *exo*-3,4,5-trithiatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (**27**), which will be referred to as trithiolane **27** (Figure 17).[95]

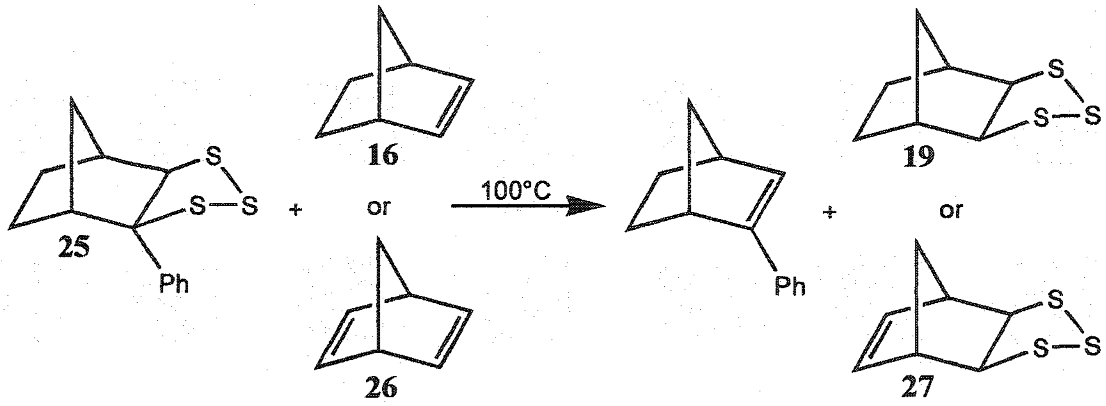

Figure 17. S_3 Transfer Reaction

Very recently, Nakayama and co-workers developed a reagent, which upon decomposition delivers S_2O units.[96] This small molecule is known to disproportionate into SO_2 and S_3.[97] The latter was indeed efficiently trapped with norbornene and good yields of trithiolane **19** were obtained.

1.2.3.2. S_6 and Larger Sulfur Rings

The synthesis of the solid sulfur allotropes has already been extensively reviewed.[98] Some of the main methods used for the preparation of sulfur rings with an update on new developments in this area will be the subject of this Section.

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[94] Gilchrist, T. L. and Wood, J. E. *J. Chem. Soc., Chem. Commun.*, **1992**, 1460.

[95] Ghosh, T. and Bartlett, P. D. *J. Am. Chem. Soc.*, **1988**, *110*, 7499.

[96] a) Ishii, A.; Nakabayashi, M. and Nakayama, J. *J. Am. Chem. Soc.*, **1999**, *121*, 7959. b) Ishii, A.; Nakabayashi, M.; Jin, Y.-N. and Nakayama, J. *J. Organomet. Chem.*, **2000**, *611*, 127.

[97] a) Hopkins, A. G.; Tang, S.-Y. and Brown, C. W. *J. Am. Chem. Soc.*, **1973**, *95*, 3486. b) Tang, S.-Y. and Brown, C. W. *Inorg. Chem.*, **1975**, *14*, 2856.

1.2.3.2.a. Extraction from Sulfur Melts

As it has been discussed, (*vide supra*) about the composition of sulfur melts, *all* rings from S_6 up to S_{26} have been detected in liquid sulfur. Some proof also exists for the presence of even larger rings such as S_{35}. This complexity in the composition of sulfur melts probably explains why it has been very difficult to design procedures that would allow the isolation of any desired ring in pure form directly from liquid sulfur. Also, some rings only exist at trace levels.

Another limitation in order to design preparative scale isolation procedures arises from the lack of suitable solvents to selectively extract one ring in preference to another when they are all present in a quenched sulfur melt. Preparative or semi-preparative scale HPLC is obviously a very appealing tool in order to achieve separation, but it is still limited in terms of the quantities that can be isolated.

Nevertheless, some preparative scale extraction procedures have been successful for a few sulfur allotropes. A total of four sulfur rings have actually been extracted from quenched sulfur melts.

In 1967, at a time when sulfur melt composition was still obscure, Schmidt and Block claimed that they had achieved the isolation of S_{12} from quenched liquid sulfur.[99] Their technique consisted in melting pure S_8 and stabilizing the melt at 200°C for 10 min prior to a fast cooling. The solid residue was then subsequently extracted in carbon disulfide (CS_2) and successive crystallization and decantation afforded pure S_{12} in *ca.* 0.1% yield. However, this procedure has been contested by the work of Steudel. "The isolation of S_{12} from sulfur melts as first reported by Schmidt and Block could not be reproduced in our laboratory, even after several attempts by different co-workers".[100] Steudel reported in the same publication not only a modified procedure, which allowed them to reproducibly extract S_{12} from sulfur melts, but also a method for the extraction of α–S_{18} and S_{20}.[100] The same authors had already published the successful isolation of

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[98] a) Steudel, R. *Top. Curr. Chem.*, **1982**, *102*, 149. b) Laitinen, R. S. and Pekonen, P. *Coord. Chem. Rev.*, **1994**, *130*, 1.

[99] Schmidt, M. and Block, H.-D. *Angew. Chem., Int. Ed. Engl.*, **1967**, *6(11)*, 955.

[100] a) Steudel, R. and Mäusle, H.-J. *Angew. Chem., Int. Ed. Engl.*, **1979**, *18(2)*, 152. b) Steudel, R. and Mäusle, H.-J. *Z. Anorg. Allg. Chem.*, **1981**, *478*, 156.

cyclo-heptasulfur (S_7) from sulfur melts.[101] Steudel's procedures appear somewhat quite similar to that of Schmidt. They usually consist in stabilizing melts of initially pure S_8 at temperatures between 140°C and 200°C and for times ranging from 5 min to 3 hr, prior to quenching in liquid nitrogen. Solid-liquid extraction in carbon disulfide, repetitive crystallization, decantation and fractional recrystallization or flotation, usually leads to the isolation of the desired cyclic species.

Table 2 summarizes some of the experimental data relative to the extraction of S_7, S_{12}, α-S_{18} and S_{20} from sulfur melts. Moreover, it compares the isolated yields to the weight % obtained by Steudel and co-workers in their quantitative study of sulfur melts by HPLC.[67]

Sulfur Allotrope	Temperature of the Melt prior to Quenching (°C)	Isolated Yield (weight %)	Concentration Observed by HPLC (weight %)[c]
S_7	159[d]	0.6-0.8	5.2
S_{12}[a]	200	0.1	0.42
S_{12}[b]	140[e]	0.2	0.48
α-S_{18}	155-159	0.02	0.09[f]
S_{20}	155-159	0.01	0.12

[a] Schmidt's procedure; ref. 99. [b] Steudel's procedure; ref. 100. [c] At the temperature at which the melt was quenched. [d] The melt was first stabilized at 200°C for 30 min. [e] The melt was first stabilized at 200°C for 5-10 min. [f] Takes into account both α– and β–S_{18}.

Table 2. Extraction of Sulfur Rings S_n ($n \neq 8$) from Sulfur Melts

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[101] Steudel, R. and Mäusle, H.-J. *Angew. Chem., Int. Ed. Engl.*, **1978**, *17(1)*, 56.

1.2.3.2.b. Metathesis Reaction

In 1965, Schmidt and co-workers introduced a general synthetic method for the preparation of sulfur allotropes.[102] This procedure is the very first one that was entirely directed towards the synthesis of specific sulfur ring sizes. This method centers on S-S bond formation by condensation of an –SH group and an –SCl group as shown in Figure 18.

Figure 18. S-S Bond Formation by Metathetic Reaction

The –SH group typically comes from sulfanes (H_2S_x) and the –SCl group from chlorosulfanes (S_yCl_2). Methods for the independent preparation of both H_2S_x and S_yCl_2 species have been designed.[103] The procedure of sulfur ring formation involves a series of condensation reactions until a mixed species of the type HS_zCl ($z \geq x+y$) is formed and undergoes self-condensation to yield the sulfur ring S_z. These reactions are usually carried out at low temperature (-78°C) and at high dilution in order to favor this intramolecular ring closure.

Cyclo-hexasulfur (S_6) was the first sulfur allotrope to be synthesized using this method.[102,104] Schmidt actually found two routes that both led to the formation of S_6. The first route involves the reaction between H_2S and S_2Cl_2. It proceeds through the sequence of reactions shown in Figure 19.

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[102] Schmidt, M. and Wilhelm, E. *Inorg. Nucl. Chem. Letters*, **1965**, *1*, 39.

[103] For H_2S_x: a) Hahn, J. *Z. Naturforsch.*, **1985**, *40b*, 263 and references cited therein. For S_yCl_2: b) Fehér, F.; Naused, K. and Weber, H. *Z. Anorg. Allg. Chem.*, **1957**, *290*, 303. c) Fehér, F. and Ristic, S. *Z. Anorg. Allg. Chem.*, **1958**, *293*, 307.

[104] a) Schmidt, M. in *Elemental Sulfur*, Meyer, B. (Ed.), **1965**, 327 and references cited therein. b) Schmidt, M. *Inorg. Macromol. Rev.*, **1970**, *1*, 101 and references cited therein.

$$H_2S + ClS\text{—}SCl \longrightarrow HS\text{—}S\text{—}SCl + HCl \qquad \text{Eq. 1}$$

$$HS\text{—}S\text{—}SCl + H_2S \longrightarrow HS\text{—}S\text{—}S\text{—}SH + HCl \qquad \text{Eq. 2}$$

$$HS\text{—}S\text{—}S\text{—}SH + ClS\text{—}SCl \longrightarrow HS\text{—}S\text{—}S\text{—}S\text{—}S\text{—}SCl + HCl \qquad \text{Eq. 3}$$

$$HS\text{—}S\text{—}S\text{—}S\text{—}S\text{—}SCl \longrightarrow S_6 + HCl \qquad \text{Eq. 4}$$

$$2\ H_2S + 2\ ClS\text{—}SCl \longrightarrow S_6 + 4\ HCl \qquad \text{(overall)}$$

Figure 19. Formation of S_6 by Metathetic Reaction

This route produced S_6 in a yield of *ca* 8%. However, Schmidt also reported a much preferred second route that involved two fewer steps than the above reaction sequence. The second route used H_2S_4 and S_2Cl_2 as the starting materials and Schmidt reported an improved yield of 30%.[104a]

Sulfur Allotrope	Sulfane	Chlorosulfane	% Yield
S_6	H_2S	S_2Cl_2	8
	H_2S_4	S_2Cl_2	25-30
S_{10}	H_2S_6	S_4Cl_2	No reported yield
S_{12}	H_2S_8	S_4Cl_2	15-20[a]
	H_2S_4	S_2Cl_2	4.2[b]
S_{18}[c]	H_2S_8	$S_{10}Cl_2$	0.7
S_{20}	H_2S_{10}	$S_{10}Cl_2$	0.4

[a] Ref. 105a. [b] Ref. 105b. [c] Steudel suggested later that this allotrope be called α–S_{18}; ref. 100.

Table 3. Yields of Sulfur Rings S_n ($n \neq 8$) Formation by Metathesis

This metathesis reaction has also been applied to the synthesis of S_{10},[102,104a] S_{12},[105] S_{18}[106] and S_{20}.[106b,107] Some of the details of these reactions are summarized in Table 3.

One of the main limitations of this technique comes from the preparation of sulfanes and chlorosulfanes. Sulfanes are difficult to obtain in pure form and are often composed of traces of either longer or shorter sulfur chain species. For example, an impure sample was actually responsible for the discovery of the second route for forming S_6. About a quarter of a sample of H_2S_3 was in fact composed of H_2S_4. When treated with S_2Cl_2, the anticipated synthesis of S_{10} did not take place and S_6 was isolated instead.[104a]

Chlorosulfanes are usually malodorous oils that are thus not very easy to handle; alternatives have been proposed. Dicyanosulfanes of the type $S_n(CN)_2$ (n=1-9)[108] have been prepared and the structures of $S_3(CN)_2$,[109] $S_4(CN)_2$,[110] $S_6(CN)_2$[111] and $S_9(CN)_2$[108b] have been determined by X-ray crystallography. Steudel replaced, for example, S_4Cl_2 by the therein mentioned "easier to handle" crystalline $S_6(CN)_2$ in the synthesis of α-S_9.[111] However, this reaction did not actually involve reaction with a sulfane but with a commonly used organometallic precursor of sulfur allotropes. This will be the topic of the next Section.

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[105] a) Schmidt, M. and Wilhelm, E. *Angew. Chem., Int. Ed. Engl.*, **1966**, *5(11)*, 964. b) Schmidt, M.; Knippschild, G. and Wilhelm, E. *Chem. Ber.*, **1968**, *101*, 381.

[106] a) Debaerdemaeker, T. and Kutoglu, A. *Naturwissenschaften*, **1973**, *60*, 49. b) Schmidt, M.; Wilhelm, E.; Debaerdemaeker, T.; Hellner, E. and Kutoglu, A. *Z. Anorg. Allg. Chem.*, **1974**, *405*, 153.

[107] Debaerdemaeker, T.; Hellner, E.; Kutoglu, A.; Schmidt, M. and Wilhelm, E. *Naturwissenschaften*, **1973**, *60*, 300.

[108] a) Fehér, F. and Weber, W. *Chem. Ber.*, **1958**, *91*, 642 and references cited therein. b) Steudel, R.; Bergemann, K.; Buschmann, J. and Luger, P. *Angew. Chem., Int. Ed. Engl.*, **1993**, *32(12)*, 1702.

[109] Bats, J. W. *Acta Crystallogr., Sect. B*, **1977**, *33*, 2264.

[110] Steudel, R.; Bergemann, K. and Kustos, M. *Z. Anorg. Allg. Chem.*, **1994**, *620*, 117.

1.2.3.2.c. Organometallic Precursors

Organometallic reagents have greatly assisted the area of chalcogen ring[112] synthesis and in particular sulfur allotropes.[98] In 1968, Schmidt and co-workers found that the controlled reaction between bis(π-cyclopentadienyl)titanium(IV) pentasulfide (**28**), also commonly called titanocene pentasulfide, and chlorosulfanes (S_nCl_2) is able to produce sulfur rings of the type S_{5+n}.[113] The preparation of **28** had previously been described.[114] Not only Schmidt and co-workers reported the synthesis of S_6, S_7 and S_{12} but they also found that **28** leads to S_{10}[113] when reacted with sulfuryl chloride (SO_2Cl_2) (Figure 20).

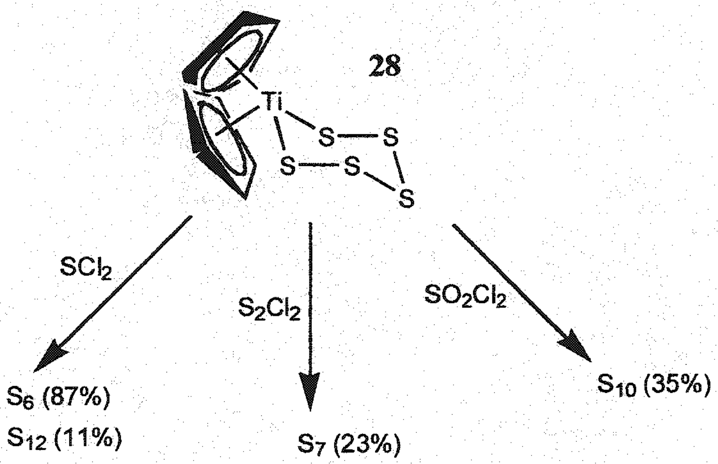

Figure 20. Titanocene Pentasulfide as a Precursor for Sulfur Rings

This ability of titanocene pentasulfide to cleanly deliver 5 sulfur atoms (S_5^{2-}) under these conditions has been greatly exploited. This reagent has unquestionably become the most versatile precursor for sulfur allotrope synthesis. Indeed, among the sulfur rings known today, only two of them (S_{18} and S_{14}) have not been produced by reaction with

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[111] Steudel, R; Bergemann, K.; Buschmann, J. and Luger, P. *Inorg. Chem.*, **1996**, *35*, 2184.

[112] For a review on mixed chalcogen rings (S, Se): Steudel, R. and Laitinen, R. *Top. Curr. Chem.*, **1982**, *102*, 177.

[113] Schmidt, M.; Block, B.; Block, H. D.; Köpf, H. and Wilhelm, E. *Angew. Chem., Int. Ed. Engl.*, **1968**, *7(8)*, 632.

[114] a) Samuel, E. *Bull. Soc. Chim. Fr.*, **1966**, *11*, 3548. b) Köpf, H.; Block, B. and Schmidt, M. *Chem. Ber.*, **1968**, *101*, 272.

28. Since the first synthesis of **28**,[114a] some modified preparations for this complex have been reported.[115] The structure of **28** has been characterized by single crystal X-ray diffraction and showed the chair conformation of the TiS_5 ring.[116]

The first step of a sulfur ring formation with this reaction involves insertion of a chlorosulfane species into the titanium-sulfur bond of **28**, followed by ring cyclisation to the desired sulfur cycle and formation of titanocene dichloride. Figure 21 shows the example of the formation of S_6.

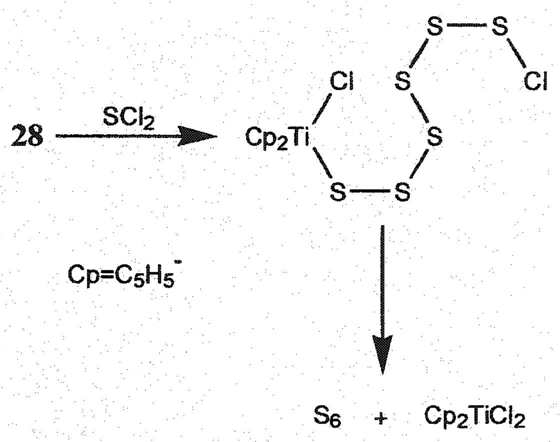


Figure 21. Formation of S_6 with Titanocene Pentasulfide

These reactions often lead, as well, to the formation of larger-sized sulfur cycles. For example, this takes place in the above reaction (Figure 21) since not only S_6 is obtained but also quite a significant amount (11%) of S_{12}.[113] This can be explained by the reaction of the intermediate shown in Figure 22 with another molecule of **28** and further reaction with sulfur dichloride (SCl_2). The different steps leading to S_{12} formation are shown in Figure 22.

---

[115] a) Köpf, H. and Block, B. *Chem. Ber.*, **1969**, *102*, 1504. b) McCall, J. M. and Shaver, A. *J. Organomet. Chem.*, **1980**, *193*, C37. c) Shaver, A. and McCall, J. M. *Organometallics*, **1984**, *3*, 1823. d) Steudel, R. and Strauss, R. *J. Chem. Soc., Dalton Trans.*, **1984**, 1775. e) Draganjac, M. and Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742 and references cited therein.

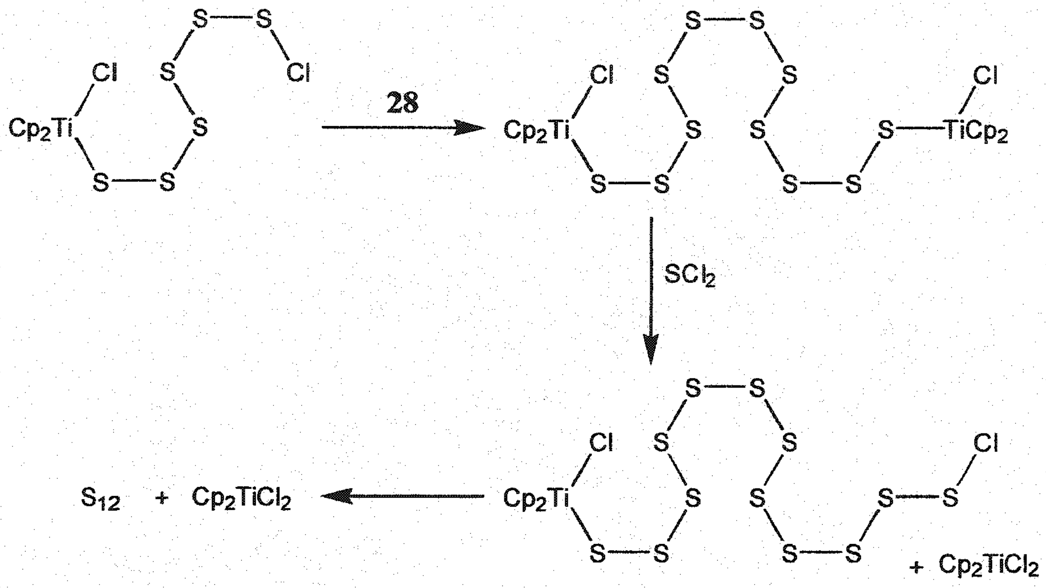
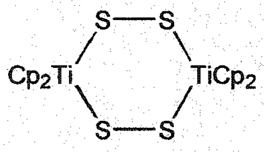
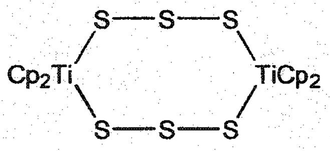


Figure 22. Formation of S_{12} with Titanocene Pentasulfide

Other titanium-based organometallic complexes have also produced sulfur allotropes. Steudel demonstrated that the dinuclear complexes **29**[117] and **30**[118] as well as titanocenedicarbonyl (**31**) can be efficient precursors of sulfur allotropes.[119]



29



30

$Cp_2Ti(CO)_2$

31

---

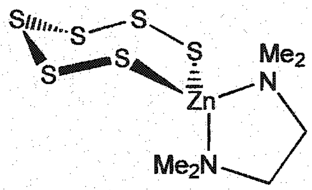
[116] a) Epstein, E. F.; Bernal, I. and Köpf, H. *J. Organomet. Chem.*, **1971**, *26*, 229. b) Muller, E. G.; Petersen, J. L. and Dahl, L. F. *J. Organomet. Chem.*, **1976**, *111*, 91.

[117] Giolando, D. M.; Rauchfuss, T. B.; Rheingold, A. L. and Wilson, S. R. *Organometallics*, **1987**, *6*, 667.

[118] Bolinger, C. M.; Rauchfuss, T. B. and Wilson, S. R. *J. Am. Chem. Soc.*, **1981**, *103*, 5620.

[119] a) Steudel, R.; Jensen, D and Papavassiliou, M. *Phosphorus Sulfur Silicon Relat. Elem.*, **1989**, *41*, 349. b) Westphal, U. and Steudel, R. *Phosphorus Sulfur Silicon Relat. Elem.*, **1992**, *65*, 151.

Recently, Rauchfuss and co-workers showed that a zinc-based complex ZnS_6(TMEDA) (TMEDA=*N,N,N',N'*-tetramethylethylenediamine) (**32**)[120] could be used as a 6 sulfur atom donor (S_6^{2-}) for the synthesis of mixed chalcogen rings.[121] Steudel and co-workers have advantageously used this property for the synthesis of yet another allotrope of elemental sulfur, *cyclo*-S_{14}.[122] This easy-to-prepare complex constitutes a new kind of sulfur transfer reagent as it is capable of delivering a fragment that was not available before and is based on zinc and not titanium.



32

Table 4 provides a convenient overview of all the sulfur allotropes synthesized with organometallic precursors. It includes original references as well as, in some cases, references for improved methods.

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[120] Verma, A. K.; Rauchfuss, T. B. and Wilson, S. R. *Inorg. Chem.*, **1995**, *34*, 3072.

[121] Verma, A. K. and Rauchfuss, T. B. *Inorg. Chem.*, **1995**, *34*, 6199.

[122] Steudel, R.; Schumann, O.; Buschmann, J. and Luger, P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37(17)*, 2377.

Organometallic Precursor	Reactant	Products	References
Cp_2TiS_5	S_nCl_2	S_{5+n} (S_6, S_7, S_9, S_{11}, S_{12}, S_{13})	123
	SO_2Cl_2	S_{10}, S_{15}, S_{20}	124
	$S_4(SCN)_2$	α–S_9	111
$Cp_2Ti(\mu\text{-}S_2)_2TiCp_2$	SCl_2	S_6	119a
$Cp_2Ti(\mu\text{-}S_3)_2TiCp_2$	S_2Cl_2	S_7, S_{10}, S_{15}*, S_{20}*	119a
$Cp_2Ti(CO)_2$	S_6/S_nCl_2	S_{8+n} (S_9, S_{10})	119b
$ZnS_6(TMEDA)$	S_8Cl_2	S_{14}	122

* Traces

Table 4. Sulfur Rings S_n ($n \neq 8$) Preparation with Organometallic Precursors

1.2.3.2.d. Miscellaneous

Reactions that do not belong to any of the three categories described above have also been used for the synthesis of some sulfur allotropes.

The reaction used for the first synthesis of an allotrope of elemental sulfur actually belongs to this category of so called miscellaneous reactions. In 1891, Engel prepared *cyclo*-hexasulfur S_6 by the reaction of concentrated hydrochloric acid (HCl) with a saturated solution of sodium thiosulfate ($Na_2S_2O_3$) at 0°C.[125] This form of sulfur was for a long time called "Engel's sulfur" or "Aten's sulfur" as Aten was the first one to identify

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[123] For S_6 and S_7: See ref. 113. For S_9: a) Schmidt, M. and Wilhelm, E. *J. Chem. Soc., Chem. Commun.*, **1970**, 1111. b) Steudel, R.; Sandow, T. and Steidel, J. *Z. Naturforsch.*, **1985**, *40b*, 594. For S_{11} and S_{13}: c) Sandow, T.; Steidel, J. and Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21(10)*, 794. d) Steudel, R.; Steidel, J. and Sandow, T. *Z. Naturforsch.*, **1986**, *41b*, 958. For S_{12}: See ref. 113.

[124] For S_{10}: See ref. 113 and a) Steudel, R.; Steidel, J. and Reinhardt, R. *Z. Naturforsch.*, **1983**, *38b*, 1548. For S_{15}: b) Strauss, R. and Steudel, R. *Z. Naturforsch.*, **1988**, *43b*, 1151. For S_{20}: See ref. 115d.

[125] Engel, M. R. *Acad. Sci., Paris*, **1891**, *112*, 866.

the crystal.[126] Bartlett optimized the procedure and developed a purification method.[127] The kinetics of the reaction have been studied.[128] "The formation of sulfur from acidified thiosulfate is consistent with a series of displacements of sulfite by thiosulfite ion leading to increasingly long ions of the type $HS_xSO_3^-$. As soon as x=6, an intramolecular displacement can occur through a sterically favored transition state, leading to hexatomic sulfur"[127] (Figure 23).

$$HS_2O_3^- + S_2O_3^{2-} \longrightarrow HS_2SO_3^- + SO_3^{2-}$$

$$HS_2SO_3^- + S_2O_3^{2-} \longrightarrow HS_3SO_3^- + SO_3^{2-}$$

$$HS_xSO_3^- + S_2O_3^{2-} \longrightarrow HS_{x+1}SO_3^- + SO_3^{2-}$$

$$HS_6SO_3^- \longrightarrow S_6 + HSO_3^-$$

Figure 23. Formation of S_6 from Acidified Sodium Thiosulfate

This procedure also leads to the formation of elemental sulfur S_8, *cyclo*-heptasulfur (S_7)[129] and other sulfur cycles.[130]

Another method for the synthesis of sulfur allotropes involves the formation of S_2I_2 from sulfur monochloride (S_2Cl_2) and potassium iodide.[131] S_2I_2 then decomposes to form a variety of sulfur rings (S_6, S_8, S_{12}, α-S_{18} and S_{20}) from which S_6 can be extracted by crystallization in 36% yield (Figure 24). The yields of S_{12} (1-2%), α-S_{18} (0.4%) and S_{20} (0.4%) are much lower. Even larger size sulfur homocycles have been detected with this method.[131,132]

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[126] Aten, A. H. W. *Z. Phys. Chem.*, **1914**, *88*, 321.

[127] Bartlett, P. D.; Colter, A. K.; Davis, R. E. and Roderick, W. R. *J. Am. Chem. Soc.*, **1961**, *83*, 109.

[128] Davis, R. E. *J. Am. Chem. Soc.*, **1958**, *80*, 3565.

[129] Steudel, R. and Mäusle, H.-J. *Z. Anorg. Allg. Chem.*, **1979**, *457*, 165.

[130] Möckel, H.-J. *J. Chromatogr.*, **1984**, *317*, 589.

[131] Mäusle, H.-J. and Steudel, R. *Z. Anorg. Allg. Chem.*, **1980**, *463*, 27.

[132] Steudel, R.; Mäusle, H.-J.; Rosenbauer, D.; Möckel, H. and Freyholdt, T. *Angew. Chem., Int. Ed. Engl.*, **1981**, *20*, 394.

$$S_2Cl_2 + 2\,KI \longrightarrow S_2I_2 + 2\,KCl$$

$$n\,S_2I_2 \longrightarrow S_{2n} + n\,I_2$$

Figure 24. Sulfur Rings Formation from Potassium Iodide and Sulfur Monochloride

Finally, a still quite unusual method for the synthesis of S_{10} involves the decomposition of oxidized forms of S_6 (presumably S_6O_2) (Figure 25) and S_7 (presumably S_7O) (Figure 26).[124a,133]

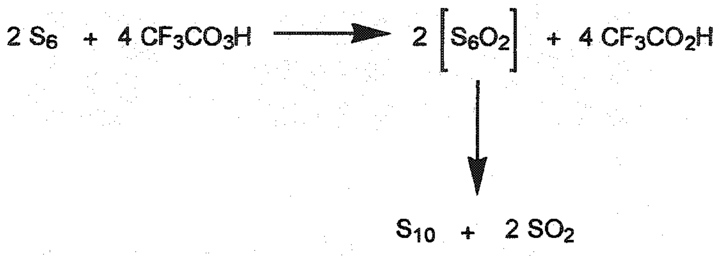

Figure 25. Formation of S_{10} by Oxidation of S_6

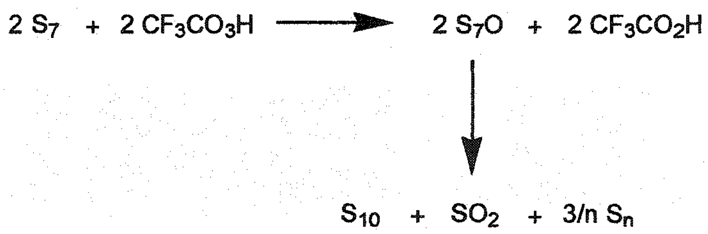

Figure 26. Formation of S_{10} by Oxidation of S_7

Slow decomposition of S_8O at -20°C in carbon disulfide has also shown to produce S_{12}.[134]

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[133] Steudel, R.; Steidel, J.; Sandow, T. and Schuster, F. *Z. Naturforsch.*, **1978,** *33b*, 1198.

[134] Steudel, R. and Rebsch, M. *J. Mol. Spectrosc.*, **1974,** *51*, 189.

1.2.4. Chemistry of the Sulfur Rings S_n with $n \geq 6$, $n \neq 8$

The chemistry of the solid allotropes of elemental sulfur (S_6 and larger rings) is surprisingly very limited.

In terms of the reactivity of sulfur allotropes, a study of interest was carried out by Bartlett and co-workers. They compared the reactivity of S_6 and S_8 towards triphenylphosphine (**33**) in a reaction that forms triphenylphosphine sulfide (**34**) (Figure 27).[127,135]

$$S_6 \; + \; \underset{\mathbf{33}}{6\,PPh_3} \longrightarrow \underset{\mathbf{34}}{6\,Ph_3P{=}S}$$

Figure 27. Reaction of S_6 with Triphenylphosphine

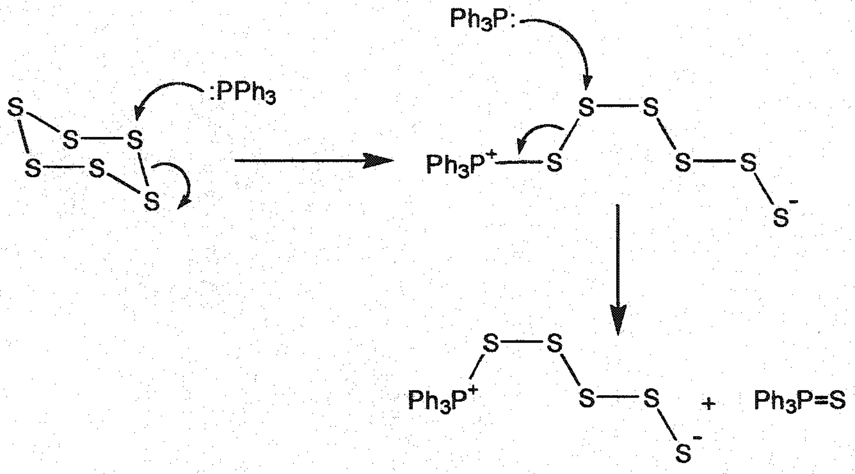

Figure 28. Mechanism for the Reaction of S_6 with Triphenylphosphine

The mechanism of this reaction likely proceeds *via* a nucleophilic opening of the sulfur ring by **33**, followed by a second attack of another molecule of **33** on the thus formed chain with displacement of **34** (Figure 28). Bartlett concluded that at the temperature used, S_6 is about 25,000 times more reactive towards **33** than S_8. This ability

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[135] a) Bartlett, P. D.; Lohaus, G. and Weis, C. D. *J. Am. Chem. Soc.*, **1958**, *80*, 5064.
b) Bartlett, P. D.; Cox, E. F. and Davis, R. E. *J. Am. Chem. Soc.*, **1961**, *83*, 103.

of **33** to cleave S-S bonds had already been studied by Bartlett[136] and then later by Harpp and co-workers, for the selective desulfurization process of trisulfides.[137]

Another main contribution to the chemistry of sulfur allotropes comes from the oxidation reaction of sulfur rings with trifluoroperacetic acid CF_3CO_3H in order to form the corresponding oxides or dioxides. As it was reported in the previous Section, this type of reaction has also been used for the synthesis of S_{10}.[124a,133] Sulfur rings S_6, S_7, S_8, S_9 and S_{10} have all been subjected to oxidation and the corresponding S_6O,[138] S_7O,[139] S_8O,[140] S_9O[123b] and $S_{10}O$[123b] have been synthesized. S_7O_2 has also been isolated from the oxidation of S_8 with excess CF_3CO_3H.[141] The structures of some of these sulfur oxides have been determined by single crystal X-ray diffraction.[142] It is interesting to note that early methods for the formation of sulfur ring oxides used the reaction between thionyl chloride $SOCl_2$ and polysulfanes HS_nH as shown by the very first synthesis of S_8O.[143] The chemistry of homocyclic sulfur oxides has been reviewed.[144] Two related sulfur oxide-metal complexes, $S_8O{\cdot}SbCl_5$[145] and $S_{12}O_2{\cdot}2SbCl_5{\cdot}3CS_2$,[146] have also been prepared and their structures determined.

---

[136] Bartlett, P. D. and Meguerian, G. *J. Am. Chem. Soc.*, **1956**, *78*, 3710.

[137] Harpp, D. N. and Smith, R. A. *J. Am. Chem. Soc.*, **1982**, *104*, 6045.

[138] Steudel, R. and Steidel, J. *Angew. Chem., Int. Ed. Engl.*, **1978**, *17*, 134.

[139] Steudel, R. and Sandow, T. *Angew. Chem., Int. Ed. Engl.*, **1976**, *15*, 772.

[140] a) Steudel, R. and Latte, J. *Angew. Chem., Int. Ed. Engl.*, **1974**, *13*, 603. b) Steudel, R. and Sandow, T. *Inorg. Synth.*, **1982**, *21*, 172.

[141] Steudel, R. and Sandow, T. *Angew. Chem., Int. Ed. Engl.*, **1978**, *17*, 611.

[142] For S_7O: a) Steudel, R.; Reinhardt, R. and Sandow, T. *Angew. Chem., Int. Ed. Engl.*, **1977**, *16*, 716. For S_8O: b) Steudel, R.; Luger, P.; Bradaczek, H. and Rebsch, M. *Angew. Chem., Int. Ed. Engl.*, **1973**, *12*, 423. c) Luger, P.; Bradaczek, H.; Steudel, R. and Rebsch, M. *Chem. Ber.*, **1976**, *109*, 180.

[143] a) Steudel, R. and Rebsch, M. *Angew. Chem., Int. Ed. Engl.*, **1972**, *11*, 302. b) Steudel, R. and Rebsch, M. *Z. Anorg. Allg. Chem.*, **1975**, *413*, 252.

[144] Steudel, R. *Comments Inorg. Chem.*, **1982**, *1*, 313.

[145] Steudel, R.; Sandow, T. and Steidel, J. *J. Chem. Soc., Chem. Commun.*, **1980**, 180.

[146] Steudel, R.; Steidel, J. and Pickardt, J. *Angew. Chem., Int. Ed. Engl.*, **1980**, *19*, 325.

Finally, in order to close this part on the known chemistry of sulfur allotropes, it is interesting to mention that S_6 has been used as a catalyst in a sulfur extrusion reaction.[147]

1.2.5. Project Outline

Although some sulfur allotropes have been known for a long time, it seems that there have been relatively few investigations in terms of their reactivity. They appear not to have been systematically studied as reagents in organic reactions.

Sulfuration reactions of simple or conjugated alkenes constitute a very active area of research and new sulfur transfer reagents are constantly being developed. These sulfuration methods usually involve either the use of diatomic sulfur (S_2) transfer reagents or the direct use of elemental sulfur in polar or amine solvents. Examples for each category will be further detailed in Chapter 2.

It was thought that certain sulfur allotropes could be used for such transformations. Attention was first focused on *cyclo*-decasulfur (S_{10}). It was anticipated that its degradation under appropriate conditions could in fact lead to a net 2-sulfur atom transfer, elemental sulfur S_8 being the only side product of such a process as shown in Figure 29.

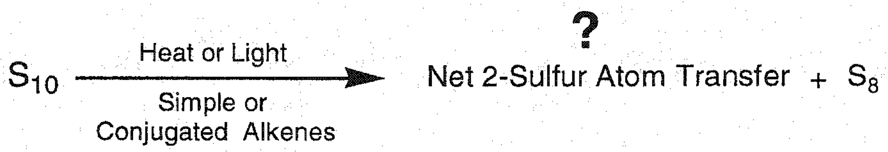

Figure 29. S_{10}: A Net 2-Sulfur Atom Donor ?

Such reactions could then also be extended to other sulfur allotropes.

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[147] Davis, M. and Tonkin, K. C. *Aust. J. Chem.*, **1981**, *34*, 755.

CHAPTER 2. SOME CHEMISTRY OF S_{10}

2.1. Background

As described in the previous Chapter, S_{10} was first synthesized *via* the metathetic reaction between sulfanes and chlorosulfanes in 1965.[104] Although it seems that S_{10} was unequivocally obtained with this method, no yield was reported and this procedure was quite inconvenient. Soon after, the synthesis of S_{10} was achieved with the use of titanocene pentasulfide (**28**) (Figure 30).[113]

$$\mathbf{28} + SO_2Cl_2 \xrightarrow[-78°C]{CS_2} S_{10}, S_{15}, S_{20}$$

Figure 30. Synthesis of S_{10} from Titanocene Pentasulfide

However, this reaction also produces significant amounts of S_{15} and S_{20}; for the separate synthesis of these allotropes, variations of the reaction have been designed.[124b,115d]

A detailed mechanism of the reaction between **28** and sulfuryl chloride (SO_2Cl_2), as described by Steudel, is shown in Figure 31 and explains the formation of S_{15} and S_{20}.[115d]

A third method for the synthesis of S_{10} is the one shown in the previous Chapter in Figures 25 and 26. It involves the slow decomposition of S_7O and S_6O_2 species.[133] This method is actually very convenient when only small quantities of S_{10} are needed.

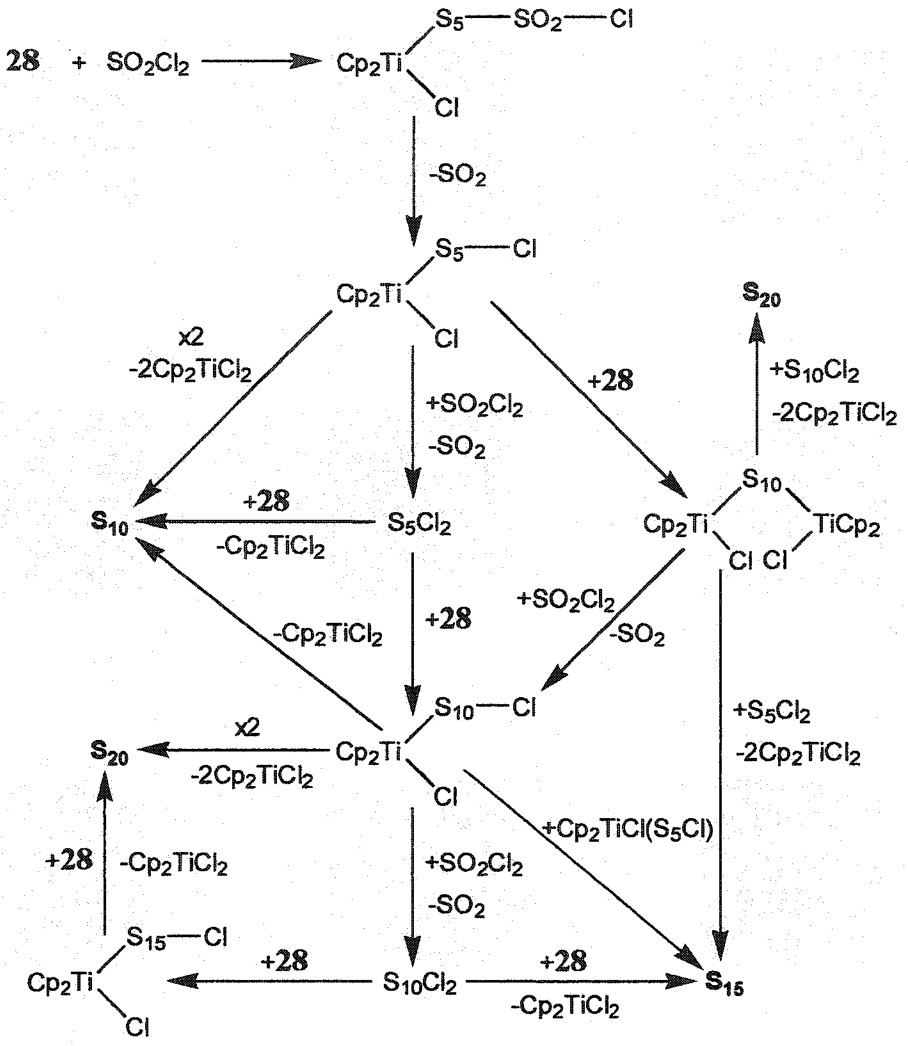

Figure 31. Mechanism for the Formation of S_{10}, S_{15} and S_{20} from Titanocene Pentasulfide

S_{10} is an intense yellow solid. Schmidt observed that S_{10} does not have a sharp melting point but decomposes with polymerization at *ca.* 60°C.[113] Steudel later showed that decomposition occurs at higher temperatures and over a wide range, 90-110°C.[148] S_{10} can, however, be stored almost indefinitely without any apparent decomposition when kept at –40°C in the dark. Indeed, some samples that were prepared in the course of this study seemed unchanged even after 2 or 3 years of storage under these conditions.

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[148] Steudel, R.; Passlack-Stephan, S. and Holdt, G. *Z. Anorg. Allg. Chem.*, **1984**, *517*, 7.

The structure of S_{10} has been studied by X-ray diffraction of a single crystal. Preliminary work on the structure[149] was achieved by Steudel and co-workers who later discussed it in further detail.[124a] The structures for the existing sulfur rings usually belong to two classes. The first class contains highly symmetrical rings that possess almost equal bond distances (205 ± 2 pm), bond angles close to 105° (± 3°) and torsion angles around 85° (± 15°). Sulfur cycles such as S_6,[150] S_8,[151] S_{12},[152] S_{14}[122] and α-S_{18}[106] belong to this group.

The second class of molecules contains less symmetrical sulfur rings that usually have alternating bond distances, which vary greatly in some cases (from 200 pm to 218 pm for S_7), and torsion angle variations as large as 108° within the same molecule. S_7,[153] α-S_9,[111] S_{11},[154,123d] S_{13},[123d] β-S_{18}[155] and S_{20}[106b,107] belong to this second group.

Contrary to theoretical predictions,[156] S_{10} actually belongs to the less symmetrical group of sulfur rings. It exhibits the rare point group symmetry D_2. Its crystal structure possesses three orthogonal two fold axes of rotation as the only elements of symmetry. Figure 32 shows a representation of the structure of S_{10} while some of the parameters are summarized in Table 5.

---

[149] Reinhardt, R.; Steudel, R. and Schuster, F. *Angew. Chem., Int. Ed. Engl.*, **1978**, *17*, 57.

[150] a) Donohue, J.; Caron, A. and Goldish, E. *J. Am. Chem. Soc.*, **1961**, *83*, 3748. b) Steidel, J.; Pickardt, J. and Steudel, R. *Z. Naturforsch.*, **1978**, *33b*, 1554.

[151] For orthorhombic α-S_8: See refs. 8 and 9; for monoclinic β-S_8: See ref. 10; for monoclinic γ-S_8: See refs. 11, 12 and 13.

[152] a) Kutoglu, A. and Hellner, E. *Angew. Chem., Int. Ed. Engl.*, **1966**, *5*, 965. b) Steidel, J.; Steudel, R. and Kutoglu, A. *Z. Anorg. Allg. Chem.*, **1981**, *476*, 171.

[153] a) Steudel, R.; Reinhardt, R. and Schuster, F. *Angew. Chem., Int. Ed. Engl.*, **1977**, *16*, 715. b) Steudel, R.; Steidel, J.; Pickardt, J.; Schuster, F. and Reinhardt, R. *Z. Naturforsch.*, **1980**, *35b*, 1378.

[154] Steidel, J. and Steudel, R. *J. Chem. Soc., Chem. Commun.*, **1982**, 1312.

[155] Debaerdemaeker, T. and Kutoglu, A. *Cryst. Struct. Commun.*, **1974**, *3*, 611.

[156] a) Tuinstra, F. *J. Chem. Phys.*, **1967**, *46*, 2741. b) Kao, J. and Allinger, N. L. *Inorg. Chem.*, **1977**, *16*, 35.

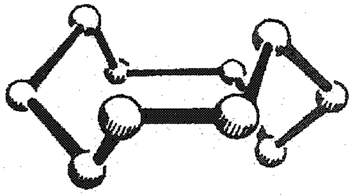

Figure 32. Structure of S_{10}

Molecule	Interatomic Distances (pm)	Bond Angles (°)	Torsion Angles (°)
S_{10}	203-208	103-110	75-124

Table 5. Some Parameters of the Structure of S_{10}

Interestingly, S_{10} co-crystallizes with S_6 to give a new allotropic modification, which was studied by X-ray diffraction.[124a] Other structures such as $S_{12}•CS_2$[123e] and S_∞[157] have also been obtained by X-ray diffraction. Finally, some allotropes have been proven to exist in different crystal packing or polymorphs by Raman spectroscopy. Depending on the crystallization conditions, S_7 exists in four different crystalline states (α, β, γ and δ),[158] while S_9 exists in two crystalline states (α and β).[159] The geometry of S_7 and S_9 cycles in these different crystal lattices seems quite similar contrary to α-S_{18} and β-S_{18}, which have completely different conformations.

2.2. Synthesis and Characterization of S_{10}

The method used for the synthesis of S_{10} in the course of this study has been the one involving titanocene pentasufide (**28**). The exact procedure used was the so-called "improved synthesis" of S_{10} designed by Steudel.[124a]

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[157] Lind, M. D. and Geller, S. *J. Chem. Phys.*, **1969**, *51*, 348.

[158] Steudel, R. and Schuster, F. *J. Mol. Struct.*, **1978**, *44*, 143.

[159] Steudel, R.; Sandow, T. and Steidel, J. *Z. Naturforsch.*, **1985**, *40b*, 594.

Two different methods have been utilized for the synthesis of precursor **28**. The method of Shaver and McCall[115c] involves the intermediate pentasulfide dianion that is generated *via* the method designed by Gladysz.[160] Gladysz's method consists in reacting a known molar ratio of elemental sulfur S_8 and a strong base, SuperHydride ($LiEt_3BH$). A mixture of lithiated polysulfide dianions of different lengths is thus obtained, the major component of the mixture being the polysulfide having the desired length. Shaver and McCall used this method to generate LiS_5Li, which, upon further reaction at room temperature with titanocene dichloride (Cp_2TiCl_2), produced the desired precursor **28** (Figure 33). Overall yields of 88% of **28** were obtained in the course of this study with this method.

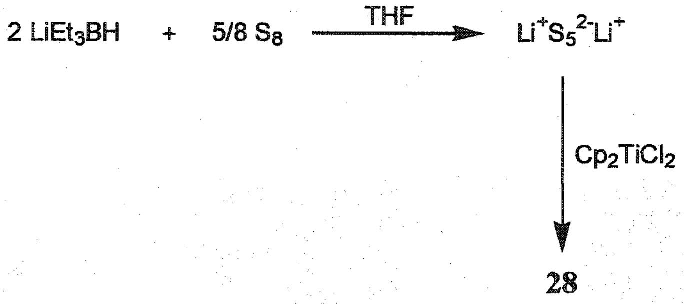

Figure 33. First Method used for the Preparation of Titanocene Pentasulfide

A second method for the preparation of **28** is a procedure first described by Köpf and Block,[115a] and modified by Steudel.[115d] It involves the *in situ* generation of diammonium pentasulfide prior to reaction with titanocene dichloride. This procedure's main disadvantage is the use of H_2S gas, which has a lethal dose of only 10 ppm in the atmosphere. As a consequence, an adequate experimental setup is required in order to be safe and is well described in the experimental part of this thesis. However, this method for the synthesis of **28** presents the advantage of being much cheaper for the preparation of bulk quantities. This procedure permits the preparation of as much as 50 g of **28** in one pot, as opposed to one-tenth of this with the SuperHydride method, although the yields are identical. It has thus quickly become the method of choice despite the disadvantage

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[160] a) Gladysz, J. A.; Hornby, J. L. and Garbe, J. E. *J. Org. Chem.*, **1978**, *43*, 1204. b) Gladysz, J. A.; Wong, V. K. and Jick, B. S. *Tetrahedron*, **1979**, *35*, 2329.

of having to handle H_2S gas. The synthetic pathway for **28** using this method is shown in Figure 34.

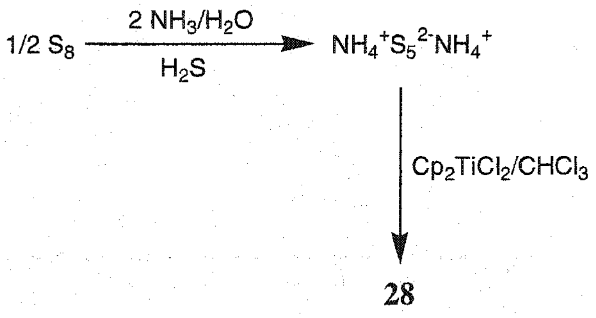

Figure 34. Second Method used for the Preparation of Titanocene Pentasulfide

Similarly to the SuperHydride method, the stoechiometry of the reaction is adjusted in order to obtain polysulfide mixtures having as a main constituent the desired pentasulfide dianion. Contrary to earlier suggestions, the size of the polysulfide ring in **28** cannot be adjusted by the nature of the polysulfide reagent.[115e] Imbalances in the stoichiometry simply result in decreased yields of **28**. Diammonium pentasulfide $(NH_4)_2S_5$ and more generally polysufide dianion solutions have been studied by vibrational spectroscopy.[161] The structure of $(NH_4)_2S_5$ has been fully determined by X-ray diffraction.[162]

The procedure used for the synthesis of S_{10} was essentially identical to the one described by Steudel.[124a] HPLC grade carbon disulfide (CS_2) was used as the solvent in most cases. The use of HPLC grade solvent avoided the inconvenience of having to distill the extremely flammable CS_2. On some occasions, newly opened bottles of reagent grade CS_2 were used for the synthesis of S_{10} without any apparent decrease in yields. The yields of S_{10} averaged 35%, in good agreement with the ones reported by Steudel.

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[161] a) Steudel, R. and Schuster, F. *Z. Naturforsch.*, **1977**, *32a*, 1313. b) Dubois, P.; Lelieur, J. P. and Lepoutre, G. *Inorg. Chem.*, **1988**, *27*, 1883. c) El Jaroudi, O.; Picquenard, E.; Demortier, A.; Lelieur, J.-P. and Corset, J. *Inorg. Chem.*, **2000**, *39*, 2593.

[162] Von Schnering, H. G.; Goh, N. K. and Peters, K. *Z. Kristallogr.*, **1985**, *172*, 153.

S_{20} was also isolated during these reactions and separated from S_{10} by the solubility difference in CS_2, which was not only used as the reaction solvent but also as a crystallization or recrystallization solvent.

The characterization of the thus synthesized S_{10} was achieved with FT-Raman spectroscopy and HPLC. These two techniques constitute probably the best tools to qualitatively and quantitatively analyze different-sized sulfur rings.

The FT-Raman instrument used was equipped with a Nd-YAG laser emitting in the near infrared region at 1064 nm and spectra were recorded with a resolution of 2-4 cm^{-1}. Analysis was performed at room temperature on a sample placed in a small capillary tube. Similar analyses have been reported earlier on sulfur allotropes, but used different laser sources. For example, Steudel very often used the red line of a krypton laser, which avoids the photodecomposition of these light sensitive materials. The analyses were also usually conducted at -90°C.[124a]

S_{10}[a]			S_{10}[b]		
		85 (76)	495 (6)	255 (5)	85 (33)
485 (33)		70 (100)	487 (16)	246 (sh)	73 (100)
	242 (57)		481 (sh)	243 (24)	51 (6)
466 (87)			469 (36)	231 (3)	39 (37)
	177 (70)		466 (sh)	178 (31)	29 (26)
424 (39)			425 (18)	155 (2)	
	129 (48)		403 (2)	131 (20)	
	97 (54)			100 (19)	

[a] FT-Raman/Nd-YAG laser/1064 nm/2.6 cm^{-1}/room temperature.
[b] Ref. 124a; Cary 82 Raman spectrometer/Krypton laser/647 nm/ 1.5 cm^{-1}/-90°C.

Table 6. Raman Spectra of S_{10}

Table 6 compares the vibrational bands detected for S_{10} in this study to those previously reported by Steudel[124a] and thus offers indisputable evidence for the nature of the sulfur ring.

The vibrations reported in Table 6 can be separated into three main categories. The region 400-500 cm^{-1} corresponds to the stretching modes of the S-S bonds of S_{10}. The bending modes are found in the region 100-270 cm^{-1} while the vibrations found at lower wavenumbers correspond to the lattice and torsional modes.

HPLC has also been routinely used in the course of this study in order to assign the purity of S_{10} batches. As we have seen in Chapter 1, Steudel was the first to advantageously use reverse phase HPLC as a separation tool for sulfur rings.[66] In this study, a reverse phase BDS-C18 column was used with mixtures of methanol and cyclohexane as an eluant. Solvent composition varied from methanol/cyclohexane 90:10 to 70:30 mixtures. Each batch of S_{10} was always freshly recrystallized prior to use. The purity of these batches was examined by HPLC. The presence of residual S_8 and traces of S_x ($x<10$) were detected but the purity based on the % area of the peaks always exceeded 90%. This purity turned out to be sufficient for this study as the results were reproducible and consistent. Details on the instrument used as well as a sample run can be found in the Experimental and in the Appendix.

2.3. Reaction of S_{10} with 1,3-Dienes

2.3.1. The Model Reaction: The Reaction of S_{10} with 2,3-Diphenyl-1,3-Butadiene

The goal of this part of the work was highly exploratory and was intended at designing a so called "model reaction" for which the experimental parameters would be well optimized and would thus serve as a starting base for future reactions. These future reactions could not only be reactions between S_{10} and other olefins but also parallel reactions involving other sulfur allotropes.

2.3.1.1. Introduction

The choice of 2,3-diphenyl-1,3-butadiene (**12a**) as a model substrate in order to optimize the possible reaction of S_{10} with olefins was motivated by the fact that this molecule has been extensively used in the past in reactions with sulfur species. These reactions can be classified into two categories.

One group of reactions uses **12a** as a trapping agent in Diels-Alder reactions with singlet diatomic sulfur ($^1S_2$). As it was discussed in Chapter 1, Steliou and co-workers were the first to show that such reactions could take place in reasonable yields.[82]

A second group of reactions takes place between **12a** and other sulfur transfer reagents (non-diatomic sulfur type precursors) or elemental sulfur (S_8) itself. The reaction of **12a** with the latter has actually been recently reinvestigated by Harpp and Rys.[163] They found new conditions for the sulfuration of 1,3-dienes with S_8 in polar or amine solvents at temperatures between 115°C and 125°C and proposed a mechanism. A catalytic version of 1,3-diene sulfuration that combines the complementary action of S_8 and metallocene polysulfides has also been optimized by the same authors.[164] The mechanistic data are however not entirely clear as to which group this reaction belongs to as two different sulfuration pathways were envisaged.[164]

2.3.1.2. Optimization of the Model Reaction

The initial reactions between 2,3-diphenyl-1,3-butadiene and S_{10} were carried out at 78°C in refluxing benzene under a nitrogen atmosphere. S_{10} was directly used in its solid form and simply added to the reaction flask prior to heating. The yields were estimated by comparison with 1,3,5-tri-*tert*-butylbenzene, which was used as an internal standard and products were identified by NMR comparison with authentic samples. This first set of reactions[81c] turned out to be promising since a reaction occurred between equimolar amounts of diene **12a** and S_{10} under these conditions. 4,5-Diphenyl-3,6-dihydro-1,2-

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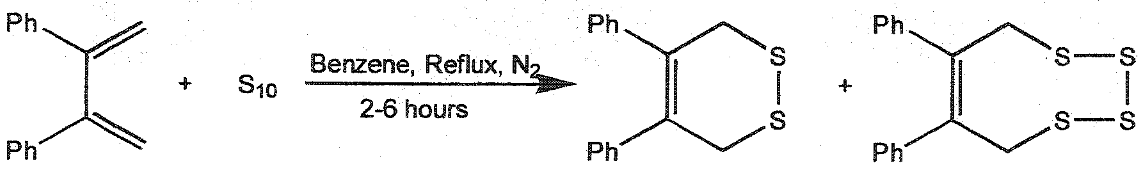
[163] Rys, A. Z. and Harpp, D. N. *Tetrahedron Lett.*, **1997**, *38*, 4931.

dithiin (**13a**) and 6,7-diphenyl-5,8-dihydro-1,2,3,4-tetrathiin (**35**) were identified as reaction products, as shown in Figure 35.



12a **13a** **5.5:1** **35**

3-29%

Figure 35. Product Yields and Ratios for the Reaction of 1,3-Diene **12a** with S_{10} in Benzene; Inconsistencies over 15 Reactions.

However, a major drawback very quickly became evident with this reaction. As it is shown in Figure 35, this trapping reaction did not seem to be at all reproducible. In the best case, overall combined yields for **13a**+**35** as high as 29% could be observed but in other cases, yields went down to as low as 3%. Unreacted diene **12a** accounted for the remaining part of the reaction mixtures.

The ratio between the two products was also quite erratic within the same batch of S_{10} as well as from one batch to another. It appeared to vary between a low 2:1 and a high 7:1 (average 5.5:1), in favor of disulfide adduct **13a**. Despite an obvious lack in reproducibility in the ratios, the high selectivity towards disulfide **13a** observed in some reactions seemed very promising as it had been anticipated that S_{10} would act as a clean 2-sulfur atom source.

Two main aspects of this irreproducible reaction were studied in order to explain the inconsistencies that were obtained.

The first main factor had to do with the purity of S_{10} itself. Steudel[165] as well as Bartlett[127,135] pointed out the sensitivity of elemental sulfur allotropes towards traces of base or nucleophiles. Traces of the strong bases that were used in the synthesis of **28**

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[164] Rys, A. Z. and Harpp, D. N. *Tetrahedron Lett.*, **1998**, *39*, 9139.

(ammonia, super-hydride) could have possibly been carried on into the different batches of S_{10} even if **28** seemed of good enough purity for bulk preparation of S_{10}. This could be responsible for partial decomposition of S_{10} in the early stages of the trapping reaction, thus explaining why yields were so inconsistent and low. Although no experimental evidence was obtained to prove that such traces were present or not in the different batches of S_{10}, from then on, **28** was systematically purified by column chromatography (see Experimental). The batches of S_{10}, as well as the other sulfur allotropes that were synthesized from this precursor were obtained in reproducible yields and all seemed homogeneous in terms of purity when analyzed by both FT-Raman and HPLC (see Appendix for selected spectra).

In order to limit the risks of base contamination, it was also decided that all glassware would be washed in dilute HCl baths prior to sulfur allotrope synthesis or trapping reactions. Coating of the glassware with silicon oils was also attempted. It did not result in significant improvements on the model reaction yields and was abandoned.

The second main aspect of the reaction between 2,3-diphenyl-1,3-butadiene and S_{10} that was modified in order to obtain a reproducible reaction had to do with the homogeneity of the reaction itself. S_{10} is only slightly soluble in benzene at room temperature and even when the solvent was heated, S_{10} never went fully into solution. The reaction between 2,3-diphenyl-1,3-butadiene and S_{10} was thus heterogeneous and only occurred at the surface of the particles of sulfur that were in suspension in the stirred reaction mixture. These particles of S_{10} often aggregated into bigger particles thus decreasing the surface area for the reaction to take place.

The stability of S_{10} at the temperature of refluxing benzene (*ca.* 80°C) was then studied in order to better estimate the lifetime of S_{10} under the reaction conditions. Steudel and co-workers very precisely determined the decomposition pattern of 10 allotropes of sulfur by HPLC.[148] They showed that S_{10} decomposes in a matter of minutes at 120°C. Figure 36 shows their results.

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[165] Steudel, R., Chemistry Department Seminar, University of Vermont, Burlington, VT, October **1996**.

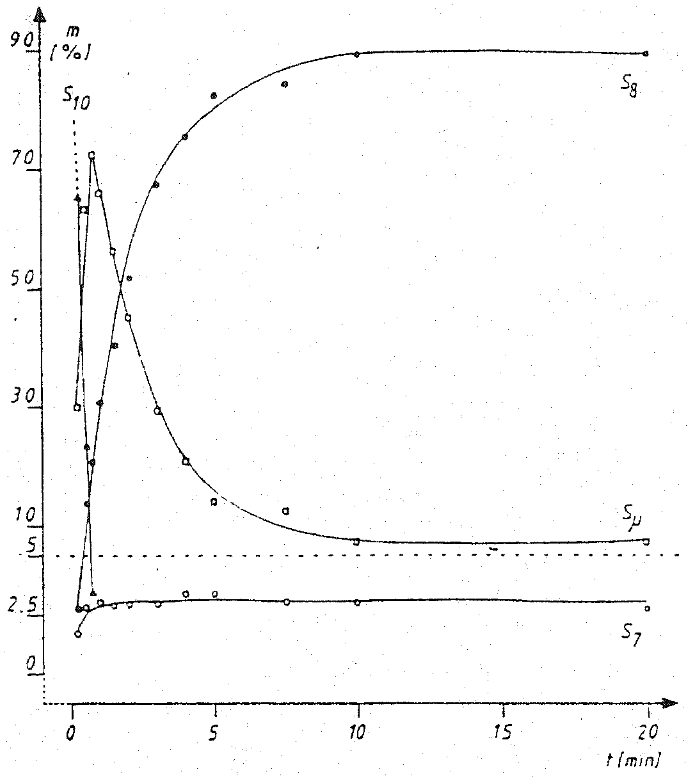

Figure 36. Decomposition of S_{10} at 120°C

An interesting aspect of this study is the characterization of polymeric sulfur S_μ as a key intermediate in the thermal decomposition pathway of S_{10} and other sulfur allotropes. Upon heating, cleavage of the S-S bonds leads to the polymerization of S_{10} and the formation of long sulfur chains (S_μ), which then depolymerize into elemental sulfur S_8 upon further heating. *Cyclo*-octasulfur S_8 is the end product of the decomposition. S_7 was also found in quantities that had been underestimated until Steudel's work.

In order to estimate the speed of decomposition of S_{10} at 80°C, we used a customized heating cell in which a capillary tube containing a fresh sample of S_{10} was placed. The temperature of the cell was maintained at 80°C with a thermocouple. A FT-Raman spectrum of the sample was taken at 5 minutes intervals during the first hour of decomposition and then at longer intervals. The acquisition time was the same for each spectrum (50 scans, 3 minutes). A resolution of 2.6 cm^{-1} was used. Selected spectra acquired in the course of this experiment are shown in Figure 37. A spectrum of S_8 is also included in this figure.

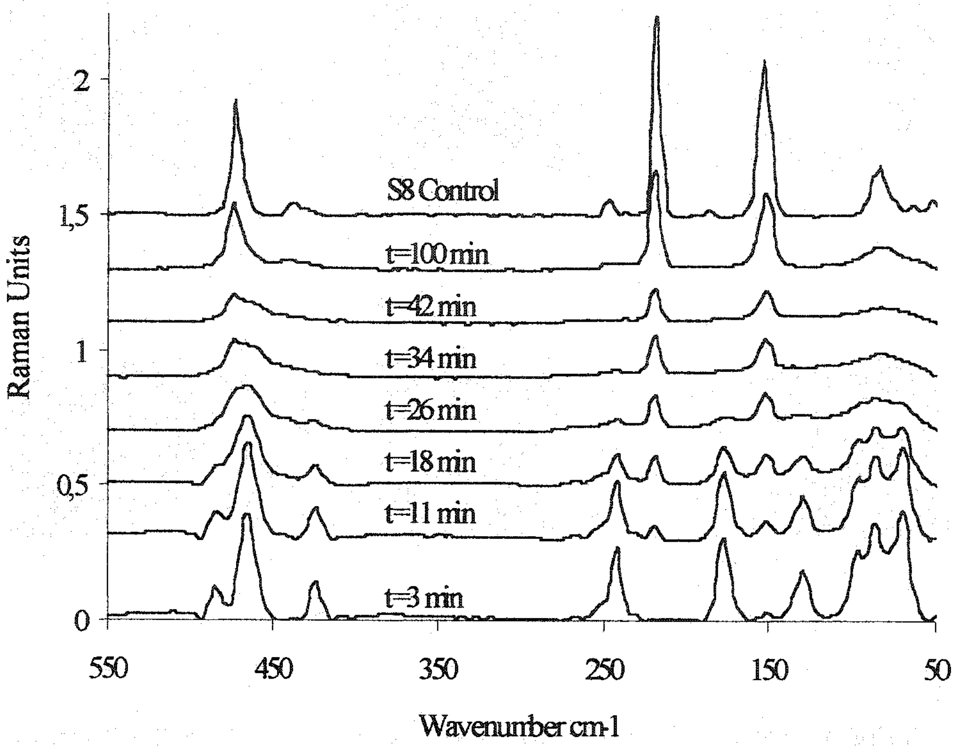

Figure 37. Decomposition of S_{10} at 80°C

This experiment only allowed a rough determination of the exact time when all S_{10} fully decomposed under these conditions. However, it was concluded with certainty that S_{10} was completely decomposed in 35 to 40 minutes at 80°C. This result was of sufficient accuracy for the purpose of this study.

The trapping reaction between 2,3-diphenyl-1,3-butadiene and S_{10} in benzene was thus not only heterogeneous but it was also concluded that the particles of S_{10} that were in suspension, changed composition very rapidly under the reaction conditions. In other words, S_{10} had probably all decomposed before it was even given a chance to react with the substrate. It was demonstrated that polymeric sulfur was completely unreactive towards 1,3-diene **12a** in the experimental conditions used in this study. Indeed, in a series of control reactions, S_{μ}, which was synthesized in parallel, did not form *any* detectable sulfuration adduct with **12a** when stirred in refluxing benzene or toluene. Contrary to what was observed in refluxing benzene, S_{μ} went fully into solution within

1.5 hour when heated at 110°C in toluene. At that temperature, depolymerization transformed the insoluble polymeric sulfur into the more soluble S_8. Further, this proved that even during its depolymerization process S_μ did not react with 1,3-diene **12a**.

In order to overcome the very limiting factor of the heterogeneity of the model reaction, it was decided to dissolve S_{10} in an appropriate solvent prior to reaction with the substrate. An obvious candidate was carbon disulfide CS_2. It is a very good solvent for small sulfur rings. For example, S_8 has a solubility of 37.4 g/100 mL of CS_2 at room temperature.[166] Thus, a solution of S_{10} in CS_2 was injected in the reaction flask over a refluxing solution of 2,3-diphenyl-1,3-butadiene.

Different reaction parameters such as amount of CS_2, addition time, reaction time and dilution were then very carefully optimized for selected solvents. Optimal conditions for a typical small scale reaction are presented in Table 7.

	Reaction with 0.1 mmol of **12a**
Amount of S_{10}	0.1 mmol
Volume of Solvent[a]	10 mL
Volume of CS_2	500 μL + 100 μL[b]
Injection Time for S_{10}/CS_2	*ca.* 30 sec
Reaction Time	2-3 hr

[a] Selected solvents were benzene, toluene or chlorobenzene.
[b] This extra volume was used to further rinse the flask that contained S_{10} and was combined to the refluxing mixture.

Table 7. Optimized Parameters for the Reaction of S_{10} with 2,3-Diphenyl-1,3-butadiene

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[166] Schmidt, M. and Block, H.-D. *Z. Anorg. Allg. Chem.*, **1971**, *385*, 119.

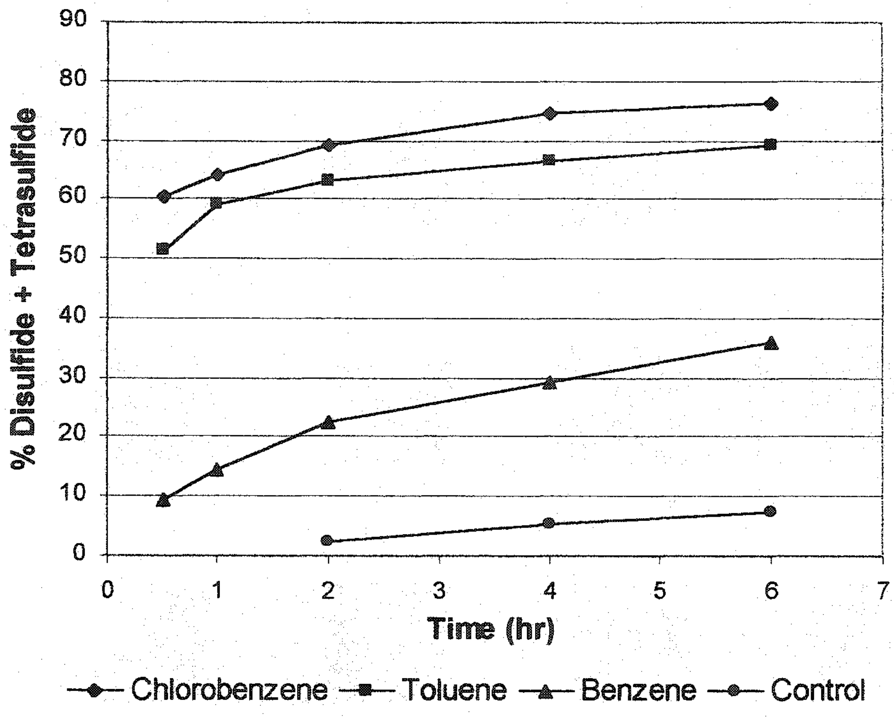


Figure 38. Effect of Temperature on S_{10} Trapping by 2,3-Diphenyl-1,3-butadiene

The model reaction was carried out in the selected solvents and the reaction analyzed at various times by ^{1}H-NMR. Due to the presence of the low boiling CS_2 in the reaction mixture, it was determined that the actual temperature inside the flask was *ca.* 15°C lower than the boiling point of the solvent. For example, the temperature of the trapping reaction in chlorobenzene (bp. 130°C) was measured at *ca.* 115°C. Yields of the two products disulfide **13a** and tetrasulfide **35** were estimated with 1,3,5-tri-*tert*-butylbenzene or 9-methylanthracene as internal standards. Results are presented in Figure 38.

The ratios of disulfide adduct **13a**/tetrasulfide adduct **35** obtained in these optimized conditions of the model reaction averaged to 6-7:1, very much in favor of disulfide **13a**. Contrary to the initial heterogeneous trapping reactions, this ratio was essentially constant throughout the reactions at different sampling times. This ratio also oscillated within the same narrow range when variations in reaction temperatures were applied during trapping reactions in toluene or benzene.

Figure 38 also presents a control reaction in which S_{10} was substituted by the same weight amount of S_8. The trapping reaction was carried out under the same conditions as with S_{10} in chlorobenzene. The very low yields of trapping compounds obtained with S_8 (*ca.* 2-3% every 2 h) clearly differs from the sulfuration reaction that takes place with S_{10} under the same conditions. Moreover, the ratio **13a/35** in this control reaction only averaged 4:1. It is interesting to note that the slope of the curve showing the amount of disulfide **13a** and tetrasulfide **35** produced in the case of S_{10} trapping reactions correlates with the control curve after 2 or 3 hours of reaction. As shown by the decomposition experiment of S_{10} at 80°C and also by HPLC analysis of this crude reaction mixture, at this time in the reaction, S_{10} is no longer present in the reaction mixture and any residual trapping reaction results from the presence of S_8. The line between each point in Figure 38 is only there to guide the eye. The curve corresponding to the reaction in chlorobenzene is an average of six different sets of data.

A series of control reactions was then carried out. Control trapping reactions between S_{10} and 2,3-diphenyl-1,3-butadiene in the presence of traces of sodium hydroxide showed combined yields as low as 20% after two hours in chlorobenzene, while the same reaction with equimolar amounts of pyridine as the base, showed no trapping at all. The experiment with the hydroxide contamination reiterates the fact that the presence of even residual quantities of base almost completely quenches the trapping reaction between S_{10} and diene **12a**. The decomposition reaction of S_{10} by hydroxide ions seems considerably faster than the sulfuration reaction of 2,3-diphenyl-1,3-butadiene by S_{10}. It was also shown that both 1,3,5-tri-*tert*-butylbenzene and 9-methylanthracene are completely unreactive with S_{10} in the reactions conditions used in this study. Similarly, reactions between CS_2 and diene **12a** did not reveal the formation of any detectable amount of a possible adduct.

Another set of control reactions also revealed that no equilibrium exits between disulfide adduct **13a** and tetrasulfide adduct **35**. Indeed, an attempted reaction between a sample of disulfide **13a** containing less than 2% of tetrasulfide **35** and S_{10} in the presence of an internal standard at *ca.* 115°C for 3 hours in chlorobenzene/CS_2, did not show the formation of any significant amount of tetrasulfide **35** (<1%). Disulfide **13a** was 96% recovered and small amounts of diene **12a** were formed (*ca.* 4%). Similarly, it was also proven that heating tetrasulfide **35** for extended periods of time does not yield the corresponding disulfide **13a**. Compounds **13a** and **35** are thus completely separate products from the sulfuration reaction of diene **12a** with S_{10}, as summarized in Figure 39.

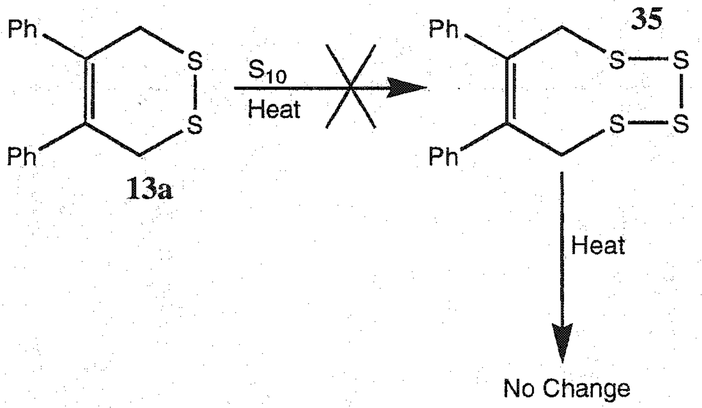
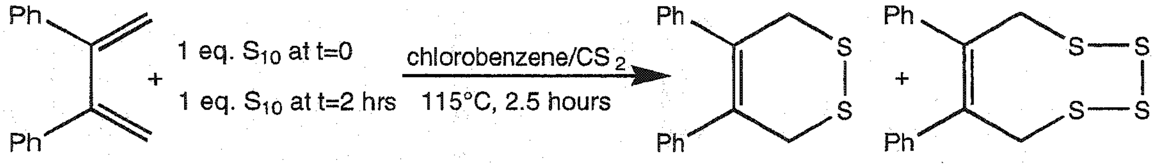


Figure 39. Non-Equilibrium between Disulfide **13a** and Tetrasulfide **35**

It is important to note that higher combined yields for disulfide **13a** and tetrasulfide **35** were obtained when more than one equivalent of S_{10} was used in the model reaction. The increase in overall yield was only modest (from *ca.* 70% to 75% in 2 hours at 115°C in chlorobenzene/CS_2) when two equivalents of S_{10} were directly reacted with one equivalent of 1,3-diene **12a**. Much improved yields were observed when the addition of the second equivalent of S_{10} was performed at a later stage in the reaction. As an example, the same small scale reaction of 1,3-diene **12a** with two equivalents of S_{10}, the second equivalent being added after 2 hours of reaction, showed an average of 86% combined yield of **13a** and **35** over 5 reactions after 2.5 hours overall reaction time. Despite the addition of a second equivalent of S_{10}, the ratios **13a/35** stayed constant around 6-7:1 in favor of disulfide **13a**, thus further showing that the formation of disulfide **13a** and tetrasulfide **35** results from two separate processes. Figure 40 summarizes these experiments.



12a **13a** **6-7:1** **35**

86%

Figure 40. Reaction of 2,3-Diphenyl-1,3-butadiene with 2 Equivalents of S_{10}

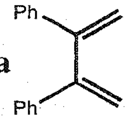
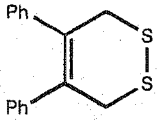
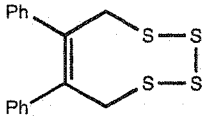
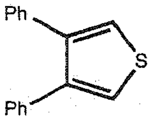
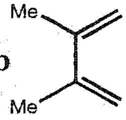
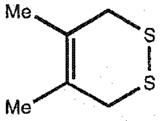
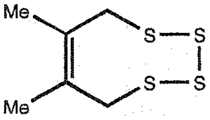
These mixtures of disulfide **13a** and tetrasulfide **35** can then be efficiently converted to yield only disulfide adduct **13a** by the use of triphenylphosphine (PPh_3) to convert **35** to **13a**.[91,137,163] A major inconvenience of this reaction was the presence in the trapping reaction mixtures of large quantities of S_8, which also reacts with PPh_3. It was found that in order to avoid the use of excess PPh_3, extraction of the products and residual diene could be achieved by trituration in methanol, which is a poor solvent for S_8. Conversion of tetrasulfide **35** to disulfide **13a** was achieved in the course of this work with 85% efficiency on isolated mixtures of the two adducts and is described in the Experimental.

Having optimized the model reaction, efforts were then concentrated on scaling up this reaction in order to fully isolate the products. Other substrates were also used in order to enlarge the scope of the trapping reactions with S_{10}.

2.3.2. Reaction of S_{10} with other 1,3-Dienes and Scale-up

Once fully optimized, the model reaction was scaled-up (10x). This was done in order to check that the methodology developed would be applicable to larger quantities and would thus provide an easy access to the resulting heterocycles. The scale of the reaction was still quite low as it only involved 1.0 mmol of the diene and 1.0 mmol of S_{10}. This scale was however sufficient to get reproducible isolated yields and this sulfuration reaction was extended to other substrates.

The results of the isolation of the products for the reaction of S_{10} with 2,3-diphenyl-1,3-butadiene (**12a**) as well as with 2,3-dimethyl-1,3-butadiene (**12b**) are reported in Table 8.[167]

1,3-Diene		Conditions (hr)	Product Yield
12a		2[a]	 **13a**, 38%  **35**, 4%  **37**, 3%
12b		3[b]	 **13b**, 36%  **36**, 6%

[a] Solvent: xylenes/CS_2; temperature maintained at 120°C by an oil bath.
[b] Solvent: toluene/CS_2; temperature *ca.* 100°C (heating mantle).

Table 8. Isolated Product Yields for the Reaction of S_{10} with 1,3-Dienes **12a** and **12b**

Scaling up the reaction between S_{10} and 2,3-diphenyl 1,3-butadiene (**12a**) was not straightforward and the reaction conditions had to be readjusted in order for the reaction to proceed in a moderate 45% isolated yield. Indeed, large scale reaction yields estimated by ^{1}H-NMR of the crude mixture and then confirmed by isolation, initially amounted to less than 20% in either chlorobenzene or toluene. The reasons for such a difference between small scale reaction and large scale reaction were carefully investigated but remained uncontrolled. The dilution of the model reaction had been carefully examined in the small scale case and appeared fully optimized.

Nevertheless, it was discovered that on a larger scale, the best results could only be obtained in a medium four times more concentrated when xylenes were used as a solvent and kept at 120°C with an oil bath (see Experimental). Under these new conditions, ^{1}H-NMR analysis of large scale crude reaction mixtures after two hours showed average

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[167] Lesté-Lasserre, P. and Harpp, D. N. *Tetrahedron Lett.*, **1999**, *40*, 7961.

yields of 50% for disulfide **13a** and tetrasulfide **35**. These ^{1}H-NMR yields tend however to be slightly overestimated without internal standard, as they are calculated from the integral values of **13a**, **35** and leftover diene **12a**. From these crude reaction mixtures, disulfide **13a** and tetrasulfide **35** were isolated as a mixture in a reproducible manner in 42% yield and identified by NMR comparison with authentic samples. Separation by column chromatography also afforded 3,4-diphenylthiophene (**37**) in 3% yield. Compound **37** had not been detected in the small scale experiments and was identified from its NMR and MS data (see Experimental).[168] This compound has already been reported as a decomposition product of disulfide adduct **13a**.[169] A loss of hydrogen sulfide gas H_2S from disulfide **13a** very likely occurred under the experimental conditions. The result is the aromatization of **13a** to thiophene **37**.

Prior to being scaled up in xylenes, the reaction between 1,3-diene **12a** and S_{10} was mainly studied under these new experimental conditions. Combined yields for **13a** and **35**, measured with 9-methylanthracene as internal standard, averaged 58% over 11 reactions after 2 hours at 120°C as shown in Figure 41. These yields were slightly lower than the optimum ones observed for this reaction in chlorobenzene (*vide supra*, *ca.* 70% in 2 hours for **13a+35**, see Figure 38). Isolated yields obtained from the same reaction on a larger scale thus remained quite moderate with only 45% overall yield. This discrepancy between small and large scale reaction was only observed for this specific substrate. As it will be discussed further, the reaction of S_{10} with 2,3-dimethyl-1,3-butadiene (**12b**) revealed some differences, that could be easily explained, while reaction with norbornene, for example, gave almost identical results in both small and large scale.

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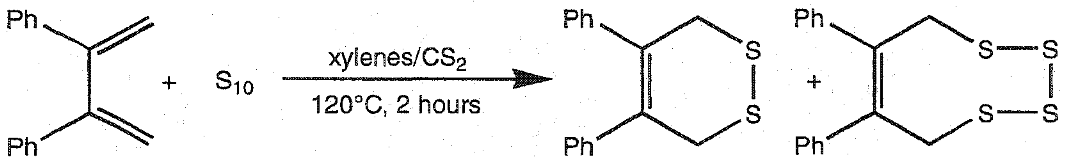
[168] Grunwell, J. R.; Foerst, D. L. and Sanders, M. J. *J. Org. Chem.*, **1977**, *42*, 1142.

[169] a) Ando, W.; Sonobe, H. and Akasaka, T. *Tetrahedron Lett.*, **1987**, *28*, 6653. b) Ando, W.; Sonobe, H. and Akasaka, T. *Tetrahedron*, **1990**, *46*, 5093.



12a **13a** **9:1** **35**

58%

Figure 41. Small Scale Reaction of S_{10} with 2,3-Diphenyl-1,3-butadiene in Xylenes

The ratio **13a/35** stayed constant upon scaling up and oscillated around 9:1 (Figure 41 and Table 8). The formation of disulfide adduct **13a** over tetrasulfide adduct **35** was thus even more favored with these new experimental conditions.

As a reminder, ratios **13a/35** of 6-7:1 were observed in the model reaction in refluxing chlorobenzene, toluene or benzene. These ratios were calculated from the integration values of the peaks corresponding to the methylene protons adjacent to sulfur for each molecule. The deshielding of these methylene protons varies depending on the number of adjacent sulfur atoms. This phenomenon allows, for example, a clean distinction of all the components of linear di-alkyl polysulfide mixtures.[170] Similar observations have been made in cyclic cases.[171] The deshielding effect of the sulfur atoms on adjacent protons is, however, not directly proportional to the number of sulfur atoms in the chain and decreases as the size of the sulfur chain increases. Similar behavior is also observed in ^{13}C-NMR spectra. It is important to note that in the course of this study, disulfide **13a** and tetrasulfide **35** were isolated as mixtures. Although separation conditions by chromatography are known, they usually lead to large numbers of mixed fractions thus lowering the isolated yields; polysulfide mixtures are well-known to be difficult to separate.

The optimized conditions found for the model reaction were also applied to the reaction between 2,3-dimethyl-1,3-butadiene **12b** and S_{10}. The corresponding 4,5-dimethyl-3,6-dihydro-1,2-dithiin (**13b**) and 6,7-dimethyl-5,8-dihydro-1,2,3,4-tetrathiin

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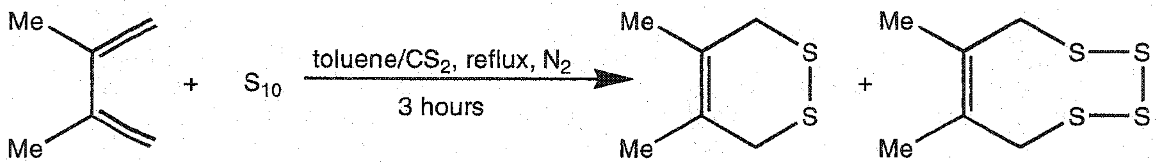
[170] Derbesy, G. Ph.D. Thesis, McGill University, **1994**.

[171] Kustos, M. and Steudel, R. *J. Org. Chem.*, **1995**, *60*, 8056.

(**36**) adducts were identified as reaction products with a combined 58% yield as shown in Figure 42.



12b **13b**, 51% **36**, 7%

Figure 42. Small Scale Reaction of S_{10} with 2,3-Dimethyl-1,3-butadiene

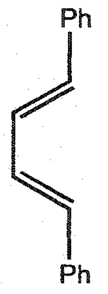
Both products were once again identified by NMR comparison with authentic samples and the yields were estimated with the use of 9-methylanthracene as an internal standard.

This reaction between **12b** and S_{10} was in turn scaled-up, which allowed isolation of both products as a mixture. The experimental conditions used in the large scale reaction were directly adapted from the small scale case. As shown in Table 8, disulfide **13b** and tetrasulfide **36** were isolated with a moderate overall (42%) yield. Isolated yields were thus slightly lower than the ones observed in the small scale version of the reaction, which could in part be explained by losses of products during the isolation process. However, contrary to the reaction between **12a** and S_{10}, this reaction did not decrease as much in yield upon scaling-up and did not need a change in experimental conditions.

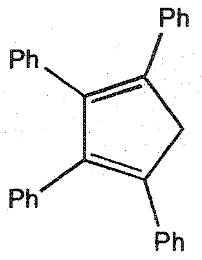
The ratio **13b/36** was determined by integral comparison of the isolated mixture ^{1}H-NMR spectrum. The change in reaction scale did not seem to affect the product ratio **13b/36**, which stayed reasonably steady around 6-7:1. No thiophene was isolated or detected in this experiment.

Lower temperatures were chosen for this reaction because of the volatility of diene **12b**, which has already been interpreted as a cause of decreased yields when high temperature conditions were applied in trapping experiments.[163]

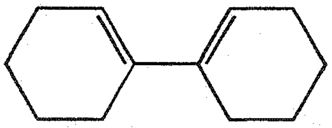
Other available 1,3-dienes were used as possible substrates for sulfuration with S_{10}. Some dienes such as **38** and **39** turned out to be completely unreactive towards S_{10} under these conditions. Reaction with 1,3-diene **40** produced a complex mixture that could not be resolved. It is however important to note that the starting material **40** was recovered as the main component of the mixture and that disulfide **41** was not detected. Disulfide **41** has been obtained in the past as the only product of trapping reactions involving likely diatomic sulfur producing processes.[81c,82,86,169,172]



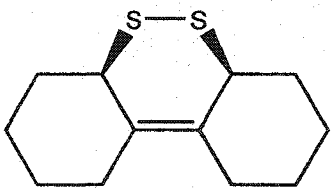
38



39



40

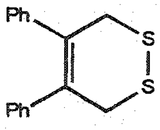
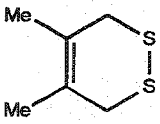
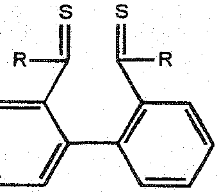
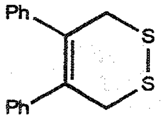
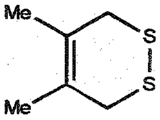
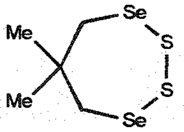
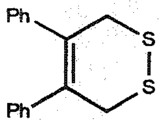
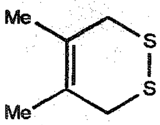
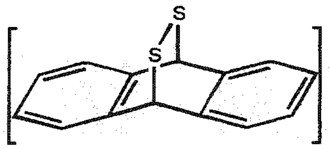
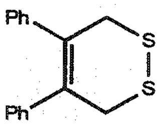
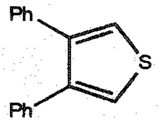
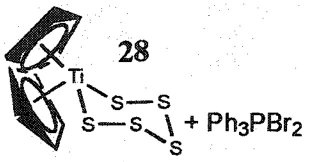
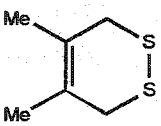
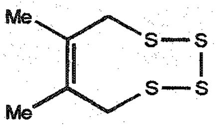


41

2.3.3. Discussion

In view of the results from the reaction of S_{10} with 1,3-dienes, a few points of discussion can be raised. Differences as well as common characteristics with sulfuration methods of 1,3-dienes by either diatomic sulfur S_2 or elemental sulfur S_8 will thus be addressed in this Section.

As a starting point for a comparison between different methods of sulfuration, Table 9 presents a chronological summary of the main diatomic sulfur precursors that have been designed over the years. Only the methods that are likely to have produced diatomic sulfur by trapping reaction are reported in Table 9. The sulfuration efficiency of almost all these methods has been tested towards either 2,3-diphenyl-1,3-butadiene **12a** or 2,3-dimethyl-1,3-butadiene **12b**. Depending on the data available, the best yields of trapped products as well as the experimental conditions for one or both 1,3-dienes are reported.

S_2 Precursor	Conditions (°C)	Products Yield[a]	Ref.
$R_3MSSSMR_3 + Ph_3PBr_2$ M=Si, Ge; R=C_6H_5, C_6H_{11}, *p*-C_6H_4Me	25	 **13a**, 20% (42%)[b]	82
	25	 **13b**, 35%	82
14  R=C_6H_5, *p*-C_6H_4OMe	80-110	 **13a**, 85%	86
	80-110	 **13b**, 60%	86
	130	 **13a**, 54%	172
	130[c]	 **13b**, 48%	172
	55[c]	  **13a**, 25% **37**, 40%	169
28  + Ph_3PBr_2	25	  **13b**, 21% **36**, 31%	173

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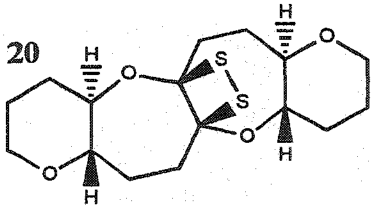
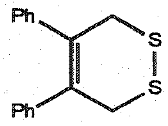
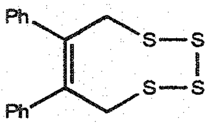
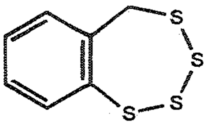
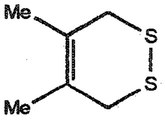
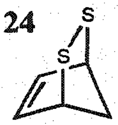
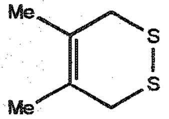
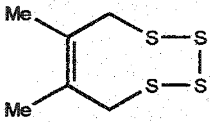
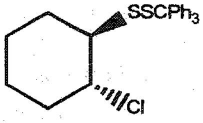
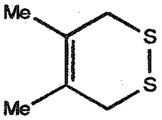
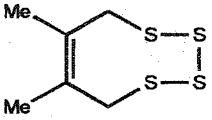
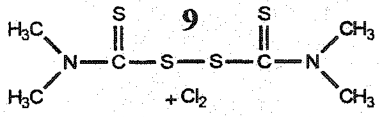
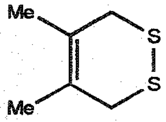
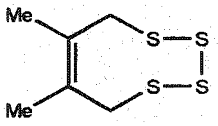
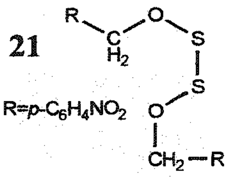
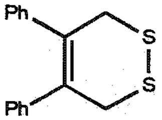
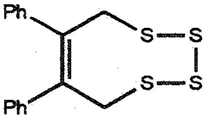
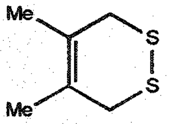
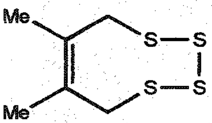
[172] Schmidt, M. and Görl, U. *Angew. Chem. Int. Ed. Engl.*, **1987**, *26*, 887.
[173] Harpp, D. N. and MacDonald, J. G. *J. Org. Chem.*, **1988**, *53*, 3812.

20 	100^c	  **13a**, 25% **35**, 28%	90
	150^c	 **13b**, 50%	174
24 	150-160^c	  **13b**, low yield **36**, detected^b	94
	77	  **13b**, detected^b **36**, 35%	92a,175
9 	60^c	  **13b**, 8% **36**, 33%	176
21 	130	  **13a**, 13% (26%)^b **35**, 28% (30%)^b	91
	100^c	  **13b**, 28% (31%)^b **36**, 17% (19%)^b	91

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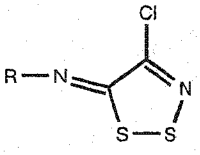
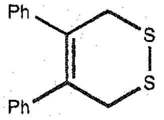
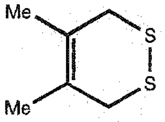
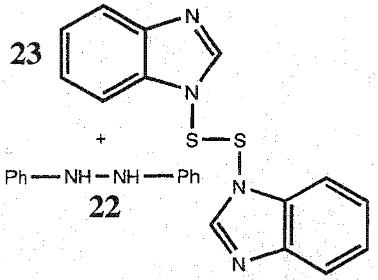
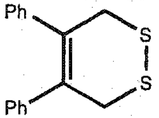
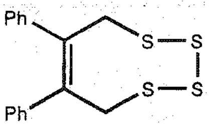
[174] Sato, R.; Satoh, S. and Saito, M. *Chem. Lett.*, **1990**, 139.

[175] a) Abu-Yousef, I. A. and Harpp, D. N. *Tetrahedron Lett.*, **1993**, *34*, 4289. b) Abu-Yousef, I. A. and Harpp, D. N. *Tetrahedron Lett.*, **1994**, *35*, 7167.

[176] Chew, W. and Harpp, D. N. *Sulfur Lett.*, **1993**, *16*, 19.

 R=Ar, Me	140-150^c	 **13a**, 29%	177
	140-150^c	 **13b**, 19%	177
 **23** + **22**	77	 **13a**, 9%^{b}  **35**, 8%^{b}	92b

^{a} Unless mentioned, yields are all isolated and based on 1 equivalent of S_2 precursor. ^{b} By ^{1}H-NMR. ^{c} Olefin was used in excess.

Table 9. Diatomic Sulfur Precursors: Reaction with 1,3-Dienes **12a** and/or **12b**

Other claims of diatomic sulfur involvement in the decomposition of some reagents have been made.[178] However, the decomposition pathway of these compounds remains, for the most part, quite obscure; the proposed mechanisms for the production of diatomic sulfur were not conclusively supported by trapping reactions.

Of the 13 diatomic sulfur precursors reported, six of them show overall isolated yields of trapping products lower than 40% with 1,3-dienes **12a** and **12b**; while another six reagents show a 40% to 60% conversion range. The dithione methodology

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[177] a) Rakitin, O. A.; Rees, C. W. and Vlasova, O. G. *Tetrahedron Lett.*, **1996**, *37*, 4589. b) English, R. F.; Rakitin, O. A.; Rees, C. W. and Vlasova, O. G. *J. Chem. Soc., Perkin Trans. 1*, **1997**, 201. c) Konstantinova, L. S.; Rakitin, O. A.; Rees, C. W.; Sivadasan, S. and Torroba, T. *Tetrahedron*, **1998**, *54*, 9639.

[178] a) Jahn, R. and Schmidt, U. *Chem. Ber.*, **1975**, *108*, 630. b) Orahovatz, A.; Levinson, M. I.; Carroll, P. J.; Lakshmikanthan, M. V. and Cava, M. P. *J. Org. Chem.*, **1985**, *50*, 1550. c) Chenard, B. L.; Harlow, R. L.; Johnson, A. L. and Vladuchick, S. A. *J. Am. Chem. Soc.*, **1985**, *107*, 3871. d) Ando, W.; Kumamoto, Y. and Tokitoh, N. *Tetrahedron Lett.*, **1987**, *28*, 4833.

investigated by Steliou and co-workers seems to be the only one that provides sulfuration rates consistently higher than 60% when a maximum of 1 equivalent of diatomic sulfur precursor *vs.* 1,3-diene is used.[179] A record 85% conversion of 2,3-diphenyl-1,3-butadiene is even reported by Steliou.[86] In view of Table 9, S_{10} trapping reactions with equimolar amounts of 1,3-dienes, despite their moderate isolated yields, compete quite well with most of the results obtained with diatomic sulfur reagents.

Moreover, it is also worth comparing the results obtained when excess sulfurating agent is used. The dialkoxydisulfide method, for example, shows a maximum 85% ^{1}H-NMR yield of disulfide **13a** and tetrasulfide **35** when 5 equimolar amounts of sulfurating agent are used.[91] In the case of 2,3-dimethyl-1,3-butadiene, yields up to 84% have been observed.[91] In comparison, ^{1}H-NMR yields of 86% (Figure 40) for the sulfuration of 2,3-diphenyl-1,3-butadiene with 2 equivalents of S_{10} were also obtained, which further shows the potential of S_{10} as an effective sulfurating reagent. This comparison is, of course, only viable if it is assumed that S_{10} transfers two sulfur atoms like dialkoxydisulfide.

In terms of the identity of the products obtained in the sulfuration of 1,3-dienes with S_{10}, an obvious comparison can be made with the diatomic sulfur case. The same Diels-Alder like disulfide adduct **13a** or **13b** was obtained as the main product with 1,3-diene **12a** or **12b**, respectively.

Smaller amounts of tetrasulfide **35** or **36** have also been isolated. Interestingly, early reports on the reaction between diatomic sulfur and 1,3-dienes did not mention this compound as a product. Nicolaou first reported the X-ray structure of tetrasulfide **35**, which he isolated as a trapping product from the thermal decomposition of dithiatopazine in the presence of 2,3-diphenyl-1,3-butadiene.[90a] Harpp and Williams were the second ones to unambiguously identify the structure of this type of adduct. They isolated tetrasulfide **36** as a product of the reaction between triphenylmethanethiosulfenyl

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[179] Ando's method (ref. 169) also provided an overall 65% conversion of 1,3-diene **12a**, but compound **37** was proven to be a decomposition product of the expected trapping product **13a**.

chloride (**38**) and 2,3-dimethyl-1,3-butadiene.[180] They found that a first molecule of sulfenyl chloride **38** can add across diene **12b** at the 1,4-position to form adduct **39**. A stable triphenylmethyl cation is then eliminated, the remaining anion further reacts with another molecule of sulfenyl chloride and cycloelimination with loss of another triphenylmethyl cation yields tetrasulfide adduct **36** as shown in Figure 43. Adduct **36** clearly results in this case not from diatomic sulfur but from a 4-sulfur insertion.

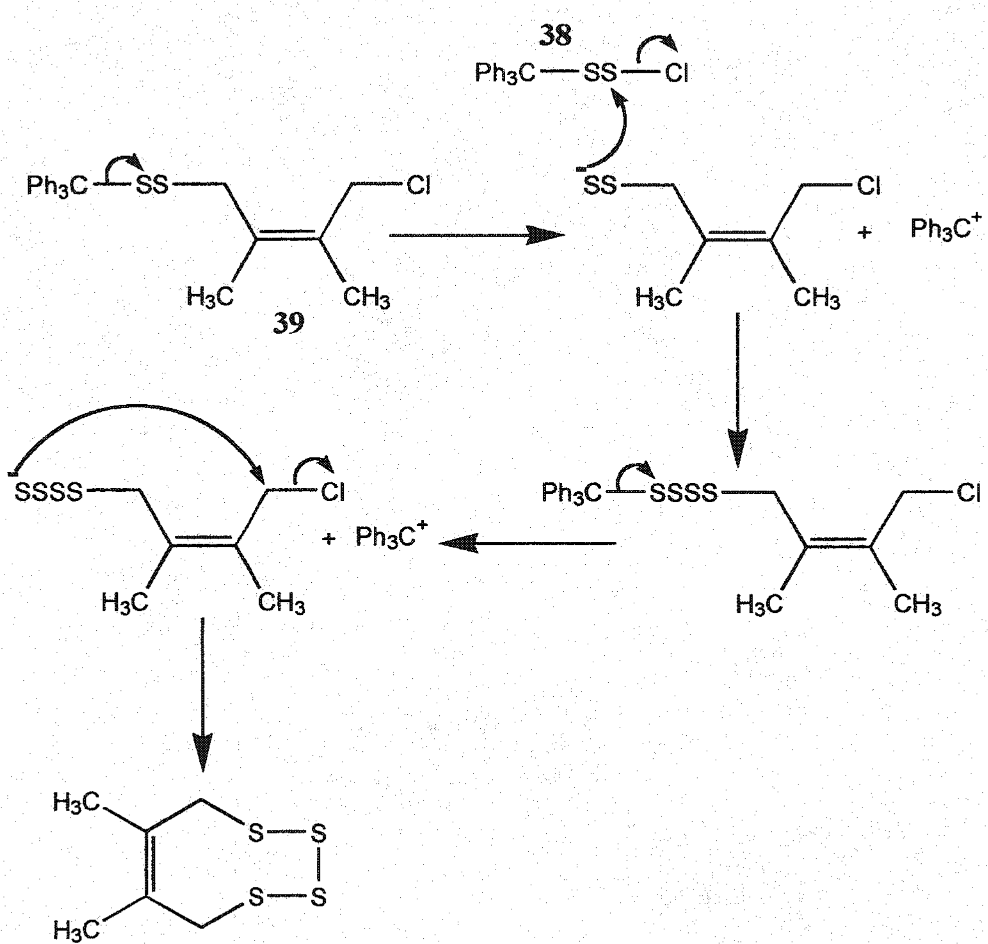

Figure 43. Parallel Synthesis of Tetrasulfide **36**

This parallel synthesis of tetrasulfide **36** allowed Harpp and co-workers to identify *a posteriori* this compound as a product of trapping reactions they carried out between titanocene pentasulfide **28** used as a diatomic sulfur precursor and 1,3-diene **12b**.[180] This

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

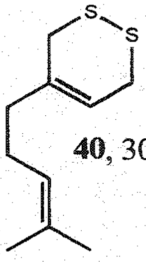
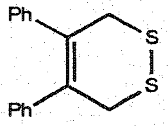
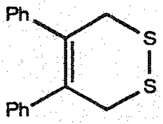
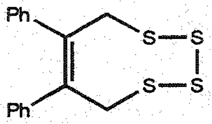
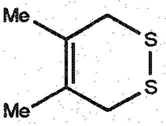
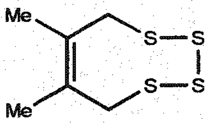
adduct had initially been assigned as a "polymer".[173] Gilchrist had also found traces of this "polymer" in his trapping reactions.[94]

Since then, all reported trapping reactions of diatomic sulfur with 1,3-dienes **12a** and **12b**, but one,[177] have identified a tetrasulfide adduct as an end product of the reaction. The presence of these tetrasulfide adducts has been explained and demonstrated. Harpp and Tardif showed that the tetrasulfide formation is a result of the insertion of an S_2 molecule into the sulfur-sulfur bond of the previously formed disulfide adduct, which serves as a competitive entity with regard to the diene.[91] The relative ratios of disulfide adduct *vs.* tetrasulfide adduct do not seem to obey to any determined law and seem to vary greatly from one precursor to another. While some authors reported ratios of *ca.* 1:1,[91] others noticed almost exclusively the formation of a tetrasulfide addduct.[92a,175,176]

The reactions between S_{10} and 1,3-dienes **12a** and **12b** showed the presence of tetrasulfide adducts **35** and **36** in small quantities in the trapping reaction mixtures (Table 8). In comparison to the most recent S_2 precursors, a quite unusually high ratio of disulfide *vs.* tetrasulfide, very much in favor of disulfide adducts **13a** and **13b**, was observed; 9.5:1 and 6:1 respectively. Moreover, as reported in the control reaction, the reaction between S_{10} and disulfide adduct **13a** did not yield any significant amount of tetrasulfide adduct **35**, as could have been expected from a diatomic sulfur precursor.

Without being fully conclusive, these first comparisons tend to indicate that S_{10} might behave very differently from a true diatomic sulfur precursor in 1,3-dienes sulfuration processes. Mechanistic aspects will be further discussed in Chapter 4.

A comparison with the sulfuration methods of 1,3-dienes by elemental sulfur S_8 will now be addressed. Table 10 shows a brief overview of the main methods developed.

Sulfuration Method	Conditions (°C)	Product Yield[a]	Ref.
S_8 DMF/Pyridine/NH_3	100-105	 **40**, 30%	181
S_8 DMF/Pyridine/NH_3	110	 **13a**, 69%	182
S_8/DMSO	125	 **13a**, 4.1[b]  **35**, 1[b] 80%[c]	163
S_8/NaH/Phase Transfer Catalyst	110	 **13b**, 45%  **36**, 7%[d]	183

[a] Isolated yield. [b] Ratio disulfide/tetrasulfide. [c] Isolated yield of disulfide after treatment of the mixture with triphenylphosphine. [d] Estimated by HPLC and ^1H-NMR.

Table 10. Sulfuration of 1,3-Dienes with S_8

The reactions of Table 10 all present a similar characteristic as they were carried out either in the presence of a strong base, in amine or very polar solvents. Elemental sulfur

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[181] Elvidge, J. A.; Jones, S. P. and Peppard, T. L. *J. Chem. Soc., Perkin Trans. 1*, **1982**, 1089.

[182] Fulcher, B. C.; Hunter, M. L. and Welker, M. E. *Synth. Commun.*, **1993**, *23*, 217.

[183] Okuma, K.; Kuge, S.; Koga, Y.; Shioji, K.; Wakita, H. and Machiguchi, T. *Heterocycles*, **1998**, *48*, 1519.

(S_8) used under these conditions is usually referred to as "activated" sulfur.[181,184] Mechanistic studies suggest solvent participation into these sulfuration processes.[185] Harpp and Rys proposed a mechanism that directly implicates very polar solvents such as dimethyl sulfoxide (DMSO) into the opening of the sulfur ring as shown in Figure 44.[163] The two main products **13a** and **35** of this reaction are the same as the ones isolated in the reaction between diatomic sulfur and 1,3-diene **12a**. Other polysulfide species **41** have also been observed in this sulfuration process, which does not exclude the participation of discrete S_x (x=2, 3, 4 or 5) units in this type of reaction.

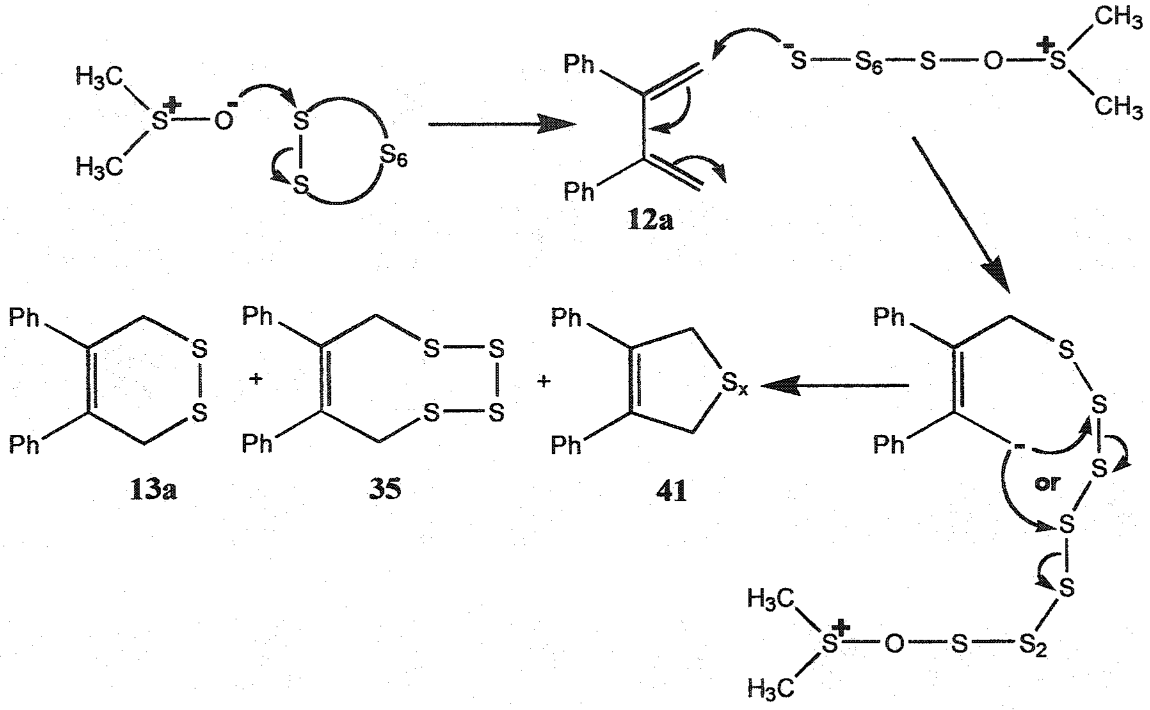

Figure 44. Mechanism for the Sulfuration of 1,3-Diene **12a** with S_8 in DMSO

The last entry of Table 10 reports the work of Okuma and co-workers.[183] Despite the claim made by the authors that their method allowed the generation of diatomic sulfur S_2 from elemental sulfur S_8, it appears more appropriate to classify this method into the

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[184] a) Shields, T. C. and Kurtz, A. N. *J. Am. Chem. Soc.*, **1969**, *91*, 5415. b) Chiacchio, U.; Corsaro, A.; Rescifina, A.; Testa, M. G. and Purrello, G. *Heterocycles*, **1993**, *36(2)*, 223. c) Chiacchio, U.; Corsaro, A.; Pistara, V.; Purrello, G. and Rescifina, A. *Heterocycles* **1998**, *48(1)*, 41.

ones of "activated" sulfur. Indeed, catalytic amounts of a strong base (NaH) are used in this process, in clear contradiction with likely demonstrated diatomic sulfur generation methods.

For most of the examples shown in Table 10, disulfide and tetrasulfide adducts are obtained as sulfuration products. Yields vary from moderate (30%) to good (80%). Ratios of disulfide/tetrasulfide adduct (3.5:1 to 6:1) vary from one method to another within a more consistent range compared to the results obtained with diatomic sulfur precursors. Another noticeable aspect of these sulfuration methods is the fact that apart from Okuma's methodology, they all make use of one or less molar equivalent of elemental sulfur compared to the diene.

In comparison with the methods reported in Table 8, S_{10} sulfuration of 1,3-dienes seems slightly less effective, as isolated yields obtained with **12a** and **13a** are lower. The same disulfide and tetrasulfide adducts have been identified as products by both S_{10} and S_8 sulfuration methods, at least if comparison is made with the most recent examples of S_8 sulfuration.[163,183] An important similarity between both methods lies on the enhanced selectivity of disulfide adduct formation *vs.* tetrasulfide adduct.

As opposed to diatomic sulfur chemistry,[81c] disulfide adducts do not seem to compete with the parent 1,3-diene for sulfuration, thus explaining this improved selectivity. S_{10} appears even more as a true 2-sulfur atom donor as ratios of disulfide adduct/tetrasulfide adduct are the highest of the three methods.

Finally, S_{10} sulfuration of 1,3-dienes completely differs from S_8 sulfuration reactions in terms of their behavior towards nucleophiles or bases. S_{10} does not support any kind of "activation" and the presence of even traces of a base almost completely quenches any sulfuration process, as opposed to what is required for S_8 sulfuration methods to proceed in good yield.

As with comparisons made with diatomic sulfur precursors, S_{10} also seems to behave quite differently from elemental sulfur S_8 in sulfuration reactions of 1,3-dienes. Mechanistic aspects will be further discussed in Chapter 4.

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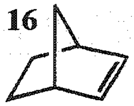
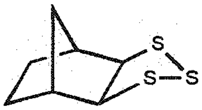
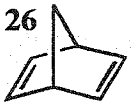
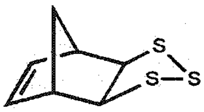
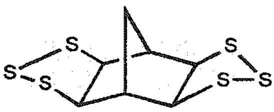
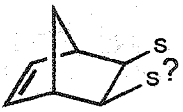
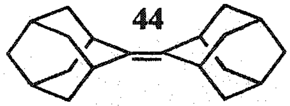
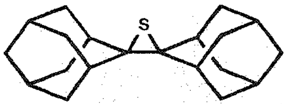
[185] Davis, R. E. and Nakshbendi, H. F. *J. Am. Chem. Soc.*, **1962**, *84*, 2085.

2.4. Reaction of S_{10} with Alkenes

2.4.1. Results

The study of the reactivity of S_{10} has also been extended to simple alkenes. The conditions for these reactions are similar to the optimized conditions that were used for reactions with 1,3-dienes. Details of the experimental protocol can be found in the Experimental Section.

Alkene	Conditions (hr)	Product Yield[a]
16 	3[b]	 **19**, 85%
26 	3[b]	 **27**, 59%  **42**, 17%  **43**, 6%[c]
44 	3[b]	 **45**, 40%

[a] Isolated yields. [b] Toluene/CS_2; Temperature *ca.* 100°C (heating mantle). [c] Yield calculated from the molecular weight of the fragment.

Table 11. Isolated Product Yields for the Reaction of S_{10} with Alkenes **16**, **26** and **44**

Table 11 summarizes the results obtained with selected olefins that reacted with S_{10}.[167] Isolated yields of the products after extraction by column chromatography are reported. The compounds obtained during these sulfuration reactions were identified by standard spectroscopic techniques such as NMR and MS, and compared with authentic samples where possible. Spectroscopic data are summarized in Table 16, which can be found later in this Section. Compounds **42** and **43** were isolated during the sulfuration of norbornadiene and are worth mentioning as they are new molecules.

The experimental conditions for these sulfuration reactions were derived from the ones found for the small scale version of the model reaction discussed in previous Sections. It is important to note that the yield for trithiolane **19**, measured with 9-methylanthracene as internal standard, for the small scale reaction between norbornene and S_{10} amounted to 87% after three hours. This result thus shows that good sulfuration yields were obtained in both small and large scale reactions. It further validates the internal standard method used for yield calculation.

The structure of *bis*-sulfurated compound **42** was determined from its NMR, HRMS and combustion analysis data, which are reported in Table 16 as well as in the Experimental in Chapter 5. This solid material decomposes over a temperature range starting at 180°C; it is likely that polymerization takes place. A very pale yellow single crystal of suitable quality for X-ray analysis was obtained after a few weeks from the oily mixture that was collected after an unsuccessful column chromatography intended to separate compounds **27**, **42** and **43**. X-ray analysis showed that the crystal was compound **42**, for which an ORTEP drawing is presented in Figure 45. Selected bond lengths, bond angles and torsion angles are reported in Table 12. The crystal cell setting is monoclinic and belongs to the P2(1)/c space group. Despite obvious symmetry present in the thermal ellipsoid plot, the molecule contains no crystallographic symmetry. Further details on the X-ray crystallography data are given in the Appendix. *Bis*-sulfurated compound **42** is called *exo*-3,4,5-*exo*-9,10,11-hexathiatetracyclo[5.5.1.$0^{2,6}$.$0^{8,12}$]tridecane.

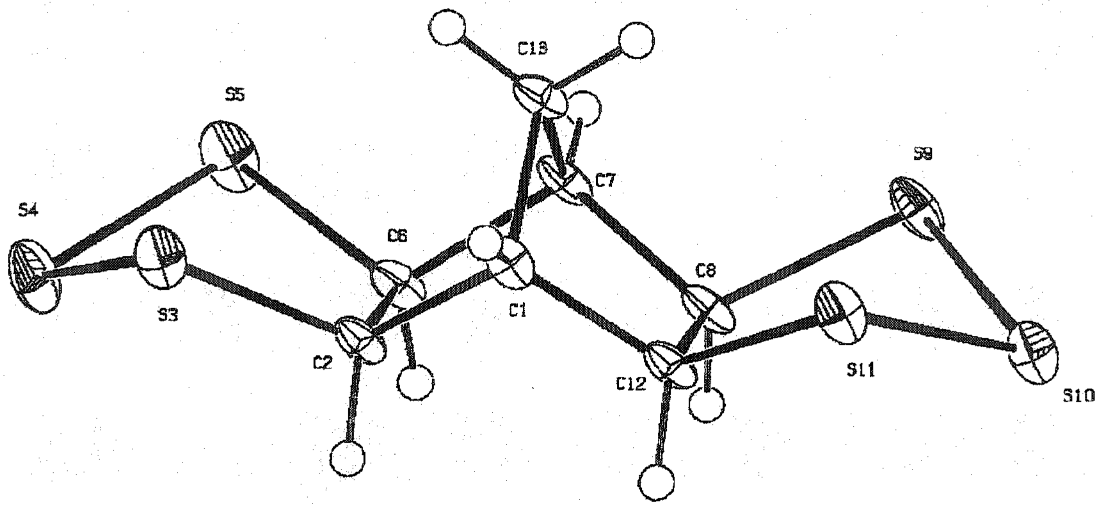
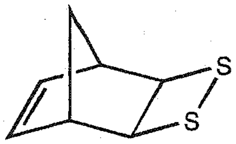


Figure 45. Ortep Drawing of *bis*-Sulfurated Compound **42**

Bond lengths (Å)			
S3-C2	1.825	S3-S4	2.0443
S4-S5	2.0561	S5-C6	1.825
S9-C8	1.831	S9-S10	2.0561
S10-S11	2.0483	S11-C12	1.830
Bond angles (deg)			
C2-S3-S4	94.36	S3-S4-S5	93.76
C6-S5-S4	94.83	C8-S9-S10	95.35
S11-S10-S9	93.28	C12-S11-S10	94.66
C6-C2-S3	113.3	C1-C2-S3	109.4
C2-C6-S5	112.7	C7-C6-S5	111.0
C12-C8-S9	112.1	C7-C8-S9	110.4
C8-C12-S11	113.4	C1-C12-S11	109.8
Torsion angles (deg)			
C2-S3-S4-S5	-49.05	S3-S4-S5-C6	48.51
C8-S9-S10-S11	-48.81	S9-S10-S11-C12	48.82
S4-S3-C2-C1	149.7	S4-S3-C2-C6	35.3
S3-C2-C6-C7	117.6	C1-C2-C6-S5	-119.8
S3-C2-C6-S5	-1.7	S4-S5-C6-C7	-146.8
S4-S5-C6-C2	-32.6	S10-S9-C8-C7	147.5
S10-S9-C8-C12	33.3	S9-C8-C12-C1	119.3
C7-C8-C12-S11	-117.7	S9-C8-C12-S11	0.9
S10-S11-C12-C1	-149.0	S10-S11-C12-C8	-34.8

Table 12. Selected Structural Parameters for *bis*-Sulfurated Compound **42**

Compound **43** was also isolated as a third product from the sulfuration reaction of norbornadiene with S_{10}. The interpretation of the different spectroscopic data led to the conclusion, with *quasi* certainty, that compound **43** contains the fragment shown in Table 11. Efforts devoted towards the formation of a single crystal of **43** remain unsuccessful. Compound **43** melts sharply at 87-89°C. All spectroscopic information are reported in Chapter 5 and Table 16. Speculations that compound **43** could actually be 1,2-dithietane **43b** have led us to investigate a possible parallel synthesis. This will be developed further at the end of this Section.

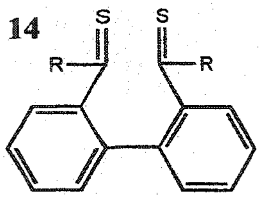
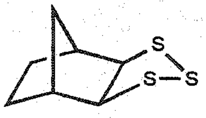
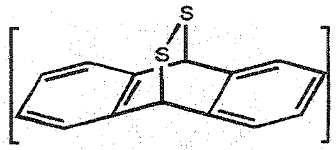
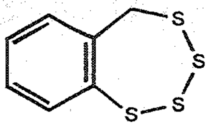
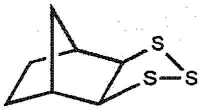
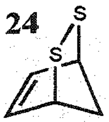
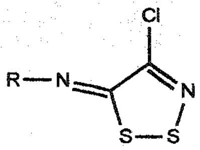
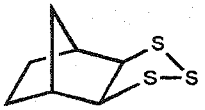


43b

2.4.2. Discussion

Of the three substrates **16**, **26** and **44** reacted with S_{10} in this part of the study, norbornene (**16**) is the one that has been the most widely used in sulfuration reactions. Similar to the 1,3-dienes, the reaction of S_{10} with **16** will thus be compared to the existing methodologies, which here as well can be divided into two main groups. The first group involves the trapping reactions of diatomic sulfur S_2 with norbornene, while the second group of reactions relates to sulfuration reactions of norbornene with elemental sulfur S_8 as the source of sulfur atoms.

Of the known diatomic sulfur precursors reported in Table 9, only some of them have been reacted with norbornene. These reactions are reported in Table 13.

S_2 Precursor	Conditions (°C)	Product Yield[a]	Ref.
14  R=C_6H_5, p-C_6H_4OMe	80-110	 **19**, 88%	84, 86
	55	No adduct	169a
	150[b]	 **19**, 89%	174
24 	150-160[b]	 **19**, 61%	94
 R=Ar, Me	140-150[b]	 **19**, 62-78%	177

[a] Yields are all isolated and based on 1 equivalent of S_2 precursor. [b] Olefin was used in excess.

Table 13. Diatomic Sulfur Precursors: Reaction with Norbornene

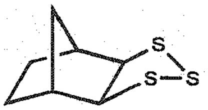
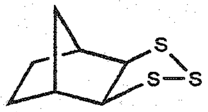
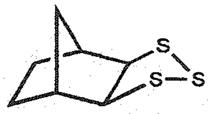
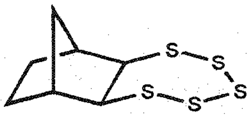
Some obvious common trends emerge between the different trapping experiments of diatomic sulfur with norbornene. Trithiolane **19** has in all cases but one[169] been isolated as the unique product of these trapping reactions. The isolated yields for **19** vary from good to very good, the best yields (88-89%) being obtained with Sato's tetrasulfide precursor[174] and Steliou's dithione methodology.[84,86] Steliou was the first to propose a mechanism explaining the formation of **19**.[84] The 1,2-dithietane **17** and the branch-bonded sulfur species **18** were proposed as intermediates of the trapping reaction as was shown in Chapter 1 (Figure 13).

One last common trend between all these trapping reactions of diatomic sulfur with norbornene is the temperature at which such reactions occur. These reactions proceed well only at quite high temperatures (above 100°C). This could be the reason why the method developed by Ando and co-workers did not yield any trapping product with norbornene (Table 13).[169] The temperature in their experiment was only 55°C, which appeared to be enough for a reaction to take place with 1,3-dienes but not with such strained olefins. Similarly, the first diatomic sulfur generation method developed by Steliou worked well at room temperature with 1,3-dienes but never showed any trace of trapping with simple olefins.[82]

At first glance, the reaction between norbornene and S_{10} compares quite well with these reactions. The same diatomic sulfur-like adduct trithiolane **19** was obtained in high reproducible yields (85%) as the unique product. In terms of reaction temperature, the reaction with S_{10} and norbornene proceeds optimally under relatively mild conditions (*ca.* 100°C). The behavior of S_{10} with norbornene thus appears to be, at least from an end result point-of-view, more closely related to that of diatomic sulfur precursors, in contrast to what was observed with 1,3-dienes.

In order to complete the discussion on trithiolane **19**, a comparison between the S_{10} reaction with norbornene and the second group of reactions, which relates to sulfuration methods with elemental sulfur S_8, will be addressed.

This second group of reactions refers to the commonly called "activated" sulfur-type reactions. As it was explained in the case of sulfuration reactions of 1,3-dienes with S_8, the latter first reacts with a strong base and/or a very polar solvent, wherein the breaking of S-S bonds appears reasonable, before the generated "active" polysulfur fragments react with the olefin. Table 14 gives a chronological overview of these methods as they have been reported in the literature.

Sulfuration Method	Conditions (°C)	Product Yield[a]	Ref.
S_8 DMF/NH_3	110	 **19**, 86%	184a
S_8 DMF/Pyridine/NH_3	110	 **19**, 35%	186
S_8 DMF or DMSO	100	  **19** 3:1[b] **46** 40%[c]	187

[a] All yields are isolated. [b] Ratio **19**/**46**. [c] Combined yield **19** + **46**.

Table 14. Sulfuration of Norbornene with S_8

All the reactions shown in Table 14 report trithiolane **19** as their main product. Trithiolane **19** was actually prepared and identified for the first time by Shields and Kurtz.[184a,188] The yields reported vary greatly, from moderate to very good. It is interesting to note that, similar to 1,3-dienes sulfuration, sulfur was not used in excess in these reactions. Other reactions involving elemental sulfur,[189] or reagents being able to deliver activated sulfur species,[93,190] have shown to produce trithiolane **19**.

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[186] Emsley, J.; Griffiths, D. W. and Jane, G. J. J. *J. Chem. Soc., Perkin Trans. 1*, **1979**, 228.

[187] Bartlett, P. D. and Ghosh, T. *J. Org. Chem.*, **1987**, *52*, 4937.

[188] The synthesis of trithiolane **19** has also appeared in a number of patents: a) Kurtz, A. N. and Shields, T. C., U.S. Patent 3586700 19710622, **1971**. b) Hay, A. S., U.S. Patent 4033982 19770705, **1977**. c) Dirlikov, S. K., U.S. Patent 4474970 A 19841002, **1984**.

[189] Inoue, S.; Tezuka, T. and Oae, S. *Phosphorus and Sulfur*, **1978**, *4*, 219.

[190] Matturro, M. G.; Reynolds, R. P.; Kastrup, R. V. and Pictroski, C. F. *J. Am. Chem. Soc.*, **1986**, *108*, 2775.

An important and new contribution to the norbornene sulfuration topic comes from the work of Bartlett and Ghosh. They found that *exo*-3,4,5,6,7-pentathiatricyclo[7.2.1.$0^{2,8}$]dodecane (**46**), which will be referred to as pentasulfide **46**, is a significant component of the sulfuration reaction of norbornene by S_8 in polar solvents.[187] The structure of pentasulfide **46** has been fully resolved by X-ray diffraction.[191] The experimental conditions used by these authors were slightly different from previous ones, as they did not use ammonia as an activator. However, the same authors obtained strong evidence for the production of such pentasulfides even in the presence of ammonia as they repeated Emsley's experiments.[187]

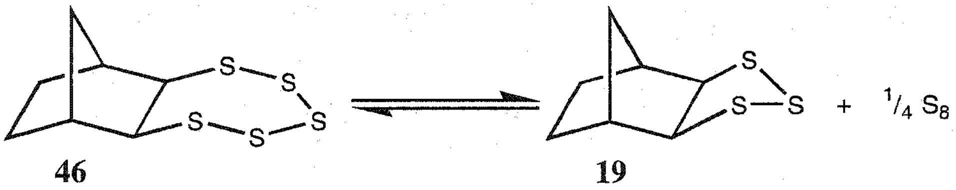

Figure 46. Equilibrium between Pentasulfide **46** and Trithiolane **19**

Further, Bartlett and Ghosh proved that an equilibrium exists between **46** and **19** under the experimental conditions that were used. This equilibrium is shown in Figure 46. Other related strained olefins have also been shown to produce pentasulfides as sulfuration products.[187]

The presence of such pentasulfides appears to be characteristic of S_8 addition to strained olefins under these conditions and these results contrast strongly with the ones obtained by S_2 chemistry. Similarly, the same remark is also true with regards to the S_{10} sulfuration of norbornene as no pentasulfide **46** was detected. The absence of pentasulfide adduct **46**, added to the fact that S_{10} does not survive the presence of an activator, enhances even more the emerging difference between S_{10} and S_8 chemistry.

Sulfuration reactions of norbornadiene are even more rare than those with norbornene. In this case as well, the same two methods of diatomic sulfur chemistry and elemental sulfur in polar solvents have been used.

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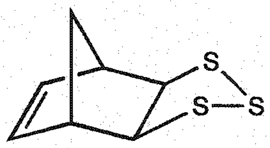
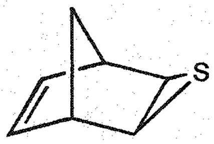
[191] Pickardt, J.; Kustos, M. and Steudel, R. *Acta Cryst.*, **1992**, *C48*, 190.

The groups of Steliou and Sato are the only ones who attempted to trap diatomic sulfur S_2 with norbornadiene. Steliou's dithione methodology with norbornene was used under similar conditions. *exo*-3,4,5-Trithiatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (**27**), which will be referred to as trithiolane **27**, was obtained as a unique product of the reaction in 75% isolated yield.[84,86] Similarly, Sato isolated trithiolane **27** as a unique product in a more modest (26%) isolated yield.[174] The behavior of norbornadiene towards diatomic sulfur thus seems to be identical to norbornene.

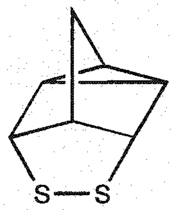
This contrasts sharply with the sulfuration experiments of norbornadiene with S_8 in polar solvents or in the presence of a base as activator. Emsley and co-workers first reported the reaction of elemental sulfur with norbornadiene. They found that in the presence of DMF, pyridine and ammonia, norbornadiene reacts with sulfur to give *exo*-2,3-epithionorborn-5-ene (**47**) in 19% yield.[186] Bartlett and Ghosh gave a more complete picture of this sulfuration reaction. In addition to episulfide **47**, they showed that trithiolane **27** as well as the more unexpected nortricyclene adducts **48** and **49**, and finally compound **50**, also formed.[187] The authors isolated and characterized each one of these compounds. Some of the spectroscopic data are reported in Table 16 at the end of this Chapter and in Table 21 in Chapter 3.



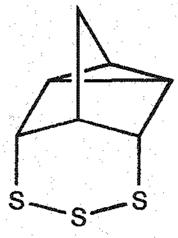
27



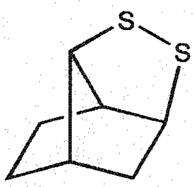
47



48



49



50

As shown earlier in Table 11, the reaction between norbornadiene and S_{10} generated trithiolane **27** as the main product in 59% isolated yield. No episulfide **47** or traces of compounds **48**, **49** and **50** were detected on the basis of the ^{1}H-NMR data of the crude reaction mixture. Two new compounds were, however, isolated from this reaction. The structure of one of them has been fully resolved, while the other one still remains unknown.

The new *bis*-sulfurated compound **42**, which was obtained in 17% isolated yield, has been fully identified and its structure solved by X-ray diffraction (Figure 45). The formation of this compound comes from the reaction of S_{10} on the free double bond of trithiolane **27**. This adduct was not observed previously either in reactions involving diatomic sulfur or elemental sulfur with norbornadiene. However, Bartlett and Ghosh isolated a similar *bis*-sulfurated compound. These authors showed that triene **51**, heated with excess S_8, gave **52** as the only product in 25% yield as summarized in Figure 47.[187]

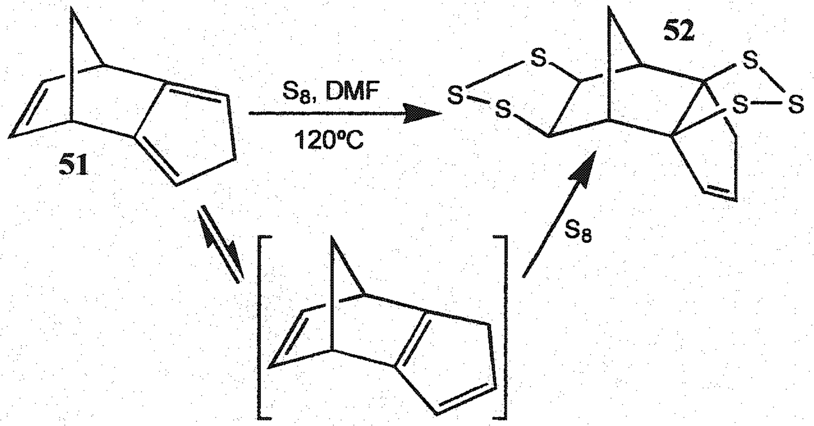
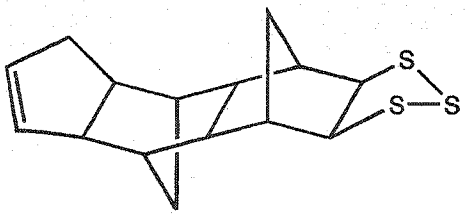


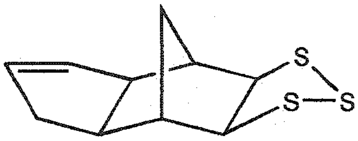
Figure 47. Sulfuration of Triene **51** with S_8

Bis-sulfurated adduct **52** was, however, not analyzed by X-ray crystallography. *Bis*-sulfurated compound **42** is thus the first compound of its kind for which an X-ray structure has been obtained.

X-ray structures for other trithiolanes having a norbornane framework have already been reported in the literature but remain quite rare. Compounds **53**[192] and **54**[193] are two examples.



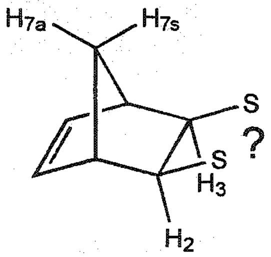
53



54

Similar to trithiolanes **53** and **54**, the two sets of three sulfur atoms of *bis*-sulfurated compound **42** are placed on the *exo* face of the norbornane framework. The two five-membered rings thus formed exhibit an envelope conformation. The sulfur atoms S4 and S10 (Figure 45) form the two flaps of the envelope. Both atoms are bent away from the methylene bridge of the norbornane with a 127.8° folding angle. This value compares well to the 123.4° and 126.4° found for **53** and **54** respectively.

The average S-S and C-S bond distances of 2.051 and 1.828 Å are also similar to the 2.045 and 1.830 Å found for **53**, or to the 2.047 and 1.836 Å for **54**. The interplanar angle of 118.7° between S3C2C6S5 and C1C2C6C7 is also very close to the 119.9° observed in **54**. This interplanar angle is actually the same on each side of **42**. Interestingly, the cyclopentene ring of **54** also exhibits the same orientation as its corresponding trisulfide unit. Finally, the average S-S-S angle of 93.5° in **42** barely differs from the 93.7° and 93.4° found for **53** and **54** respectively.



43

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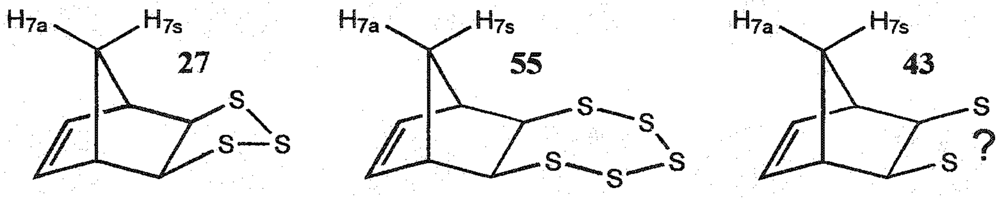
[192] Emsley, J.; Griffiths, D. W. and Osborn, R. *Acta Cryst.*, **1979**, *B35*, 2119.

The structure of compound **43** has, to date, not been fully determined. Its NMR data do not correspond to any of the adducts identified by Bartlett for the reaction of norbornadiene with S_8. The 4-line ^{13}C-NMR spectrum coupled with 5 absorptions in the ^{1}H-NMR spectrum resembles the NMR data of molecules of the type of episulfide **47** and trithiolane **27**. A triplet at 6.07 ppm in the ^{1}H-NMR spectrum and a signal at 135.48 ppm in the ^{13}C-NMR spectrum unambiguously show the presence of a free double bond on the norbornane framework. A 2.0 Hz W-coupling between the adjacent protons H_2, H_3 and the anti-proton H_{7a} of the methylene bridge indicates clearly the *exo* position of the two sulfur atoms attached to the norbornane skeleton. The chemical shift difference between syn-H_7 (H_{7s}) and anti-H_7 (H_{7a}) amounts to only 0.12 ppm, which could indicate a large number of sulfur atoms. Indeed, Bartlett and Ghosh showed that going from trithiolane **27** to its corresponding pentathiane **55**, a significant drop in chemical shift difference could be observed as shown in Figure 48.[194] This observation seems to be a common trend among structures of this type.



δH_{7s}	2.50	1.86	2.18
δH_{7a}	1.73	1.56	2.06
$\Delta\delta$	0.77	0.30	0.12

Figure 48. ^{1}H-NMR Chemical Shifts Comparison between Compounds **27**, **55** and **43**

This difference of only 0.12 ppm could suggest that a large sulfur ring with more than 5 sulfur atoms constitutes the unknown part of the structure for compound **43**. Larger sulfur rings bearing a norbornane framework, however, have never shown such a

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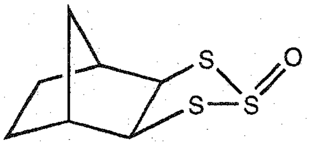
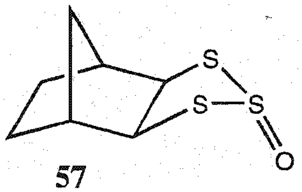
[193] Watson, W. H.; Jain, P. C.; Bartlett, P. D. and Ghosh, T. *Acta Cryst.*, **1986**, *C42*, 332.

[194] Ghosh, T., Ph.D. Thesis, Texas Christian University, **1986**.

small difference even in the heptathiane or octathiane cases studied by Steudel.[195] The chemical shifts for H_7 protons also appear to be quite deshielded in contrast to the trend observed for increasing sulfur ring size. Moreover, the low field signal associated with H_2 and H_3 at 4.65 ppm can hardly be rationalized just by a large number of adjacent sulfur atoms. It has been shown for linear[170] and cyclic[171] polysulfides that the deshielding effect of each additional sulfur atom decreases significantly as the total number of sulfur atoms increases. The presence of a sulfoxide group as in compounds **56** and **57**could in part explain such a deshielding for H_2 and H_3.[194] However, ^{13}C-NMR data do not correlate.



56



57

Analysis of compound **43** by mass spectrometry did not allow for the determination of a possible correct molecular ion. EI, CI or FAB all showed the presence of a fragment having the mass of trithiolane **27**, for which the same decomposition pattern as an authentic sample of **27** was observed. The presence of residual trithiolane **27** mixed with the sample of **43** after separation by column chromatography could perhaps explain this peak.

It could also be a fragment coming from the decomposition of a larger molecule. MALDI-TOF-MS analysis was carried out on a newly purified sample. A main peak at 155 was obtained upon direct inlet of the sample. No peak corresponding to the mass of trithiolane **27** was observed this time. From this result, it was thus speculated that compound **43** could simply be 1,2-dithietane **43b**. This led to a tentative parallel synthesis of such a compound, which will be described in the next Section.

The reaction between adamantyledeneadamantane (**44**) and S_{10} produced adamantyledeneadamantane thiirane (**45**) as a unique product in 40% isolated yield

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[195] Steudel, R. and Kustos, M. *Phosphorus, Sulfur and Silicon*, **1991**, *62*, 127.

(Table11). This result is consistent with the reaction of **44** with diatomic sulfur, as shown by previous studies,[169] including one from our group.[196] Contrary to singlet molecular oxygen chemistry, which affords a 1,2-dioxetane product via [2+2] cycloaddition,[197] no other sized ring than an episulfide has ever been observed in the reaction of S_2 and **44**. The steric hindrance of the two bulky adamantyl groups, which increases with increasing ring size, has been advanced in order to explain the formation of **45** as a unique product.[196] Similarly, **45** has also been prepared by a direct sulfuration reaction of **44** with "activated" elemental sulfur S_8.[198] The reaction proceeded in 58% yield at 150°C in refluxing DMF. In this case as well, **45** was obtained as a unique product, which was also rationalized by steric interactions.[198]

Based on these comparisons, S_{10} appears to behave similarly to diatomic sulfur and elemental sulfur towards **44**. But with the steric interactions making it impossible to produce bigger-sized sulfur rings with **44**, comparisons and differences are limited.

The results obtained in this Section on the reaction of S_{10} with simple olefins reveal a strong similarity in products isolated between S_{10} and common diatomic sulfur precursors. The unique presence of trithiolanes **19** or **27** in reaction mixtures between norbornene or norbornadiene and sulfur transfer reagents has been considered by Steliou as a good "proof" for diatomic sulfur involvement. One main difference lies in the fact that S_{10} is reactive enough to further sulfurate the remaining double bond of trithiolane **27** in order to produce the *bis*-sulfurated species **42.** On the contrary, some major differences in the nature of the adducts obtained from S_{10} and S_8 sulfuration reactions have clearly appeared. As mentioned earlier, mechanistic considerations will be discussed in Chapter 4.

Other available alkenes such as **58** and **59** or even alkynes such as **60** and **61** were also subjected to S_{10} in various reaction conditions. No adducts were isolated. Reactions

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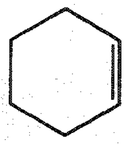
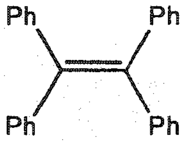
[196] a) Abu-Yousef, I. A. and Harpp, D. N. *Tetrahedron Lett.*, **1995**, *36*, 201. b) Abu-Yousef, I. A. and Harpp, D. N. *Sulfur Rep.*, **1997**, *20*, 1.

[197] a) Ando, W.; Kabe, Y. and Takata, T. *J. Am. Chem. Soc.*, **1982**, *104*, 7314. b) Kabe, Y.; Takata, T.; Ueno, K. and Ando, W. *J. Am. Chem. Soc.*, **1984**, *106*, 8174 and references cited therein.

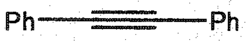
between buckminsterfullerene (**62**) and S_{10} were also carried out. The crude reaction mixtures analyzed by HPLC or MALDI-TOF-MS only revealed small fragments coming from the decomposition of the carbon cage.



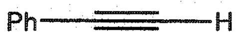
58



59



60



61

2.4.3. Parallel Synthesis

Based on the analytical data discussed in the previous paragraph, some hypotheses were made which suggest that compound **43** could indeed be 1,2-dithietane **43b**. Different synthetic routes were thus explored in order to possibly isolate and fully characterize **43b**.

There is only one reported case in the literature of a stable 1,2-dithietane. Dithiatopazine (**20**), which was described in previous Sections as a source of diatomic sulfur,[90] was synthesized by Nicolaou and co-workers and its structure fully resolved by X-ray diffraction in 1987.[88] 1,2-Dithietanes have also been proposed as intermediates in reaction mechanisms as shown in Figure 13.[84] These 4-membered rings with adjacent sulfur atoms constitute one of the few small ring compounds for which a useful synthetic method has yet to be developed. Efforts have thus been made by some groups[199] towards the development of a methodology that could provide an easy access to such structures.

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[198] Nakayama, J.; Ito, Y. and Mizumura, A. *Sulfur Lett.*, **1992**, *14*, 247.

[199] a) For a review see: Nakayama, J. and Ishii, A. *Adv. Heterocyclic Chem.*, **2000**, *77*, 221. b) Nakayama, J.; Takahashi, K.; Watanabe, T.; Sugihara, Y. and Ishii, A. *Tetrahedron Lett.*, **2000**, *41*, 8349.

A summary of the approach that was investigated in the course of this work as well as the results obtained, is presented in Figure 49.

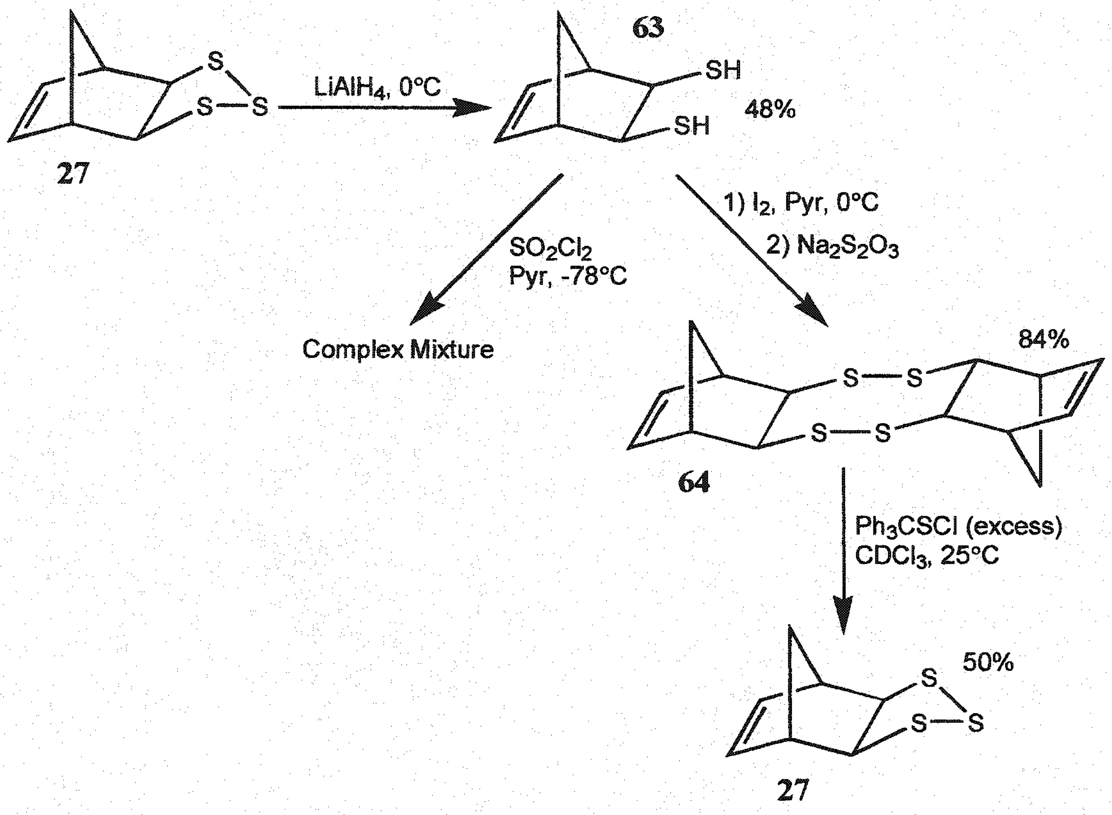

Figure 49. Results Obtained from Tentative Cyclisations of Dithiol **63**

It was envisaged that cyclisation of the parent dithiol **63** was probably the most direct approach for the synthesis of 1,2-dithietane **43b**. The controlled reduction of trithiolane **27** led to the formation of dithiol **63** in 48% yield after purification by column chromatography. Two different routes were then tried in order for S-S bond formation to take place between these two thiol groups. The method developed by Derbesy and Harpp, which is commonly used for the formation of linear disulfides,[200] gave a complex reaction mixture. NMR analysis of the mixture did not reveal any pattern resembling the one of **43**. Titrimetric cyclisation of dithiol **63** was then attempted by iodine oxidation of the two thiol groups (see Experimental). This method gave rise to the formation of a new

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[200] Derbesy, G. and Harpp, D. N. *Tetrahedron Lett.*, **1994**, *35(30)*, 5381.

compound, which was identified as dimer **64** in 84% yields. Compound **64** was fully characterized by NMR and MS analysis (see Table 16) as well as single crystal X-ray diffraction. An ORTEP drawing of **64** is shown in Figure 50 and selected bond lengths, bond angles and torsion angles are presented in Table 15. Compound **64** does not melt sharply but decomposes progressively over a range starting from 160°C. The cyclisation reaction by titrimetry was also carried out at -78°C but yielded the same major product. No trace of unknown compound **43** was detected.

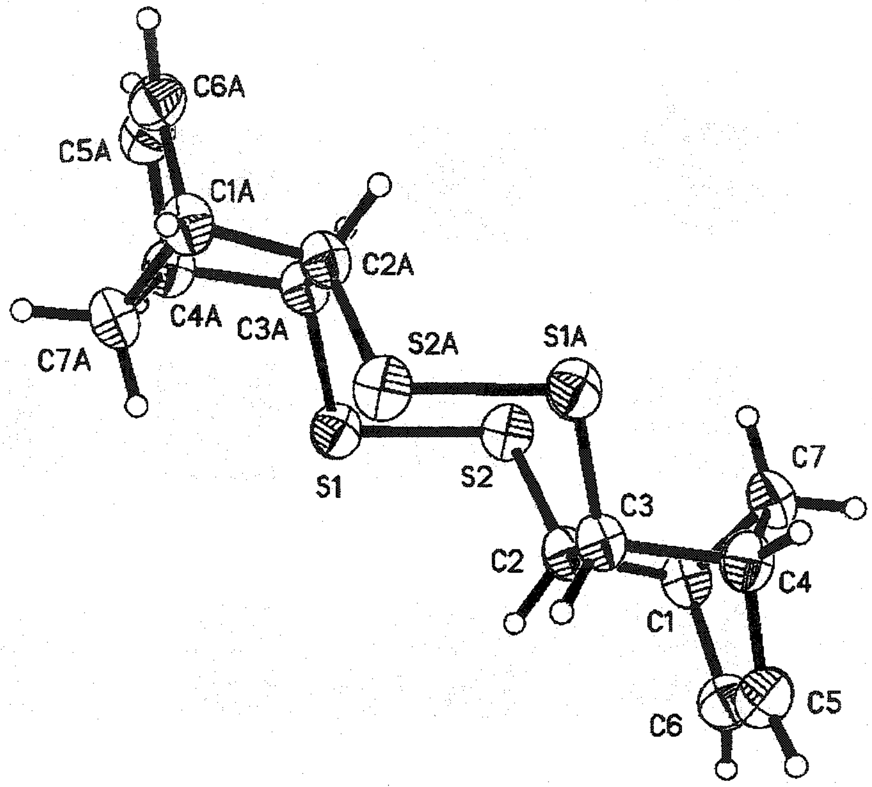

Figure 50. Ortep Drawing of Dimer Compound **64**

Bond lengths (Å)			
S1-C3A	1.817	C3-S1A	1.817
S1-S2	2.035	C2-C3	1.574
S2-C2	1.812	C5-C6	1.330
Bond angles (deg)			
C3A-S1-S2	104.8	C4-C3-S1A	106.4
C2-S2-S1	105.2	C2-C3-S1A	119.4
C1-C2-S2	106.3	C3-C2-S2	120.1
Torsion angles (deg)			
C3A-S1-S2-C2	118.2	S1-S2-C2-C1	162.5
S2-C2-C3-S1A	1.0	S1-S2-C2-C3	-82.5
S2-C2-C3-C4	-116.2	C1-C2-C3-S1A	118.1

Table 15. Selected Structural Parameters for Dimer Compound **64**

The crystal cell setting is triclinic and belongs to the $P\bar{1}$ space group. The molecule possesses a center of symmetry. Both sets of sulfur atoms S1-S2A and S2-S1A are placed on the *exo* face relative to their respective norbornene unit. The average S-S and C-S bond distances of 2.035 and 1.815 Å fall into the normal range observed for such bonds. The average interplanar angle of 117.2° between S2C2C3S1A and C1C2C3C4 is also quite close to the 118.7° observed for *bis*-sulfurated compound **42**. The 8-membered units of such compounds are usually found in various conformations. 1,2,5,6-Tetrathiacyclooctane (**65**) possesses for example a twist-boat-chair conformation where one of the C-S-S-C torsion angles is close to the ideal value of 90° (86.3°) at the expense of the other one (117.4°).[201] Others, such as the 1,2,5,6-tetrathiocin compound **66**, which has a torsion angle of 117.4°, adopt a chair conformation.[202] Compound **64** has a chair conformation with a dihedral angle C3A-S1-S2-C2 of 118.2°. Other recent examples of related structures exist in the literature.[203]

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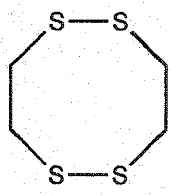
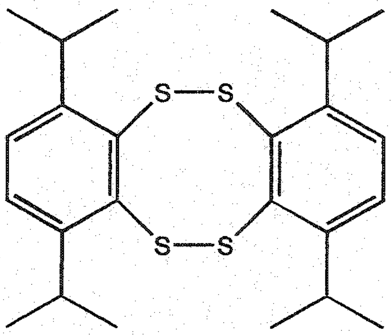
[201] Goodrow, M. H.; Olmstead, M. M. and Musker, W. K. *Tetrahedron Lett.*, **1982**, *23*, 3231.

[202] Ogawa, S.; Sugawara, M.; Kawai, Y.; Niizuma, S.; Kimura, T. and Sato, R. *Tetrahedron Lett.*, **1999**, *40*, 9101.

[203] a) Lakshmikantham, M. V.; Raasch, M. S.; Cava, M. P.; Bott, S. G. and Atwood, J. L. *J. Org. Chem.*, **1987**, *52*, 1874. b) Yang, X.; Rauchfuss, T. B. and Wilson, S.

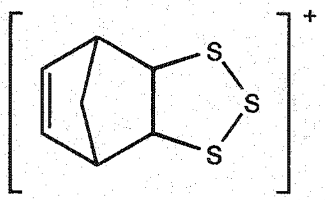


65



66

The mass spectrum (EI) of dimer **64** shows a peak at m/z 188 (40%), which corresponds to fragment **67**. Such fragmentation was observed in the case of compound **65** and comes from an intramolecular S-S coupling reaction.[201]



67

Finally, it was observed that when a small quantity of dimer **64** was treated with excess (3.5 molar equivalents) triphenylmethylsulfenyl chloride (**68**) in an NMR tube in $CDCl_3$ at room temperature, trithiolane **27** slowly formed over 2-3 days in an apparent 50% yield calculated from integral ratios. Trithiolane **27** seemed to be formed as a unique product. Compounds such as **68** are known to insert into S-S bonds and they have been the topic of recent studies in our group.[204] A mechanism explaining the formation of trithiolane **27** from dimer **64** is suggested in Figure 51.

J. Chem. Soc., Chem. Commun., **1990**, 34. c) Borisenko, K. B.; Broschag, M.; Hargittai, I.; Klapötke, T. M.; Schröder, D.; Schulz, A.; Schwarz, H.; Tornieporth-Oetting, I. C. and White, P. S. *J. Chem. Soc., Dalton Trans.*, **1994**, 2705. d) Shimizu, T.; Iwata, K. and Kamigata, N. *Angew. Chem., Int. Ed. Engl.*, **1996**, *35*, 2357.

[204] a) Rys, A. Z. and Harpp, D. N. *Tetrahedron Lett.*, **2000**, *41*, 7169. b) Hou, Y.; Abu-Yousef, I. A. and Harpp, D. N. *Tetrahedron Lett.*, **2000**, *41*, 7809.

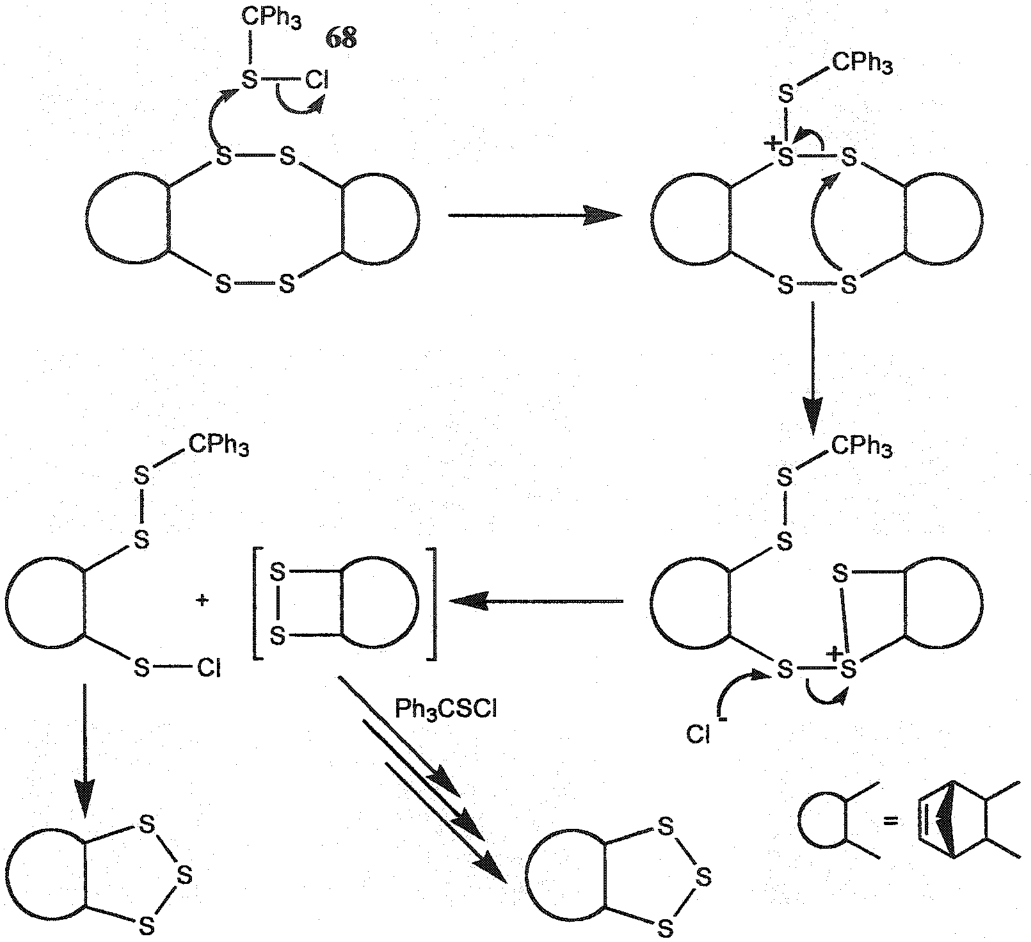
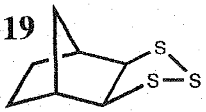
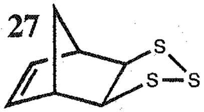
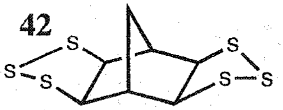
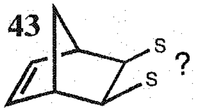
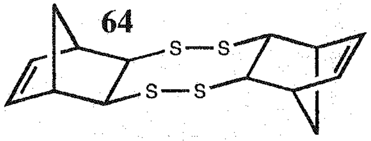


Figure 51. Proposed Mechanism for the Reaction of Dimer Compound **64** with Triphenylmethylsulfenyl Chloride

Attempts to synthesize the elusive 1,2-dithietane **43b** have remained unsuccessful. The observed MALDI-TOF spectrum for compound **43** might only show the small fragment of a bigger molecule. However, the synthetic approach that was undertaken to synthesize 1,2-dithietane **43b** allowed the isolation of the new dimer compound **64**.

Compound	^{1}H-NMR[a]	^{13}C-NMR[a]	MS[b]
19 	3.61 (d, J=2.0 Hz, 2H), 2.43 (m, 2H), 1.89 (dt, J_1=10.0 Hz, J_2=2.0 Hz, 1H), 1.70 (m, 2H), 1.24 (m, 2H), 1.03 (dt, J_1=10.0 Hz, J_2=2.0 Hz, 1H)	69.68, 40.66, 32.21, 27.49	190[c] (100), 126 (46), 125 (31), 98 (19), 97 (35), 93 (60), 92(24), 91 (45), 79 (26), 77 (31), 67 (21), 66 (65), 65 (24), 64 (28)
27 	6.36 (t, J=1.8 Hz, 2H), 4.03 (d, J=1.8 Hz, 2H), 2.89 (m, 2H), 2.45 (d, J=9.4 Hz, 1H), 1.70 (dt, J_1=9.4 Hz, J_2=1.8 Hz, 1H)	139.40, 70.85, 46.30, 43.18	188[c] (11), 124 (36), 123 (37), 122 (36), 97 (22), 92 (45), 91 (100), 79 (13), 77 (8), 66 (30), 65 (16), 64 (7)
42 	3.83 (bs, 4H), 2.63 (t, J=1.5 Hz, 2H) 1.98 (bs, 2H)	68.63, 45.61, 28.18	284[c] (51), 220 (14), 156 (14), 125 (11), 124 (100), 123 (89), 122 (25), 121 (18), 97 (52), 92 (33), 91 (94), 79 (23), 78 (13), 77 (16), 76 (26), 66 (26), 65 (16), 44 (15)
43 	6.07 (t, J=1.7 Hz, 2H), 4.66 (m, 2H), 3.17 (m, 2H), 2.18 (d, J=9.0 Hz, 1H), 2.06 (dt, J_1=9.0 Hz, J_2=2.0 Hz, 1H)	135.48, 70.72, 56.75, 46.37	155[d]
64 	6.20 (t, J=1.8 Hz, 2H), 3.46 (d, J=1.5 Hz, 2H), 2.86 (m, 2H), 1.58 (dbs, J=9.3 Hz, 1H), 1.37 (dt, J_1=9.3 Hz, J_2=1.8 Hz, 1H)	137.62, 57.00, 49.27, 44.79	312[c] (60), 188 (40), 156 (32), 124 (25), 123 (40), 122 (100), 97 (14), 92 (14), 91 (49), 79 (11), 66 (30), 65 (14), 45 (12)

[a] $CDCl_3$; δ in ppm. [b] EI-MS. [c] $M^{+\cdot}$ parent ion. [d] MALDI-TOF-MS.

Table 16. NMR and MS Data for Compounds **19**, **27**, **42**, **43** and **64**

2.5. Conclusion

The sulfuration process of simple and conjugated alkenes with *cyclo*-decasulfur S_{10} that was developed, compares well in terms of product yields with most of the existing sulfuration methodologies. Indeed, the yields of the sulfuration products fell into the same range as most diatomic sulfur precursors or sulfuration methods with elemental sulfur S_8.

The main advantage of reactions with S_{10} lies in the mild conditions required for efficient reaction to take place. S_{10} reacts at moderate temperatures with olefins and the use of harsh reagents such as bases or nucleophiles is not necessary and even has to be avoided. This methodology is also attractive as the only side product generated by the reactions is elemental sulfur. However, the presence of large quantities of S_8 could be considered as a drawback as it renders product separation more difficult in some cases.

Some differences in terms of both the selectivity and the identity of the products itself have also emerged in comparison with S_8 or S_2 sulfuration processes. Without anticipating too much on the mechanistic aspects of these reactions, which will be discussed in Chapter 4, these results show that S_{10} behaves quite differently from most known sulfurating reagents. It appears to act as the clean 2-sulfur atom transfer reagent as was anticipated.

The scope of this sulfuration methodology will now be enlarged towards other sulfur allotropes.

CHAPTER 3. SOME CHEMISTRY OF S_9, S_{12} AND S_{20}

3.1. Some Chemistry of S_9

3.1.1. Background

The first-ever synthesis of *cyclo*-nonasulfur, S_9, was performed by Schmidt *via* the organometallic route to sulfur homocycles using titanocene pentasulfide (**28**).[123a] This compound (**28**) was reacted with dichlorotetrasulfane, S_4Cl_2, under the classic conditions developed by the same authors.[113] It was only much later that Steudel discovered that S_9 can actually crystallize in two polymorphic states, α- and β-S_9. Slight modifications to the initial synthetic method allowed for the production of pure α-S_9.[123b] The same group also found that β-S_9 could be crystallized from the remaining solution of the non-oxidized portion of the oxidation reaction of S_9 (to give S_9O) with trifluoroperacetic acid (Figure 52).[123b]

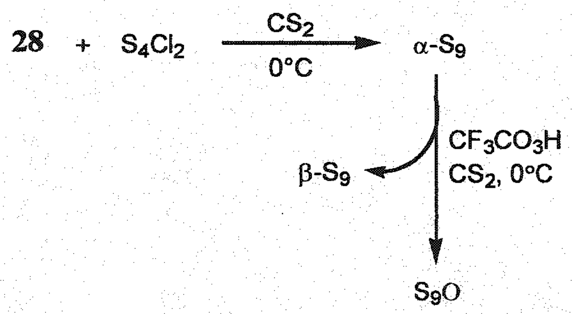


Figure 52. Synthesis of α- and β-S_9

The identification of the two phases of S_9 was deduced from the assignment of the Raman spectra, which were recorded for both pure species.[123b] The structure of α-S_9 has been determined by single crystal X-ray diffraction.[111] α-S_9 belongs to the less symmetrical group of sulfur homocycles, with alternating bond lengths and great variations in torsion angles. Some of the parameters of the crystal structure of α-S_9 are reported in Table 17.

Molecule	Interatomic Distances (pm)	Bond Angles (°)	Torsion Angles (°)
α-S_9	203-207	104-110	60-116

Table 17. Some Parameters of the Structure of α-S_9

As was mentioned in Chapter 1, the synthetic route that leads to single crystals of α-S_9 is different from the early methods. In its reaction with **28**, S_4Cl_2 was replaced by dicyanohexasulfane ($S_6(CN)_2$), the structure of which was also determined by X-ray diffraction.[111] No single crystal structure for β-S_9 has been obtained to date.

The first contribution by Schmidt reported a melting point above 50°C[123a] along with decomposition by polymerization for *cyclo*-S_9. Steudel reported later a clean melting point for α-S_9 at 65-66°C.[123b] No melting point for the β phase has been reported.

Cyclo-nonasulfur has also been quantified as a component of liquid sulfur[67] and has been detected at trace levels in solid commercial samples of S_8.[77] Photochemical decomposition of S_7 and S_8 in CS_2,[61] thermal decomposition of S_8 in CS_2[78] and thermal depolymerization of industrial polymeric sulfur S_μ[148] have all resulted in the detection of S_9. *Cyclo*-nonasulfur is also a component of the mixtures of sulfur allotropes produced by the acid decomposition of thiosulfate[130] or by reaction of SCl_2 with aqueous KI.[132] These last two reactions produce S_6 as their main component. Finally, S_9 has also been detected in a reaction involving titanocene dicarbonyl (**31**), S_6 and SCl_2.[119b] As far as S_9 chemistry is concerned, the only account is the formation and characterization of *cyclo*-nonasulfur oxide, S_9O.[123b]

3.1.2. Synthesis and Characterization

The synthetic pathway that was chosen in this study in order to produce *cyclo*-S_9 combined two procedures.

The method to yield dichlorotetrasulfane (S_4Cl_2) was the one used by Steudel[111] and not the older procedure of Fehér.[103b,c] Steudel found that the chlorination of *cyclo*-hexasulfur, S_6, with excess chlorine (3 eq. Cl_2) generates a mixture of S_4Cl_2 and S_2Cl_2. The latter can be stripped off under reduced pressure and a relatively pure sample of S_4Cl_2 is thus obtained as a malodorous orange oil in a reported 62% yield. Chlorine was dispensed in solution in carbon tetrachloride (CCl_4). These Cl_2/CCl_4 solutions were prepared by bubbling chlorine gas in carbon tetrachloride and were always used immediately after their preparation. This seemed important as losses of Cl_2 gas from the CCl_4 solution were noticed over time. In the course of this study, S_4Cl_2 was obtained in average yields of 47%, in relatively good agreement with Steudel.

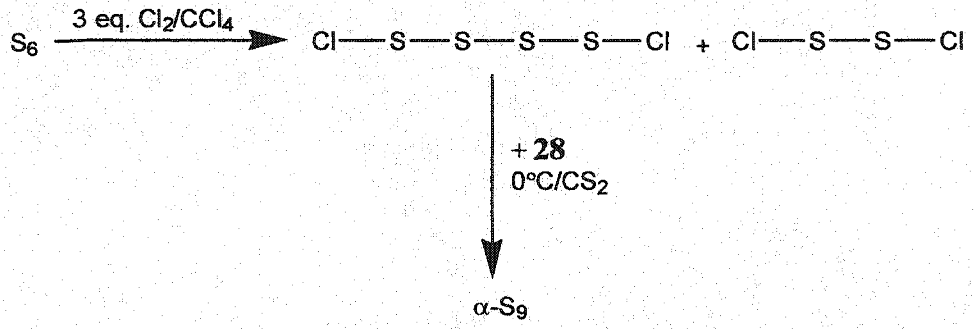


Figure 53. Preparation of α-S_9 from S_6

Dichlorotetrasulfane obtained by this method was of good enough purity to be directly reacted with titanocene pentasulfide (**28**). The experimental procedure followed classical conditions, which are described in detail in the Experimental Section. α-S_9 was obtained as a bright yellow solid that can be recrystallized from CS_2/n-pentane. The yield of pure α-S_9 was 21%, to be compared with the *ca.* 30%[123a,123b] or 18%[111] yield previously reported. Melting points for α-S_9 samples obtained in this study were measured at 61-63°C. The method for the synthesis of α-S_9 from S_6 used in the course of this study is summarized in Figure 53.

Although this was not evaluated precisely, like S_{10}, α-S_9 also decomposes in a few days at room temperature and/or with light. Samples were thus kept in the dark at -40°C and even freshly recrystallized samples were often not fully soluble in CS_2. A small fraction of insoluble polymeric sulfur always seemed to be present.

The characterization of α-S_9 was achieved by FT-Raman spectroscopy and the purity of the samples was assessed by HPLC. Table 18 compares the main vibrational bands for α-S_9 synthesized in the course of this study with those reported in the literature and shows unequivocally the identity of the sample.

	α-S_9[a]			α-S_9[b]	
	298.5 (10)	shoulder	485 (10)	297 (13)	117 (31)
477 (23)	257 (13)		477 (16)	256 (12)	111 (sh)
	245 (26)	105.5 (67)	463 (sh)	245 (23)	104 (58)
456 (100)			454 (100)	222 (26)	100 (sh)
	219 (38)	80 (62)	442 (sh)	215 (31)	78 (67)
437 (44)	186 (72)		436 (49)	188 (90)	57 (50)
417 (10)			416 (11)	181 (sh)	46 (33)
	160.5 (46)			161 (37)	43 (sh)
	157 (38)			155 (28)	41 (sh)
				151 (sh)	27 (35)

[a] FT-Raman/Nd-YAG laser/1064 nm/2.6 cm^{-1}/room temperature. [b] Ref. 123b; Cary 82 Raman spectrometer/Krypton laser/647 nm/1.5 cm^{-1}/-100°C.

Table 18. Raman Spectra of α-S_9

The purity of each S_9 sample was achieved with the standard reverse phase HPLC procedure described in the Experimental Section. An example of a run is also shown in the Appendix Section. Apart from the insoluble polymeric sulfur fraction mentioned above, no sulfur cycle other than *cyclo*-S_9 could be detected in the different batches used.

3.1.3. Reaction of S_9 with 1,3-Dienes and Norbornene

Cyclo-nonasulfur S_9 was reacted with three key substrates in order to study its reactivity with classic conjugated dienes and a strained olefin. Due to the difficulty in preparing S_9, these reactions were carried out on a small scale. Yields were measured by comparison with an internal standard and the identity of the different products was determined by spectroscopic comparison with authentic samples, which were synthesized separately if needed. These trapping reactions constitute a good starting base in order to compare the difference in reactivity and/or reaction products between the different sulfur allotropes.

The experimental protocol used in the reactions between S_9 and these substrates was similar to the one optimized for the study of S_{10}. Equimolar amounts of 1,3-diene **12a** and **12b** or norbornene (**16**) were reacted with S_9 at similar temperatures in non-polar solvents, the sulfur allotrope being initially dissolved into an appropriate amount of carbon disulfide (CS_2) and added to the refluxing olefin. Reaction times never exceeded three hours; it was checked by reverse phase HPLC that S_9 was no longer present in the reaction mixtures. The internal standard used in order to estimate the yields of reaction products by ^{1}H-NMR was 9-methylanthracene. Details of the experimental procedure are reported in the Experimental Section in Chapter 5.

The results obtained from this study are reported in Table 19. Table 20 reports two control reactions that were carried out with S_8 as the sulfurating agent; 9/8 equivalents of S_8 were used for these control reactions.

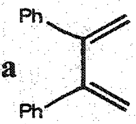
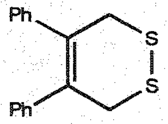
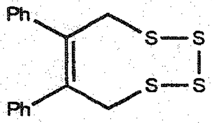
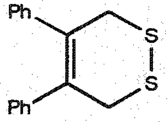
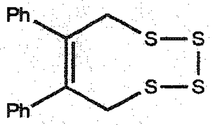
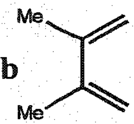
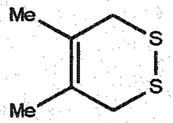
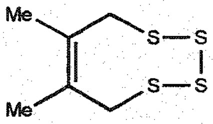
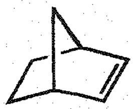
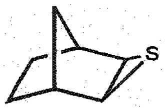
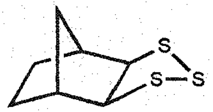
Substrate	Conditions (solv./°C/hr)	Products Yield and Ratio
12a 	Chlorobz./115/3	 **13a** 6.5:1  **35** 45%
	Toluene/100/3	 **13a** 5.5:1  **35** 31%
12b 	Toluene/100/3	 **13b** 10:1  **36** 39%
16 	Toluene/100/3	 **69** 1.5:1  **19** 26%

Table 19. Reaction of Selected Olefins with S_9

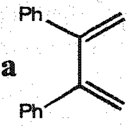
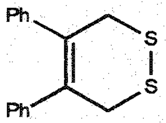
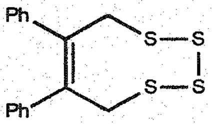
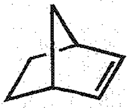
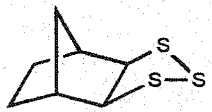
Substrate	Conditions (solv./°C/hr)	Products Yield and Ratio
12a 	Chlorobz./115/3	 **13a** 4:1  **35** 4%
16 	Toluene/100/3	 **19**, No Trace

Table 20. Control Reactions for S_9 Trapping

3.1.4. Discussion

The reaction between equimolar amounts of S_9 and 1,3-dienes **12a** and **12b** yielded the corresponding well-identified disulfide and tetrasulfide adducts in moderate yields. The product yields were lower than the ones obtained in the sulfuration reactions with S_{10} under similar conditions. The selectivity towards disulfide adduct **13a** fell into the same range as the one observed for the S_{10} sulfuration of 2,3-diphenyl-1,3-butadiene (**12a**) (*circa* 6-7:1 for **13a/35** ratio). An even greater selectivity towards disulfide **13b** was observed in the sulfuration of 2,3-dimethyl-1,3-butadiene (**12b**). In fact, the ratio disulfide **13b**/tetrasulfide **36** culminated at 10:1, to be compared with *ca.* 7:1 in the corresponding S_{10} sulfuration experiment.

A control reaction with S_8 as the sulfurating agent was carried out with 2,3-diphenyl-1,3-butadiene. The conditions used were the ones that gave the best yield of sulfuration products with S_9. This control reaction showed that, like S_{10}, S_9 reacts more efficiently than S_8 with 1,3-dienes even under mild conditions and without any sort of activation process. Only 4% of trapped products were obtained after 3 hours at 115°C in chlorobenzene/CS_2.

Yields of sulfuration products obtained for the reaction between equimolar amounts of norbornene and S_9 were even more modest than for the corresponding S_{10} sulfuration reaction (26% *vs.* 83%). However, the originality of this sulfuration reaction comes from the fact that *exo*-2,3-epithionorbornane (**69**) was obtained as one of the two products, along with almost equimolar amounts of trithiolane **19**. Compound **69** was identified within the crude reaction mixture by NMR comparison with an authentic sample. This authentic sample of **69** was synthesized by a parallel method, which is described below. Trithiolane **19** had already been isolated in pure form as the unique product of the reaction of norbornene with S_{10}.

The control reaction that was carried out between norbornene and S_8 under the same conditions as for S_9 did not show any traces of the episulfide **69** or trithiolane **19**. Once again, this demonstrates the greater reactivity of S_9 towards strained olefins compared to that of S_8. In the latter case, activation by ammonia is often required for sulfuration to take place.[184a,187,194]

In order to better understand the composition of this reaction mixture, a second set of control reactions was carried out and is summarized in Figure 54.

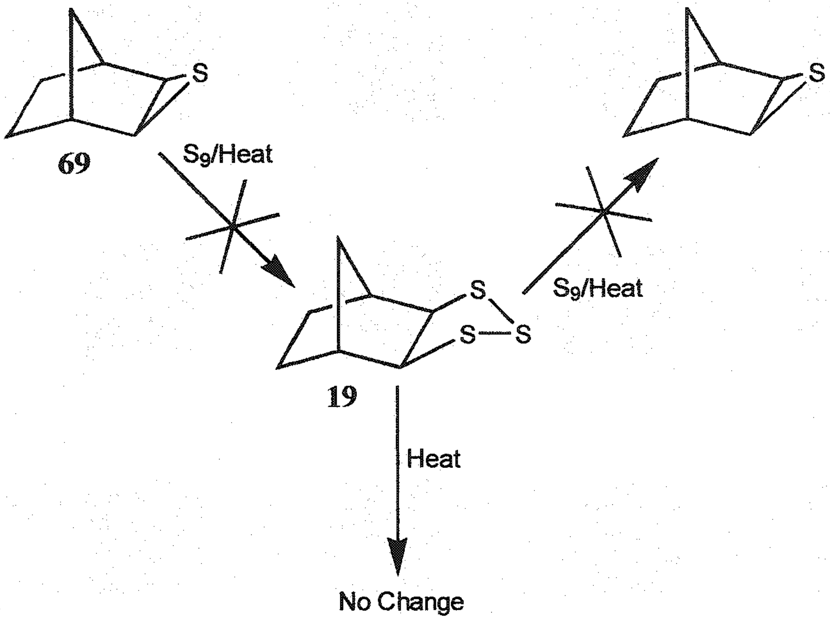


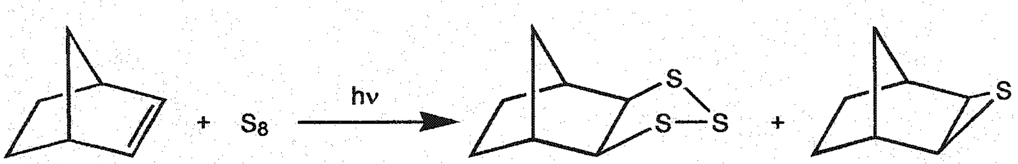
Figure 54. Non-Equilibrium between Trithiolane **19** and Episulfide **69**

The decomposition of S_9 in the presence of episulfide **69** only yielded traces (*ca.* 3%) of trithiolane **19** after 3 hours at 100°C in toluene/CS_2. Moreover, when trithiolane **19** was treated under similar conditions in the presence of S_9, no episulfide **69** was detected. Finally, a pure sample of trithiolane **19** was unchanged when heated under these conditions. It thus seems evident that both **19** and **69** are direct products of the sulfuration of norbornene with S_9. Their presence in the reaction mixture is not the consequence of thermal decomposition or further reaction with S_9.

This non-equilibrium between **19** and **69** is analogous to the one of the two products obtained from the sulfuration of 1,3-dienes **12a** and **12b** with either S_9 or S_{10}. Both disulfides **13a** or **13b** and tetrasulfides **35** or **36** are clearly separate products of the sulfuration reaction (see Figure 39). This reactivity seems to contrast with the S_8

sulfuration reaction of norbornene reported by Ghosh and Bartlett.[187,194] In this reaction, trithiolane **19** was indeed demonstrated to be in equilibrium with pentasulfide **46** as shown in Figure 46. Other accounts of such equilibrium have been reported.[205,174] It should be further noted that in the present study, no traces of pentasulfide were detected.

Very few examples of episulfide formation from direct sulfuration of an olefin with any form of sulfur have been reported. A very closely related example is the study of Inoue and co-workers. They identified episulfide **69** as well as trithiolane **19** in a solution of elemental sulfur S_8 and norbornene, which they irradiated with a sunlamp for 70 hours.[189] Trithiolane **19** and episulfide **69** were formed in yields of 77% and 8%, respectively. The authors proposed that episulfide **69** formed from the reaction of a photo-excited state of trithiolane **19** with norbornene. This example contrasts strongly with the analogous thermal sulfuration of norbornene, in which case episulfide **69** was not detected.[184a,186,187,194]



16 **19**, 77% **69**, 8%

Figure 55. Irradiation of S_8 in the Presence of Norbornene

Finally, Ghosh and Bartlett,[187,194] as well as Emsley,[186] isolated *exo*-2,3-epithionorborn-5-ene (**47**) (10%) among the reaction products of norbornadiene with S_8. In this latter case, however, S_8 was activated by ammonia.

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[205] Chenard, B. L.; Harlow, R. L.; Johnson, A. L. and Vladerchick, S. A. *J. Am. Chem. Soc.*, **1985**, *107*, 3871.

Others accounts, which report the formation of *exo*-2,3-epithionorbornane (**69**) as one of the reaction products, exist.[93,190,206] These accounts do not however use elemental sulfur as the source of sulfur atoms.

The lack of examples in the area of episulfide formation by direct sulfuration of olefins emphasizes even more the unique behavior of S_9 towards norbornene. Mechanistic aspects of this reaction will be discussed in Chapter 4.

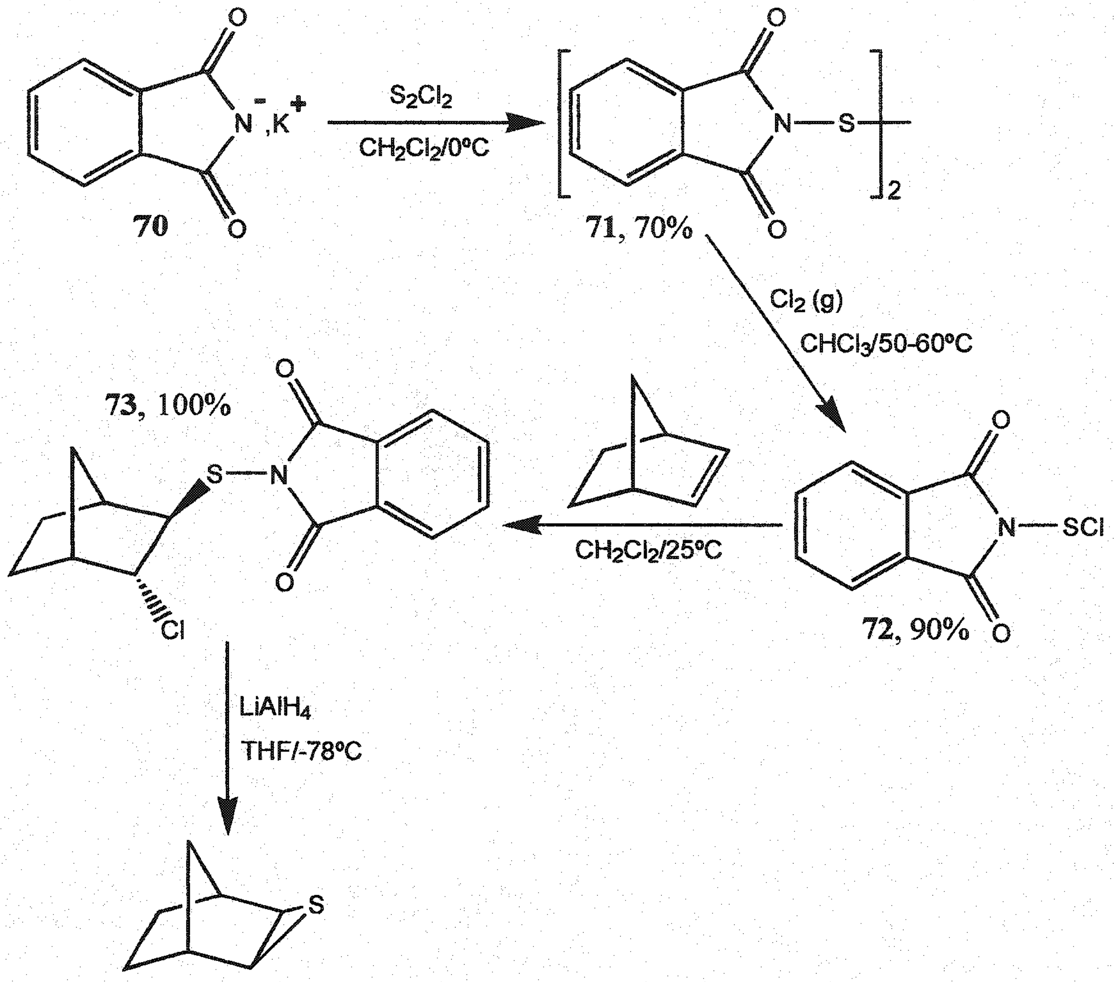
The next Section will deal with the parallel synthesis of episulfide **69**. It will also include a brief overview of other useful synthetic approaches that have been reported towards the general preparation of episulfides. Efforts towards the independent preparation of all possible sulfuration products of norbornadiene with S_9 will also be summarized.

3.1.5. Parallel Synthesis

In order to identify with certainty *exo*-2,3-epithionorbornane (**69**) within the reaction mixture, a parallel synthesis was carried out. The preparation of this authentic sample of **69** was accomplished by the reaction sequence shown in Figure 56.

---

[206] a) Schmidt, U.; Kabitzke, K.; Boie, I. and Osterroht, C. *Chem. Ber.*, **1965**, 98, 3819. b) Sidhu, K. S.; Lown, E. M.; Strausz, O. P. and Gunning, H. E. *J. Am. Chem. Soc.*, **1966**, *88*, 254. c) Leppin, E. and Gollnick, K. *Chem. Ber.*, **1970**, *103*, 2894.



69, 51%

Figure 56. Parallel Synthesis of *exo*-2,3-Epithionorbornane

This set of reactions leading to **69** has been described previously.[207] A key step of this sequence is the addition of phthalimido-N-sulfenyl chloride (**72**) to the double bond of norbornene in order to form the adduct *endo*-3-chloro-*exo*-2-(phthalimido-N-thio)bicyclo[2.2.1]heptane (**73**). Upon reduction of **73**, **69** was produced in 51% isolated yield, in good agreement with the literature. Details of the synthesis can be found in the Experimental. NMR and MS data for **69** are reported in Table 21 at the end of this Section.

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[207] Bombala, M. U. and Ley, S. V. *J. Chem. Soc., Perkin Trans. I*, **1979**, 3013.

Other methods for the synthesis of episulfides, that also make use of the ability of thiosulfenyl or sulfenyl chloride species to add across double bonds,[208] have been reported,[209] including a recent contribution by our group.[210] Earlier episulfidation methods implicated the reaction of epoxides with sulfur transfer reagents and did not directly involve the corresponding alkene.[211] One exception is the procedure developed by Lautenschlaeger and co-workers, which advantageously makes use of the reactivity of sulfur monochloride (S_2Cl_2) and sulfur dichloride (SCl_2) towards olefins.[212] This latter method can be considered as the precursor of the phthalimido-N-sulfenyl chloride procedure used in the course of this work. Other approaches towards the synthesis of episulfides have been developed but very often seem to be restricted to strained olefins.[213]

Using the synthetic method presented above, phthalimido-N-sulfenyl chloride **(72)** was reacted with norbornadiene. The initial goal was to prepare separately all the products that could potentially be formed during the reaction between norbornadiene and S_9. Based on the sulfuration of norbornene with S_9, this reaction mixture was anticipated to be complex. It thus seemed a better approach to first fully characterize all the expected products, which are shown in Figure 57, in order to more easily detect their presence in the reaction mixture by NMR.

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[208] a) Mueller, W. H. and Butler, P. E. *J. Am. Chem. Soc.*, **1966**, *88*, 2866 and references cited therein. b) Thaler, W. A.; Mueller, W. H. and Butler, P. E. *J. Am. Chem. Soc.*, **1968**, *90*, 2069. c) Mueller, W. H. and Butler, P. E. *J. Am. Chem. Soc.*, **1968**, *90*, 2075. d) Brown, H. C. and Liu, K.-T. *J. Am. Chem. Soc.*, **1970**, *92*, 3502.

[209] a) Fujisawa, T. and Kobori, T. *Chem. Lett.*, **1972**, 935. b) Fujisawa, T. and Kobori, T. *Chem. Lett.*, **1972**, 1065.

[210] Abu-Yousef, I. A. and Harpp, D. N. *Sulfur Lett.*, **2000**, *23*, 131.

[211] Sander, M. *Chem. Rev.*, **1966**, *66*, 297.

[212] a) Lautenschlaeger, F. and Schwartz, N. V. *J. Org. Chem.*, **1969**, *34*, 3991. b) Lautenschlaeger, F. *J. Org. Chem.*, **1969**, *34*, 3998.

[213] a) Adam, W.; Deeg, O. and Weinkötz, S. *J. Org. Chem.*, **1997**, *62*, 7084. b) Kendall, J. D. and Simpkins, N. S. *Synlett*, **1998**, *4*, 391. c) Adam, W. and Weinkötz, S. *J. Am. Chem. Soc.*, **1998**, *120*, 4861.

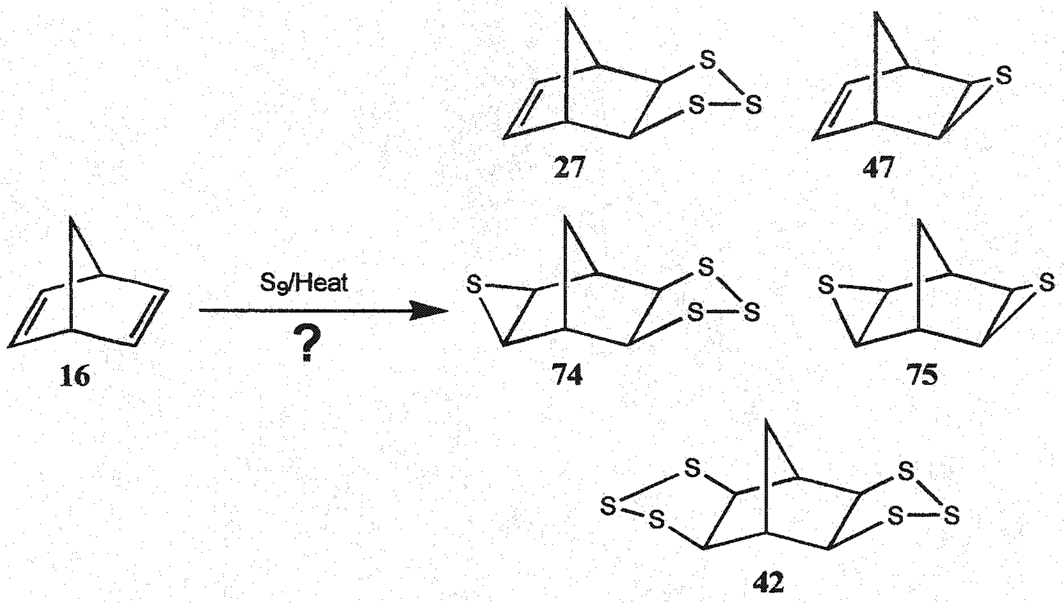

Figure 57. Expected Products for the Reaction of S_9 with Norbornene

Compounds **27** and **42** had already been obtained in pure form during the sulfuration reaction of norbornadiene with S_{10}. The proposed synthetic pathway for the preparation of the remaining compounds **47**, **74** and **75** is shown in Figure 58. However, the anticipated products were not all obtained.

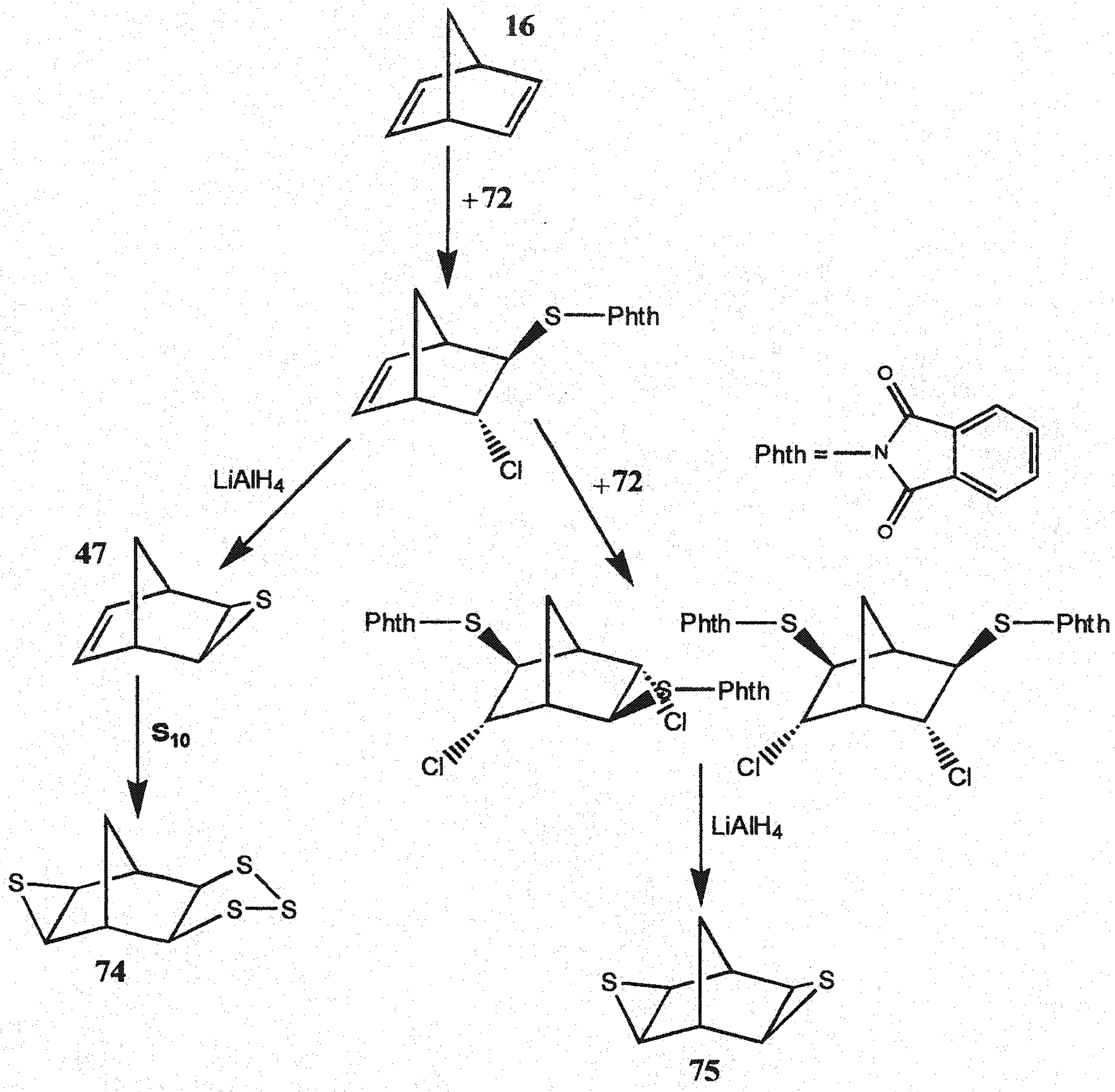

Figure 58. Proposed Pathway for the Synthesis of Compounds **47**, **74** and **75**

The reaction between phthalimido-N-sulfenyl chloride (**72**) and norbornadiene unexpectedly yielded *exo*-3-chloro-*endo*-2-(phthalimido-N-thio)bicyclo[2.2.1]hept-5-ene (**76**) in 55% isolated yield. The reduction of this adduct under standard conditions allowed for the isolation of *endo*-2,3-epithionorborn-5-ene (**77**) and nortricyclene adduct **78** in 16% and 7% yield, respectively. Figure 59 summarizes these results and NMR and MS data for compounds **77** and **78** are reported in Table 21.

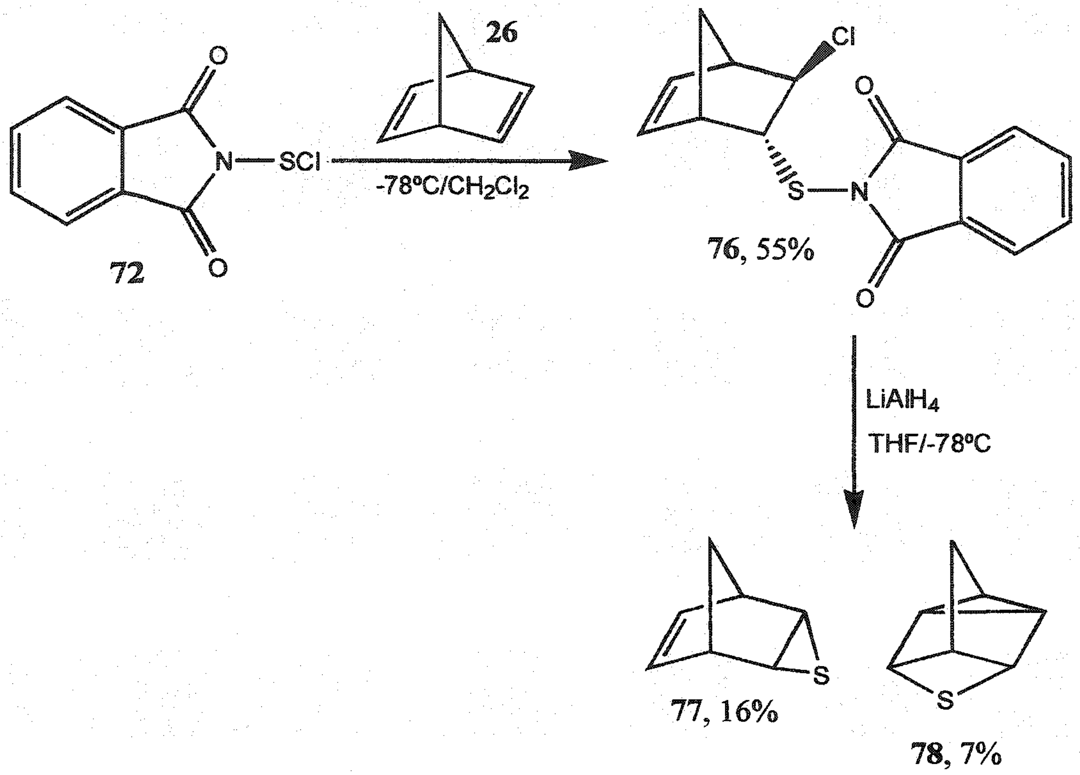

Figure 59. Addition of Sulfenyl Chloride **72** to Norbornadiene and Synthesis of *endo*-Episulfide **77** and Nortricyclene **78**

The structure for *exo*-3-chloro-*endo*-2-(phthalimido-N-thio)bicyclo[2.2.1]hept-5-ene (**76**) was determined *a posteriori* upon reduction and identification of the reduced products **77** and **78**. ^{1}H-NMR for **76** showed a typical anti-adduct pattern (J=2.7 Hz *vs* J=3.0 Hz for compound **73**[207]) for the addition of phthalimido-N-sulfenyl chloride to the double bond. However, it was not possible to give a conclusive appreciation on the orientation of the chlorine and the sulfur bearing group with regards to the plane of the norbornene unit. It is important to note that the reaction at room temperature between different arylsulfenyl chlorides (Ar-S-Cl) and norbornadiene has received considerable attention in the past.[214] These addition reactions, which were directed at studying the homoallylic double bond participation in the stabilization of the sulfonium ion transition

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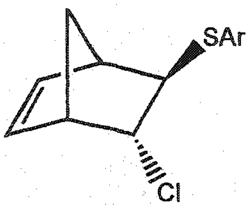
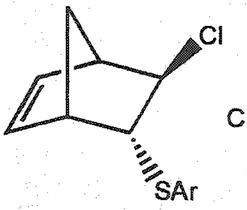
[214] a) Garratt, D. G. and Beaulieu, P. L. *J. Org. Chem.*, **1979**, *44*, 3555. b) Majewski, J. M. and Zakrzewski, J. *Tetrahedron Lett.*, **1981**, *22*, 3659. c) Zefirov, N. S.; Sadovaya, N. K.; Velikokhat'ko, T. N.; Andreeva, L. A. and Morrill, T. C. *J. Org. Chem.*, **1982**, *47*, 1468.

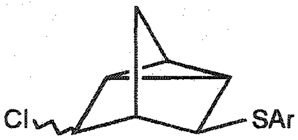
state, usually yielded complex mixtures. Adducts **79**, **80**, **81** and **82** have been characterized in these mixtures.



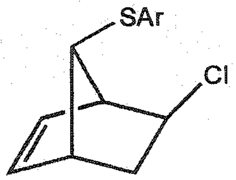
79



80



81



82

One adduct of type **80**, bearing an -S-Ar group *endo* to the norbornene plane, has been isolated and fully characterized by X-ray crystallography.[215] However, the presence of *endo*-S-Ar type compounds never exceeded 22%[214a] (by NMR) and these addition reactions produced *exo*-S-Ar type adducts as their main products. Ratios of *ca.* 80:20 in favor of the *exo* adducts were observed.[214a] In the case of phthalimido-N-sulfenyl chloride addition, compound **76** represented 74% (by NMR) of the crude reaction mixture when the reaction was carried out at -78°C and still accounted for 49% of the mixture when the addition was performed at room temperature. Two other compounds were observed in these mixtures but not isolated. One compound possessed a remaining double bond, while the other one did not. They could be the missing *exo* type adduct **79** and nortricyclene type adduct **81**. While steric effects have been advanced to explain the production of *endo* type adducts in some cases,[208d] electronic effects could explain the *endo* selectivity observed in the addition of phthalimido-N-sulfenyl chloride with norbornadiene.

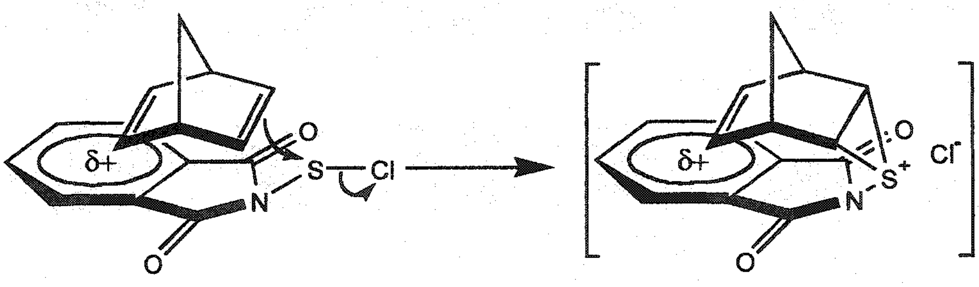


Figure 60. Proposed Intermediate for the Formation of Adduct **76**

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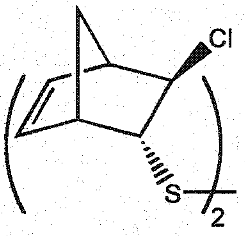
[215] Sedov, B. B.; Rau, T. F.; Rau, V. G.; Struchkoz, Y. T.; Akhmedova, R. S.; Zefirov, N. S. and Sadovaya, N. K. *Cryst. Struct. Commun.*, **1980**, *9*, 633.

We suggest that the interaction between the electron deficient phenyl ring of the phthalimido group and the free double bond directed the side of attack (Figure 60).

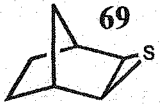
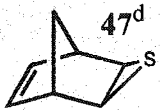
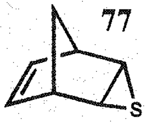
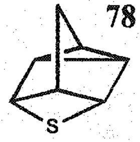
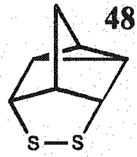
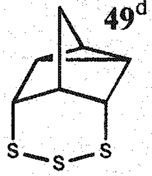
endo-2,3-Epithionorborn-5-ene (77) had been previously synthesized by the reaction of norbornadiene with sulfur dichloride. Compound **77** is actually the first episulfide bearing the norbornane-type skeleton to have been prepared.[212b] Its ^{1}H-NMR spectrum was identical to the one reported in the literature[212b] and its ^{13}C-NMR spectrum is reported for the first time. The mass spectrum of **77** shows the molecular ion as the predominant species. Two major fragmentation products come from the loss of sulfur and acetylene. The sample of **77** isolated upon reduction of **76** was actually not completely pure and traces of a probable disulfide **83** were detected by MS. The formation of such disulfides has already been observed in reduction reactions of this type in the absence of excess reducing agent.[207]



83

Nortricyclene **78** was isolated for the first time. Its structure was deduced from the interpretation of both ^{1}H- and ^{13}C-NMR data, which were also compared to the disulfide and trisulfide analogues **48** and **49** isolated by Bartlett and Ghosh (Table 21).[194] The mass spectrum of **78** shows the molecular ion as the main species. Interestingly, oxide analogues of compound **78** have already been synthesized following different routes.[212b]

Although the separate synthesis of all possible products from the sulfuration reaction of norbornadiene with S_9 was not successfully achieved, a method has been discovered which provides a selective access to *endo*-monosulfides having a norbornane skeleton.

Compound	^{1}H-NMR[a]	^{13}C-NMR[a]	MS[b]
 **69**	2.68 (s, 2H), 2.39 (bs, 2H), 1.54-1.62 (m, 2H), 1.47 (dt, J_1=10.5 Hz, J_2=2.4 Hz, 1H), 1.16-1.23 (m, 2H), 0.60 (d, J=9.9 Hz, 1H)	37.43, 37.22, 27.34, 27.30	-
 **47**[d]	6.36 (m, 2H), 3.00 (d, J=1.8Hz, 2H), 2.95 (s, 2H), 1.84 (d, J=9.5Hz, 1H), 1.28 (d, J=9.5Hz, 1H)	140.35, 43.66, 41.82, 41.72	124[c] (72), 123 (100), 97 (60), 91 (70), 79 (28), 78 (14), 77 (23), 66 (14), 65 (16)
 **77**	5.74 (J=2.1 Hz, 2H), 3.30 (t, J=1.7 Hz, 2H), 3.02 (bs, 2H), 2.13 (d, J=8.1 Hz, 1H), 2.04 (d, J=7.5 Hz, 1H)	130.32, 62.39, 43.73, 32.84	124[c] (94), 123 (84), 97 (70), 92 (14), 91 (100), 79 (57), 78 (23), 77 (31), 66 (22), 65 (20), 58 (18), 51 (12), 45 (25), 39 (26).
 **78**	3.53 (bs, 2H), 3.12 (bs, 1H), 2.26 (m, 1H), 2.21 (m, 2H), 1.42 (t, J=1.5 Hz, 2H)	56.26, 55.68, 37.95, 35.07, 28.43	124[c] (100), 123 (96), 97 (81), 92 (15), 91 (98), 79 (65), 78 (28), 77 (36), 66 (30), 65 (26), 58 (12), 51 (11), 45 (25), 39 (20)
 **48**[d]	3.50 (s, 2H), 2.50 (s, 1H), 1.83 (s, 2H), 1.55 (d, J=5.0Hz, 2H), 1.18 (d, J=5.0Hz, 1H)	55.29, 50.36, 31.08, 18.01, 10.02	156[c] (82), 123 (71), 92 (20), 91 (100), 79 (8), 78 (5), 77 (9), 66 (16), 65 (13), 45 (9)
 **49**[d]	3.00 (s, 2H), 1.95 (s, 1H), 1.72 (d, J=5.6Hz, 2H), 1.55 (d, J=5.6Hz, 1H), 1.30 (s, 2H)	47.94, 36.06, 35.75, 15.20, 12.00	188[c] (76), 156 (100), 123 (91), 122 (25), 91 (40), 66 (7), 65 (8), 64 (12), 45 (9)

[a] $CDCl_3$, δ in ppm. [b] EI-MS. [c] $M^{+\cdot}$ parent ion. [d] Isolated by Ghosh and Bartlett, ref. 187, 194.

Table 21. NMR and MS Data for Compounds **47**, **48**, **49**, **69**, **77** and **78**

3.2. Some Chemistry of S_{12} and S_{20}

Both *cyclo*-dodecasulfur (S_{12}) and *cyclo*-eicosasulfur (S_{20},) will be discussed in this Section as these sulfur allotropes share many common features.

3.2.1. Background

S_{12} and S_{20} were obtained as pure solids very early in the development of sulfur allotrope synthesis, being prepared for the first time by the methatetic method of Schmidt.[105,106b,107]

Both S_{12} and S_{20} have also been successfully extracted from sulfur melts.[100] The first-ever method for a sulfur allotrope extraction from liquid sulfur was actually developed by Schmidt[99] for S_{12}, but remains very controversial as it was never repeated successfully.

The most efficient procedure for S_{12} and S_{20} synthesis remains the organometallic route with the use of titanocene pentasulfide (**28**). Both S_{12}[113] and S_{20}[115d] are side products of the reactions leading to the synthesis of S_6 and S_{10}, respectively. Their formation can be explained mechanistically as shown in Figure 22 and Figure 31. Allotrope S_{12} is produced in isolated yields of 11% by this method. As for S_{20}, the experimental procedure leading to S_{10} can be modified slightly to give S_{20} in isolated yields of 8%.

S_{12} and S_{20} have also been produced in low yields (1-2% for S_{12} and 0.4% for S_{20}) by the reaction of S_2Cl_2 with aqueous KI.[131] This reaction mainly produces S_6. S_{20} has also been detected as a product of the reaction between the dinuclear complex **30** and S_2Cl_2.[119a] Finally, slow decomposition of S_8O at -20°C in CS_2 produces S_{12}.[134]

The structures of S_{12} and S_{20} have been determined by single crystal X-ray diffraction. S_{12} belongs to the group of highly symmetrical sulfur rings generally defined by equal bond distances (205 ± 2 pm), bond angles close to 105° (± 3°) and torsion angles near 85° (± 15°).[152] S_{20}, on the contrary, belongs to the less symmetrical group of sulfur rings that possess alternating bond distances and large variations in their torsion angles.[106b,107] Their structures are shown in Figure 61 and some of the parameters are reported in Table 22.

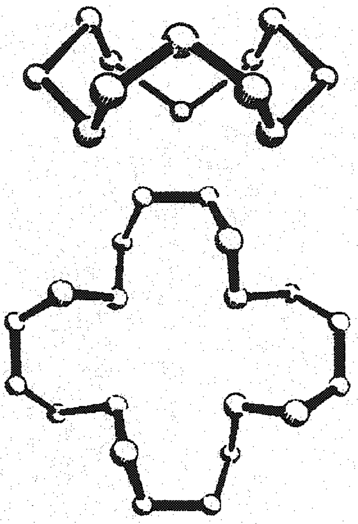


Figure 61. Structures of S_{12} and S_{20}

Molecule	Interatomic Distances (pm)	Bond Angles (°)	Torsion Angles (°)
S_{12}	205-206	105-107	86-89
S_{20}	202-210	105-108	66-90

Table 22. Some Parameters of the Structure of S_{12} and S_{20}

Needle-like single crystals of S_{12}, which can be obtained from benzene, are yellow and melt at 146-148°C.[100a] This melting point is the highest of all sulfur allotropes and is even almost 20 degrees higher than sulfur in its elemental form. The average bond distances of S_8 and S_{12} are identical, which make them structurally very close. S_{12} is thus usually regarded as the second most stable allotrope after S_8. S_{20} crystallizes as pale yellow rods and melting points between 120-130°C with decomposition have been reported.[100b,107] More details on the melting point, the stability and the decomposition behavior of S_{12} and S_{20} have been reported.[148]

3.2.2. Synthesis and Characterization

Two synthetic methods were used in the course of this study for the formation of S_{12} while only one method was used for the generation of S_{20}.

S_{12} was at first synthesized by extraction from liquid sulfur in 0.08% yield, which was lower than the one reported by Steudel (0.2%).[100] In contrast to the quite complicated custom-made apparatus[100b] designed by Steudel, the experimental setup used in this study was much simpler. Elemental sulfur (S_8) was heated in a beaker with an oil bath and the contents of the beaker simply poured into liquid nitrogen when appropriate. The temperature stabilization of the melt was probably much less accurate than that of Steudel's and the speed of quenching in nitrogen probably not as efficient. These two differences, among others, probably account for the drop in yield that was observed.

The second method to generate S_{12} used in this work was the one of Schmidt,[113] which takes advantage of the reaction between titanocene pentasulfide (**28**) and sulfur dichloride (SCl_2). As explained in Chapter 1, S_{12} is a side product of this reaction that mainly produces S_6. Yields for S_{12} obtained by this method averaged 8%, in agreement with the 11% yield reported by Schmidt. In view of the improved yield of S_{12} obtained by this method, it has quickly become the method of choice for the present work.

S_{20} was only prepared by the organometallic route, which involves the reaction between titanocene pentasulfide (**28**) and sulfuryl chloride (SO_2Cl_2), as was previously mentioned. The experimental procedure that allows for the direct isolation of pure S_{20} in 8% yield was not used.[115d] S_{20} was instead collected over time, as the side product obtained from the procedure designed to prepare S_{10}.[124a] S_{20} was separated from S_{10} by exploiting its solubility difference in CS_2. Yields for S_{20} averaged 5%. S_{20} batches were then purified either by recrystallization from CS_2 or just simply washed at room temperature with CS_2 in order to remove any remaining S_{10}. Recrystallization was avoided most of the time because large amounts of the very flammable CS_2 were needed due to the low solubility of S_{20} in this solvent. All details for the synthesis of S_{12} and S_{20} are reported in the Experimental Section in Chapter 5.

The characterization of S_{12} and S_{20} was again achieved by FT-Raman spectroscopy. Table 23 and Table 24 report the positions of the main vibrational modes observed for S_{12} and S_{20}, respectively. A comparison with existing spectra is also provided.[216]

Two representative HPLC runs for S_{12} and S_{20} are also reported in the Appendix Section and attest to the purity of each sample. Small amounts of residual S_8 could occasionally be detected along with the desired sulfur allotrope.

$S_{12}{}^a$			$S_{12}{}^b$		
	289 (13)	127 (80)	475 (vw)	289 (m)	127 (vs)
459 (100)	243 (17)		460 (vs)	245 (m)	67 (s)
448 (35)	shoulder	64 (32)	449 (s)	238 (m)	63 (vs)
				221 (vvw)	58 (m-s)
				180 (sh)	43 (vs)
	177 (22)			177 (m-s)	31 (vs)
	shoulder			170 (m)	
				156 (vvw)	

[a] FT-Raman/Nd-YAG laser/1064 nm/2.6 cm^{-1}/room temperature. [b] Ref. 216b; Cary 82 Raman spectrometer/Krypton laser/647 nm/1.5 cm^{-1}/-80°C.

Table 23. Raman Spectra for S_{12}

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[216] For S_{12}: See ref. 134 and a) Steudel, R. *Spectrochim. Acta*, **1975**, *31a*, 1065. b) Steudel, R. and Mäusle, H.-J. *Z. Naturforsch.*, **1978**, *33a*, 951. For S_{20}: See ref. 100b.

S_{20}[a]			S_{20}[b]		
	270 (28)		470.5 (41)	270 (26)	113 (4)
466.5 (100)		95 (59)	466 (100)	254 (sh)	93 (63)
	251 (28)	67 (31)	462 (sh)	250 (24)	66 (46)
			454 (9)	213 (5)	54 (31)
444 (20)	208 (8)		444 (17)	207 (5)	48 (17)
427 (10)	187 (15)		428 (8)	188 (12)	40 (sh)
			416 (3)	173 (5)	32 (34)
	169 (20)		411 (3)	167 (16)	29 (sh)
	137 (64)			136 (73)	18 (7)

[a] FT-Raman/Nd-YAG laser/1064 nm/2.6 cm^{-1}/room temperature. [b] Ref. 100b; Cary 82 Raman spectrometer/Krypton laser/647 nm/1.5 cm^{-1}/-100°C.

Table 24. Raman Spectra for S_{20}

3.2.3. Reaction of S_{12} and S_{20} with 1,3-Dienes and Norbornene

This Section reports the results obtained for the reaction between S_{12} and S_{20} with 1,3-dienes such as 2,3-diphenyl-1,3-butadiene (**12a**) and 2,3-dimethyl-1,3-butadiene (**12b**), and a strained olefin, norbornene. These substrates have already been studied in reactions with S_{10} and S_9. The results will thus be compared to the ones obtained previously and will enlarge the understanding of sulfur homocycle chemistry.

All reactions were carried out in small scale due to the difficulty of preparation of both S_{12} and S_{20}, which were only obtained in low yields. 9-Methylanthracene was used as an internal standard in order to estimate (by ^{1}H-NMR) the yields of products obtained during these reactions. All products were identified by comparison with authentic samples. Apart from pentasulfide **46**, all compounds resulting from these reactions had been identified in previous experiments of the current study.

Allotropes S_{12}[166] and S_{20} are very poorly soluble in carbon disulfide (CS_2). Because of this characteristic, a modification to the experimental protocol used for S_{10} and S_9 had to be devised. Under the usual experimental conditions, the sulfur homocycle, once dissolved into an adequate volume of CS_2, is added to the hot olefin and the mixture is thus homogeneous at all times during the reaction. In the present case, S_{12} and S_{20} had to be used directly and reaction mixtures were heterogenous. However, both S_{12} and S_{20} suspensions remained finely divided as small particles and results were reproducible.

The temperatures at which these reactions were carried out were the ones of the refluxing solvents, chlorobenzene and toluene. The reaction temperatures were thus higher than in the S_{10} and S_9 trapping reactions, for which a 15°C drop was observed due to the addition of CS_2.

For both reaction sets, heating was maintained until no more particles could be seen in suspension in the reaction mixture. At the end of each reaction it was also verified by HPLC that S_{12} and S_{20} were no longer present in the mixture.

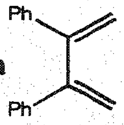
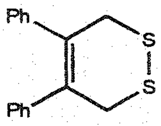
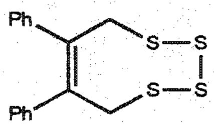
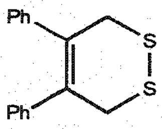
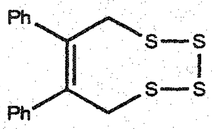
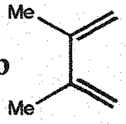
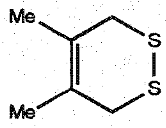
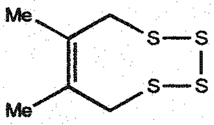
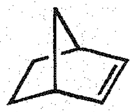
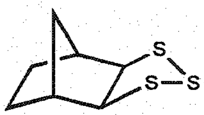
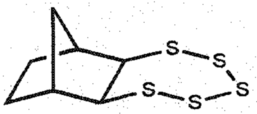
Substrate	Conditions (solv./°C/hr)	Products Yield and Ratio
12a 	Chlorobz./130/3	 **13a** 3.5:1  **35** 51%
	Toluene/115/15	 **13a** 5.5:1  **35** 65%
12b 	Toluene/115/15	 **13b** 5.5:1  **36** 50%
16 	Toluene/115/15	 **19**  **46**, Traces (*ca.* 4%) 80%

Table 25. Reaction of Selected Olefins with S_{12}

The results for the reaction between equimolar amounts of S_{12} and 2,3-diphenyl-1,3-butadiene (**12a**), 2,3-dimethyl-1,3-butadiene (**12b**) and norbornene (**16**) are reported in Table 25.

The results for the reaction between equimolar amounts of S_{20} and 2,3-diphenyl-1,3-butadiene (**12a**), 2,3-dimethyl-1,3-butadiene (**12b**) and norbornene (**16**) are reported in Table 26.

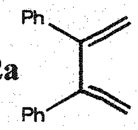
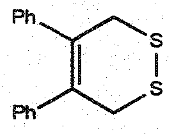
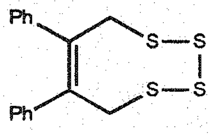
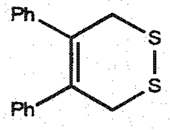
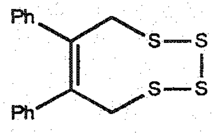
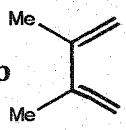
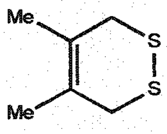
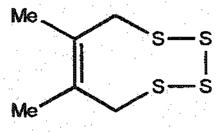
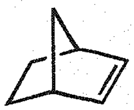
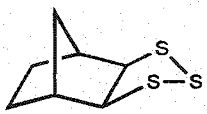
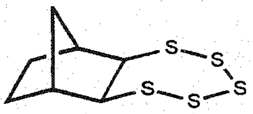
Substrate	Conditions (solv./°C/hr)	Products Yield and Ratio
12a 	Chlorobz./130/3	  **13a** 4.5:1 **35** 51%
	Toluene/115/15	  **13a** 5.5:1 **35** 67%
12b 	Toluene/115/15	  **13b** 7.5:1 **36** 64%
16 	Toluene/115/15	 **19**  **46**, Traces (< 1%) 70%

Table 26. Reaction of Selected Olefins with S_{20}

Table 27 and Table 28 summarize the results obtained for selected control reactions for S_{12} and S_{20}, respectively. These control reactions were carried out with S_8 as the sulfurating agent in order to offer a good base for comparison. All S_{12} control reactions used 3/2 equivalents of S_8 and all S_{20} control reactions used 5/2 equivalents of S_8 in order to respect the number of moles of sulfur atoms.

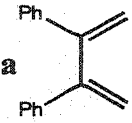
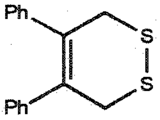
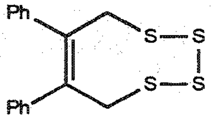
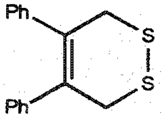
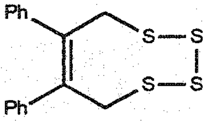
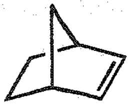
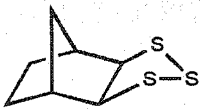
Substrate	Conditions (solv./°C/hr)	Products Yield and Ratio
12a 	Chlorobz./130/3	 **13a** 7.5:1  **35** 36%
	Toluene/115/15	 **13a** 7:1  **35** 30%
16 	Toluene/115/15	 **19** 38%

Table 27. Control Reactions for S_{12} Trapping

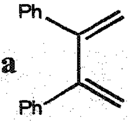
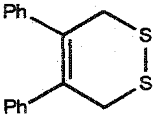
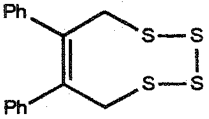
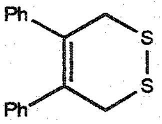
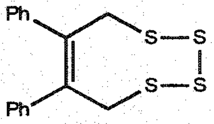
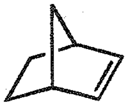
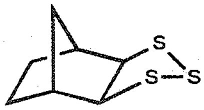
Substrate	Conditions (solv./°C/hr)	Products Yield and Ratio
12a 	Chlorobz./130/3	 **13a** 7:1  **35** 39%
	Toluene/115/15	 **13a** 6:1  **35** 42%
16 	Toluene/115/15	 **19** 36%

Table 28. Control Reactions for S_{20} Trapping

3.2.4. Discussion

From the results reported in Tables 25 and 26, a few discussion points will now be addressed in order to compare qualitatively and quantitatively the behavior of S_{12} and S_{20} with elemental sulfur as well as with S_{10} and S_9 sulfur allotropes.

The reaction of equimolar amounts of S_{12} and S_{20} with 1,3-dienes **12a** and **12b** yielded the expected disulfide and tetrasulfide adducts, thus showing no difference compared to the products obtained with S_8, S_9 or S_{10}. Overall yields of trapped products appeared to be almost identical in the case of 2,3-diphenyl-1,3-butadiene (**12a**) with both allotropes (51% at 130°C and *ca.* 66% at 115°C). The yields were however slightly more disparate in the sulfuration reaction of 2,3-dimethyl-1,3-butadiene (**12b**). These overall yields varied from moderate to good and fell into the same range as the ones observed with S_9 or S_{10}. Despite the heterogeneity of the reaction medium, trapping reaction proceeded efficiently. S_{12} and S_{20} stayed as small particles and did not agglomerate, which, contrary to what was observed with S_{10}, explains why yields were reproducible. It is important to note though that the number of mole equivalents of sulfur atoms is greater in the case of S_{12} and S_{20} compared to S_9 and S_{10}. Trapping reaction with two equivalents of S_{10} and 1,3-diene **12a** resulted, for example, in a much better 86% overall yield (at *ca.* 115°C in chlorobenzene/CS_2 for 2.5 hr), as opposed to a maximum 67% (at 115°C in toluene for 15 hr) with one equivalent of S_{20}. When compared to the results obtained by their respective control reactions with elemental sulfur (S_8), S_{12} and S_{20} actually appear to be quite poor sulfurating agents towards 1,3-dienes. Figure 62 presents the yield increase obtained with the different sulfur allotropes compared to their respective control reaction yields with S_8 during the small scale sulfuration reaction of 2,3-diphenyl-1,3-butadiene (**12a**). These reactions were all carried out at *ca.* 115°C in refluxing toluene for S_{12} and S_{20} and in chlorobenzene/CS_2 for S_9 and S_{10}. Reaction times varied widely, however, from 2-3 hours for S_{10} and S_9 respectively and up to 15 hours for S_{12} and S_{20}. The reaction time depends on how quickly the sulfur ring decomposes at the temperature of the reaction. Figure 62 shows a large difference in sulfuration efficiency between the different allotropes. Switching from S_8 to S_{20} or S_{12} only amounts to a *ca.* 60% and 120%

increase in yield, respectively, whereas the same comparison for S_{10} reveals a yield increase close to 2700%. This comparison thus demonstrates that within the experimental conditions that were used, S_{10} appears to be *45 times* more efficient than S_{20} and *22 times* more efficient than S_{12} at sulfurating 1,3-diene **12a**. The same calculations for S_9 show that this allotrope is *11* and *5 times* more efficient than S_{20} and S_{12}, respectively.

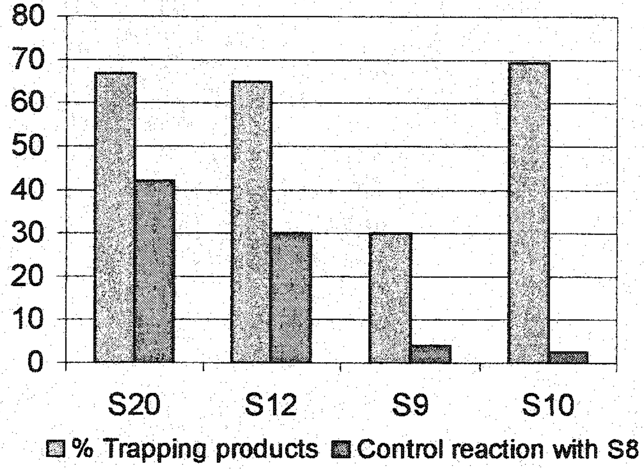


Figure 62. Sulfuration of 2,3-Diphenyl-1,3-butadiene: Comparison of S_9, S_{10}, S_{12} and S_{20}

Table 25 and 26 reveal that during the reaction of S_{12} or S_{20} with 2,3-diphenyl-1,3-butadiene (**12a**), higher yields of trapped products were obtained when lower temperatures were used; 51% trapping at 130°C and an average 66% at 115°C. This phenomenon does not seem to be solvent related. Indeed, control reactions with S_8 show a more expected behavior, higher yields being obtained at high temperatures (see Table 27 and 28). It should however be mentioned that the value observed for the S_{20} control reaction in chlorobenzene seems abnormally low. The rapid decomposition of S_{12} and S_{20} at high temperatures is probably the main reason for such behavior. Steudel showed that both allotropes decompose quite rapidly at 130°C.[148] Similarly to S_{10} or S_9, S_{12} and S_{20} rings open to form polymeric sulfur (S_μ), which depolymerizes upon further heating to finally yield S_8. Similarly to what was observed in the first steps of the optimization of the model reaction with S_{10}, S_{12} and S_{20} polymerization process competes with the trapping reaction itself, thus explaining the observed decreased yields. S_μ was proven to be totally unreactive towards 1,3-dienes at these temperatures (see Chapter 2); at 115°C, however, the decomposition of S_{12} and S_{20} is slower and trapping reaction can more efficiently occur.

In terms of the ratios of disulfide/tetrasulfide adducts, the case of S_{12} is particularly interesting as a general pattern seems to evolve from the interpretation of the data. Indeed, sulfuration of 1,3-dienes **12a** and **12b** with S_{12} consistently produced tetrasulfide adducts **35** and **36** in larger amounts than what was observed for S_{10}, S_8 or even S_9. Ratios of *ca.* 5.5:1 of disulfide/tetrasulfide were obtained at 115°C for both 1,3-dienes **12a** and **12b**, which contrasts strongly with the maximum 9.5:1 ratio observed with S_{10} (see Table 8) and the 7:1 ratio observed with S_8 (see Table 27). The selectivity of S_{12} towards the formation of disulfide adducts **13a** and **13b**, thus seems to be decreased.

Further, this trend is even emphasized when higher reaction temperatures were used. The ratio **13a/35** dropped to a low 3.5:1 at 130°C. The same ratio stayed steady throughout the experiments at 115°C and 130°C for both S_{10} and S_8. A quick decomposition of S_{12} thus seems to result in an increased tetrasulfide selectivity. This selectivity is not however totally inverted as was first thought.[81c] Mechanistic aspects of this reaction will be discussed in Chapter 4 and will qualitatively explain this behavior.

In the case of S_{20}, the results obtained for the ratios of disulfide/tetrasulfide were more erratic. Although some of these results seem to follow a similar pattern to what was concluded for S_{12}, as a loss in disulfide adduct formation selectivity was also observed, it is more difficult to be fully conclusive.

It is interesting to note that the control reactions for both S_{12} and S_{20} revealed that in pure chlorobenzene or toluene, the ratios of disulfide/tetrasulfide obtained from the sulfuration of 1,3-diene **12a** with S_8 were as high as 7.5:1. These ratios contrast with the ones obtained for S_{10} or S_9 control reactions in chlorobenzene/CS_2 or toluene/CS_2, which were much lower at *ca.* 4:1.

The reaction between equimolar amounts of S_{12} or S_{20} with norbornene proceeded at 115°C in good overall yields (80% for S_{12} and 70% for S_{20}) as shown in Table 25 and 26. Trithiolane **19** was identified as the major product in both cases. Similarly to what was obtained for 1,3-dienes, the sulfuration efficiency of these two allotropes does not appear to be as high as the one of S_{10}. Indeed, control reactions with S_8 under similar experimental conditions also produced significant amounts of trithiolane **19**. The results obtained with S_9 were more modest as it was discussed in previous Sections. Figure 63 compares S_{12}, S_{20}, S_{10} and S_9 with respect to their control reaction with S_8. The reaction between norbornene and S_{12} or S_{20} was carried out at 115°C in refluxing toluene for 15 hours, while the same reaction with S_{10} and S_9 proceeded at *ca.* 100°C in a co-solvent toluene/CS_2 for only 3 hours.

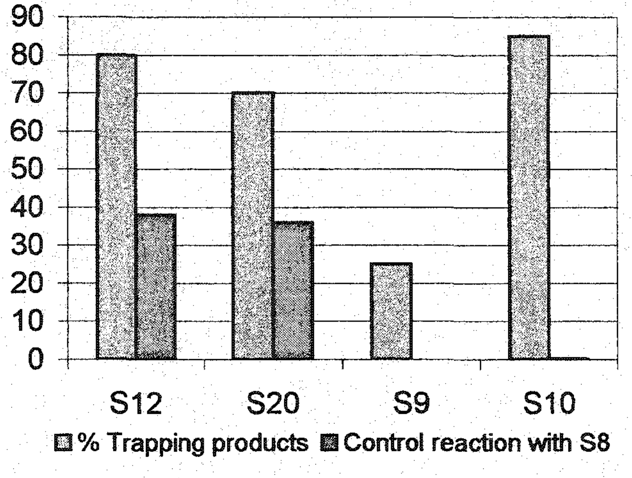


Figure 63. Sulfuration of norbornene: Comparison of S_9, S_{10}, S_{12} and S_{20}.

The control reactions for S_9 and S_{10} produced only trace amounts of trithiolane **19**, if any, under the mild conditions used. Only 0.25% trithiolane **19** was estimated to have formed in the control reaction for S_{10} by comparison with an internal standard, while no traces of this adduct were detected for S_9 control reaction. Relatively low (110% and 95%) yield increases were observed when S_{12} or S_{20} was used as a sulfurating agent instead of S_8. The use of S_{10} thus appears to be considerably more efficient. It also provides a milder and faster reaction.

An interesting aspect is the presence in low concentration of pentasulfide **46** in the crude reaction mixtures from the sulfuration of norbornene with S_{12} and S_{20}. In contrast, no traces of pentasulfide **46** were detected in the same sulfuration reactions with S_9 or S_{10}. Even control reactions with S_8 did not produce **46** under these non-polar conditions, which is different from what was observed by Ghosh and Bartlett in polar solvents.[187,194]

This result seems to indicate the ability of S_{12} and S_{20} to liberate longer polysulfide chains than the other sulfur allotropes.

3.3. Conclusion

The results obtained in this Chapter have shown that, in terms of yields, S_9, S_{12} and S_{20} are not as good sulfurating agents as S_{10} towards 2,3-diphenyl-1,3-butadiene (**12a**) and 2,3-dimethyl-1,3-butadiene (**12b**), or norbornene (**16**). These allotropes are more rare and difficult to synthesize than S_{10}, which makes them less appealing and useful for methodology purposes.

However, they have revealed very interesting properties with regards to the qualitative results that were obtained. S_9 has the ability to deliver a single sulfur atom to norbornene. On the other hand, S_{12} and to a lesser extent S_{20}, show an increased selectivity towards the production of tetrasulfide adducts when reacted with 1,3-dienes **12a** or **12b**, or more generally an ability to deliver longer polysulfide chains.

CHAPTER 4. CONCLUSION and MECHANISTIC STUDY

Reaction sequences to account for the products of the reactions between sulfur allotropes and olefins will be proposed in this Section.

4.1. Background

The mechanistic study of the reactions involving S_{10}, S_9, S_{12} and S_{20} sulfur allotropes with simple or conjugated alkenes is very closely related to the way in which sulfur homocycles decompose. Processes such as sulfur polymerization or sulfur ring interconversion will be discussed.

As already mentioned in Chapter 2, thermal homopolymerization of elemental sulfur S_8 is a well-known process that was first described by Tobolsky and Eisenberg[73] and was also studied by other groups.[74] When a sulfur melt is heated above its critical polymerization temperature of 159°C,[71] the sulfur rings are fully transformed into longer sulfur chains or very large sulfur rings. Polymeric sulfur S_∞ is formed. A radical chain reaction has been postulated in order to explain the formation of S_∞ by polymerization of S_8.[217] An initiation step, which consists of the homolytic cleavage of an S-S bond, is then followed by a propagation step as shown in Figure 64.

$$S_8^R \longrightarrow S_8^C$$

$$S_8^C + S_8^R \longrightarrow S_{16}^C$$

$$S_{16}^C + n\,S_8^R \longrightarrow S_\infty$$

R=ring
C=chain

Figure 64. S_8 Polymerization

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[217] a) Cordery, R. *Phys. Rev. Lett.*, **1981**, *47*, 457. b) Steudel, R. *Z. Anorg. Allg. Chem.*, **1981**, *478*, 139. c) Wheeler, J. C. and Pfeuty, P. *Phys. Rev.*, **1981**, *24a*, 1050. d) Kennedy, St. J. and Wheeler, J. C. *J. Chem. Phys.*, **1983**, *78*, 953.

The presence of free radicals detected by ESR in sulfur melts at temperatures higher than 172°C supports this theory.[218] At temperatures below 172°C, a sudden drop in radical concentration is observed, but radicals can still be observed in melts at temperatures as low as 153°C. Also, sulfur radicals have been detected in quenched sulfur vapors or quenched liquid sulfur, as well as in irradiated α-S_8, at temperatures of 27°C.[219] Koningsberger even observed sulfur radicals in quenched sulfur melts which had been stored at room temperature for some weeks, thus showing the stability of some of these species. The structure of sulfur radicals has been discussed.[219]

Other sized sulfur rings S_n ($n \neq 8$) have been shown to play an important role in the polymerization process of S_8. The presence of small quantities of sulfur allotropes such as S_6 or S_7 in sulfur melts below the polymerization temperature has been studied (see Chapter 1). These less stable sulfur rings have been proposed to act as radical initiators for the polymerization process.[220] The decomposition behavior of ten sulfur allotropes and especially S_{10}, S_{12} and S_{20} has been studied by Steudel.[148] It was shown that these metastable rings all decompose at temperatures well below the polymerization temperature of S_8. In all cases, polymeric sulfur was isolated as an intermediate in the decomposition process of these allotropes as presented in Figure 36 for S_{10}.

The mechanism for the low temperature polymerization of sulfur allotropes S_n ($n \neq 8$) has not been established with certainty. A radical pathway does not appear to be a good candidate because no free radical has ever been detected in sulfur melts below 153°C, although the dissociation energy of long sulfur chains appears to be quite low (150 kJ/mol[220] for long S_n chains *vs.* 265 kJ/mol[221] for organic disulfides). Steudel and others

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[218] a) Gardner, D. M. and Fraenkel, G. F. *J. Am. Chem. Soc.*, **1956**, *78*, 3279. b) Van Aken, J. E. *Physica*, **1968**, *39*, 107. c) Koningsberger, D. C. and De Neef, T. *Chem. Phys. Lett.*, **1970**, *4*, 615. d) Kennedy, S. J.; Wheeler, J. C.; Osuch, C. and Wasserman, E. *J. Phys. Chem.*, **1983**, *87*, 3961.

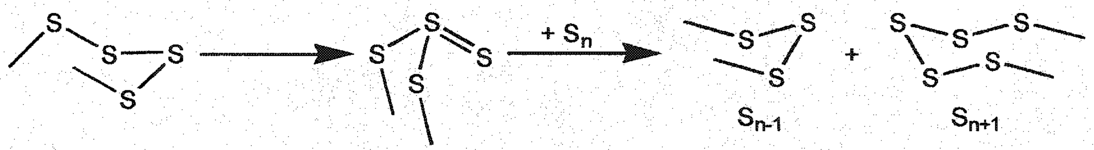
[219] Steudel, R.; Albertsen, J. and Zink, K. *Ber. Bunsenges. Phys. Chem.*, **1989**, *93*, 502 and references cited therein.

[220] Steudel, R. *Phosphorus, Sulfur*, **1983**, *16*, 251.

[221] Steudel, R. *Angew. Chem., Int. Ed. Engl.*, **1975**, *14*, 655.

have proposed alternative paths in order to explain sulfur-ring interconversion and low temperature polymerization for elemental sulfur allotropes.[98,148]

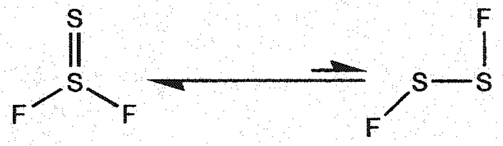
The capacity of sulfur rings to be in equilibrium with their corresponding thiosulfoxide parent compounds **84** has been advanced as one possible route for the interconversion between sulfur rings. These hypervalent sulfur species, which resemble their corresponding oxides S_nO, are thought to be key intermediates, for example to explain the formation of S_7 in quite substantial amounts when a pure sample of S_8 is being heated. This is summarized in Figure 65.



84

Figure 65. Intermediacy of Hypervalent Sulfur Species in Sulfur Ring Interconversions

Stable thiosulfoxide compounds, often referred to as branch-bonded sulfur species, have been isolated. One of the best-known examples is that of thiothionyl fluoride $F_2S{=}S$, a colorless gas.[222] It exists predominantly at room temperature in its branch-bonded form **85** rather than in its linear form **86** as shown in Figure 66.



85 **86**

Figure 66. Thiothionyl Fluoride Equilibrium

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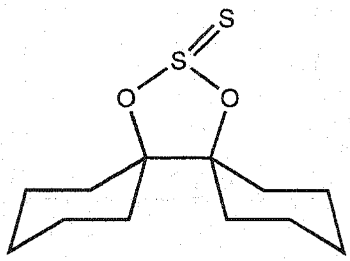
[222] a) Seel, F. and Budenz, R. *Chimia*, **1963**, *17*, 355. b) Seel, F. and Gölitz, H. D. *Z. Anorg. Allg. Chem.*, **1964**, *327*, 32. c) Marsden, D. J.; Oberhammer, H.; Lösking, O. and Willner, H. *J. Mol. Struct.*, **1989**, *193*, 233.

Harpp and co-workers have also obtained a single crystal X-ray structure for thionosulfite compound **87**.[223] Branch-bonded type compounds have been extensively reviewed.[224]



87

Spirocyclic species **88** have also been postulated as possible intermediates in order to explain sulfur ring interconversions or sulfur allotropes polymerization at low temperatures. Two possible paths have been advanced for the formation of intermediate **88** as shown in Figure 67. A first one involves thiosulfoxide **84** while a second possible path involves an insertion reaction that resembles the known insertion reaction of dialkyl sulfides R_2S into the covalent single bond of chlorine.[225] It is interesting to note that polymeric sulfur formed in this process would consist mainly of very large sulfur rings.

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[223] a) Harpp, D. N.; Steliou, K. and Cheer, C. J. *J. Chem. Soc., Chem. Commun.*, **1980**, 825. b) The structure of a second thionosulfite has also been determined where the two rings of **87** are 7-members: Abrams, C. and Harpp, D. N., unpublished results.

[224] Kutney, G. W. and Turnbull, K. *Chem. Rev.*, **1982**, *82*, 333.

[225] Baenzinger, N. C.; Buckles, R. E.; Maner, R. J. and Simpson, T. D. *J. Am. Chem. Soc.*, **1969**, *91*, 5749.

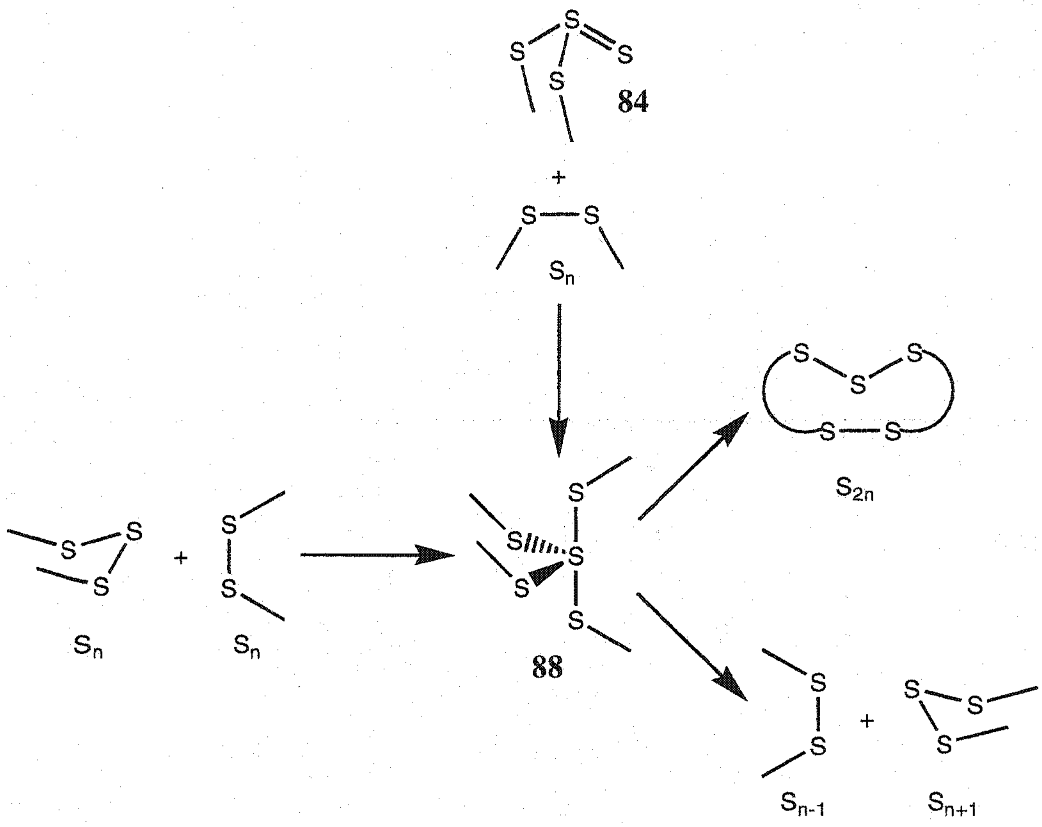
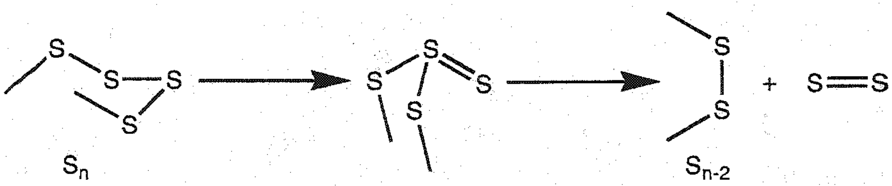


Figure 67. Intermediacy of Spirocyclic Sulfur Species in Sulfur Ring Interconversions

One last mechanism postulated in order to explain sulfur ring interconversions or low temperature polymerization involves the direct generation of S_2 units from sulfur allotropes as shown in Figure 68. This mechanism resembles the process of extrusion of sulfur monoxide from thiirane oxides.[226] This path appears, however, very unlikely as it would be a highly energy demanding process.[98a] Moreover, only sulfur rings having even numbers of sulfur atoms would result from such reactions. This is not consistent with the polymerization mechanism as S_7 was detected in the thermal decomposition of sulfur allotropes.[148] In the course of the present study, it was also conclusively demonstrated that S_{10} does not produce diatomic sulfur S_2. No tetrasulfide **35** was detected when S_{10} was reacted with disulfide **13a** (see Figure 39) contrary to what is observed for known S_2 chemistry, in which diatomic sulfur inserts into the S-S bond of disulfide **13a** thus forming its tetrasulfide analogue **35**.[81c]



84

Figure 68. Direct S_2 Generation from Sulfur Rings

All these possible mechanisms have been the topic of theoretical studies.[227] Hypervalent species **88** have been advanced as the preferred intermediates in order to explain both sulfur ring interconversions and low temperature polymerization processes.[227b]

However, in view of the experimental results reported in Chapters 2 and 3 of the present study, it appears that the path of radical decomposition of sulfur allotropes by homolytic cleavage of S-S bonds was worthy of investigation. The following paragraphs will report the results obtained that show intermediates sulfur radicals in the decomposition of S_{10}, even at the quite low temperatures used in this study.

4.2. Evidence for the Radical Nature of the Decomposition Reaction of S_{10}

Different methods have been used in this study in order to implicate sulfur radicals in the decomposition reaction of S_{10} or during its reaction with olefins.

4.2.1. Use of Radical Scavengers.

Traditional radical scavengers were utilized in this study in order to examine their effect on the rates and the yields of the reactions between olefins and S_{10}. 2,6-Di-*tert*-

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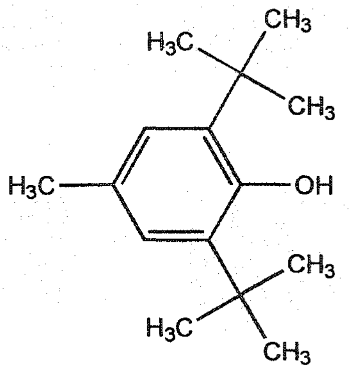
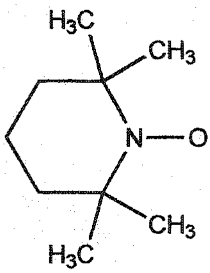
[226] Abu-Yousef, I. A. and Harpp, D. N. *J. Org. Chem.*, **1997**, *62(24)*, 8366 and references cited therein.

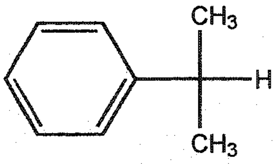
butyl-4-methyl phenol also commonly called butylated hydroxytoluene or BHT (**89**)[228] and 2,2,6,6-tetramethyl-1-piperidinyloxy free radical also referred to as TEMPO (**90**)[229] were used as radical traps in the model reaction between equimolar amounts of S_{10} and 2,3-diphenyl-1,3-butadiene (**12a**). Cumene (**91**), which is known for its hydrogen atom donor capability towards sulfur radicals,[230] was also used as a solvent instead of xylenes in the same model reaction.



89



90



91

The yields of the expected products disulfide **13a** and tetrasulfide **35** were measured by internal standard comparison with 9-methylanthracene after 2 hours of reaction and are summarized in Table 29. For each one of these experiments, a control reaction was carried out in the same conditions without the addition of any radical trap. Carbon disulfide (CS_2) was used as usual in order to dissolve S_{10} prior to its addition to the hot diene.

---

[227] a) Laitinen, R. S.; Pakkanen, T. A. and Steudel, R. *J. Am. Chem. Soc.*, **1987**, *109*, 710. b) Steudel, R.; Drozdova, Y.; Miaskiewicz, K.; Hertwig, R. H. and Koch, W. *J. Am. Chem. Soc.*, **1997**, *119*, 1990.

[228] Janzen, E. G.; Wilcox, A. L. and Manoharan, V. *J. Org. Chem.*, **1993**, *58*, 3597.

[229] a) Yoshimura, Y.; Inomata, T.; Nakazawa, H.; Kubo, H.; Yamaguchi, F. and Ariga, T. *J. Agric. Food Chem.*, **1999**, *47(11)*, 4653. b) Matsuhashi, T.; Liu, X.; Karbowski, M.; Wozniak, M.; Antosiewicz, J. and Wakabayashi, T *Free Radical Biol. Med.*, **1997**, *23(2)*, 285. c) Step, E. N.; Buchachenko, A. L. and Turro, N. J. *J. Am. Chem. Soc.*, **1994**, *116(12)*, 5462. d) Root, K. S.; Hill, C. L.; Lawrence, L. M. and Whitesides, G. M. *J. Am. Chem. Soc.*, **1989**, *111(14)*, 5405.

[230] a) Pryor, W. A. and Griffith, M. G. *J. Am.Chem. Soc.*, **1971**, *93*, 1408. b) Pryor, W. A.; Gojon, G. and Stanley, J. P. *J. Am.Chem. Soc.*, **1973**, *95*, 945. c)

Radical Trap	Conditions (solv./°C/hr)	Yields[a] of **13a**+**35**	Ratio **13a**/**35**
BHT[b]	Toluene/100/2	58%	9
Control	Toluene/100/2	63%	6-7
TEMPO[c]	Chlorobz./115/2	13%	4
Control	Chlorobz./115/2	69%	6-7
Cumene[d]	Cumene/130/2	29%	1
Control	Xylenes/130/2	60%	7.5

[a] Yields are all based on 1 equimolar amount of 2,3-diphenyl-1,3-butadiene (**12a**). [b] 4 equimolar amounts. [c] 2 equimolar amounts. [d] Used as a solvent.

Table 29. Effect of Selected Radical Scavengers on S_{10} Trapping with 1,3-Diene **12a**

The results reported in Table 29 all show that the reaction between 1,3-diene **12a** and S_{10} was altered by the addition of radical traps in the reaction medium. All yields were lower than the ones reported in the respective control reactions. While the use of BHT only slightly affected the yields of disulfide **13a** and tetrasulfide **35** after 2 hours of reaction, the use of TEMPO as a radical trap or of cumene as a solvent showed a greater effect with an 80% and a 50% drop in yields, respectively.

However, the reaction with BHT as a radical scavenger was more altered in the earlier stage of the reaction (*ca.* 30% decrease in product yields after 0.5 hr) than what it appears in Table 29 after 2 hours. A comparison between this reaction and its control reaction is shown in Figure 69.

Miyashita, T.; Iino, M. and Matsuda, M. *Bull. Chem. Soc. Jpn.*, **1977**, *50*, 317. d) Pryor, W. A.; Gojon, G. and Church, D. F. *J. Org.Chem.*, **1978**, *43*, 793.

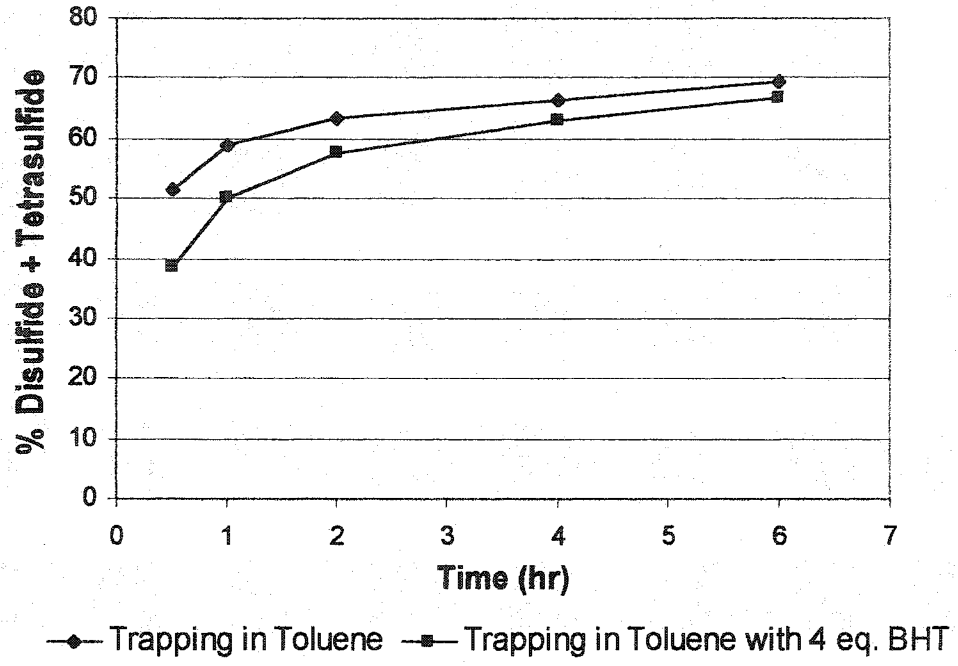


Figure 69. Effect of BHT on S_{10} Trapping Reaction with 1,3-Diene **12a**

It is important to recognize that when S_{10} was reacted with BHT alone, a 15-20% loss in the intensity of the OH signal of BHT was measured in the ^{1}H-NMR spectra that were taken at regular intervals during the first 2 hours of reaction. Any possible addition product between S_{10} and BHT was not detected though.

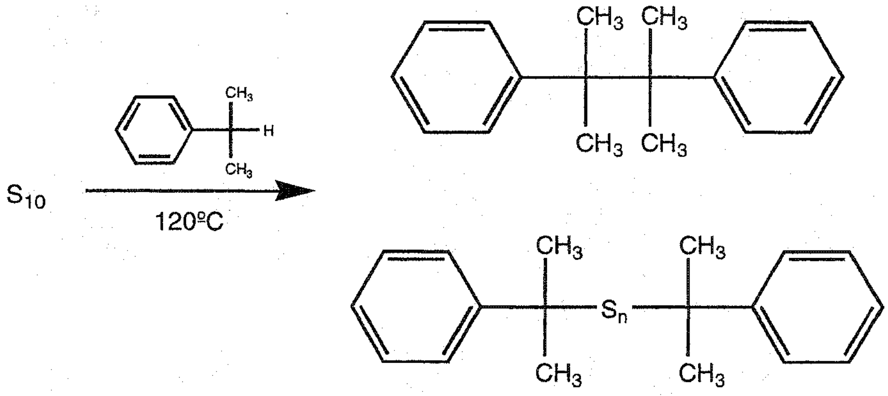
The ratios between disulfide adduct **13a** and tetrasulfide adduct **35** were also affected by the use of radical traps. The most drastic changes were observed in the case of cumene for which almost equal amounts of the two products **13a** and **35** were formed.

The reaction between S_{10} and 1,3-diene **12a** was thus affected by the use of radical scavengers, which constitutes a first sign of the radical nature of such reactions or at least of the implication of radicals species. The reactions were not actually completely quenched by the use of radical traps or even when cumene was used as a reaction solvent. 1,3-Diene **12a** was obviously a good competing entity for the radical traps that were used. 1,3-Butadiene has been used in the past as an efficient trap for radicals in the gas phase.

4.2.2. Reaction between Cumene and S_{10}

As reported in the previous paragraph, the reaction between 1,3-diene **12a** and S_{10} was altered when cumene was used as a solvent. This indicated that possible sulfur radicals abstracted the hydrogen atom of cumene to form hydrosulfanes HS_nH and cumyl radicals.

It was thus decided to decompose S_{10} dissolved in carbon disulfide (CS_2) in a cumene solution kept at 120°C by an oil bath. After 2 hours, the reaction was stopped and column chromatography of a complex mixture allowed the isolation of bicumyl (**92**) in 4% yield, as well as what was identified as a mixture of di-cumyl polysulfides (**93**). This is shown in Figure 70. All details for the reaction conditions are reported in the Experimental Section in Chapter 5.



92

93

Figure 70. Decomposition of S_{10} in Cumene at 120°C

Bicumyl was identified by comparison of ^1H-NMR data with data already reported in the literature.[231] Analysis of the sample by CI-MS showed a most abundant peak corresponding to half of the parent molecule at 119. ^1H-NMR data for compound **92** is reported in Table 30 along with a ^1H-NMR of pure cumene as a comparison.

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[231] Kratt, G.; Beckhaus, H.-D.; Lindner, H. J. and Rüchardt, C. *Chem. Ber.*, **1983**, *116*, 3235.

The identification of compound **93** was more difficult as it appeared to be a mixture of at least five polysulfides. Indeed, the ^{1}H-NMR spectrum for **93** showed six signals corresponding to the methyl groups and six signals for carbon C_α in the corresponding ^{13}C-NMR. These differences in chemical shifts were attributed to the deshielding effect of increasing sulfur chain lengths between cumyl groups. One compound (corresponding to the least deshielded ^{1}H-NMR signal for $C_\beta H_3$ and ^{13}C-NMR signal for C_α) appeared to be more abundant than the others in the mixture (*ca.* 30% by integral comparison). NMR data for compound **93** as well as a comparison with 2,2,3,3-tetramethyl butane[232] and di-*tert*-butyl polysulfides[170] is provided in Table 30. The analysis of compound **93** by CI-MS showed peaks corresponding to all cumyl-S_n (n=0-4) fragments. No parent ion was observed.

Moreover, evolution of H_2S gas was detected during the thermal decomposition of S_{10} in cumene as darkening of paper moistened in a lead acetate solution was observed during the course of the reaction.[167] Polysulfanes HS_nH (n>1) are known to decompose with the production of H_2S gas.[233]

The isolation of compounds **92** and **93** as well as the evolution of H_2S gas as a result of the reaction between S_{10} and cumene at 120°C strongly implicates the presence of sulfur radicals during the thermal decomposition process of S_{10}. Indeed, from these results, it seems apparent that cumyl radicals, which were formed from hydrogen abstraction by sulfur radicals, either recombined or further reacted with sulfur.

4.2.3. Nature of the Products of the Reaction between Norbornadiene and S_{10}

One last demonstration for the radical nature of the decomposition reaction of S_{10} simply resides in the identity of the products obtained from its reaction with norbornadiene.

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[232] http://www.tciamerica.com/

[233] Moeckel, H. J. *Fresenius' Z. Anal. Chem.* **1984**, 318, 116-20.

As it was discussed in Chapter 2, only trithiolane **27** and *bis*-sulfurated compound **42** were isolated. This contrasts strongly with the set of products identified by Bartlett and Ghosh in the sulfuration reaction of norbornadiene with S_8 in polar solvents (see compounds **27**, **47**, **48**, **49** and **50**).[187] An ionic pathway was proposed for this reaction as shown in Figure 71.[194] Compounds resulting from double bond participation (compounds **48** and **49**) as well as 1,2-vinyl migration (compound **50**) were isolated, in agreement with other ionic reactions with norbornadiene, such as the addition of arylsulfenyl chloride already discussed in Chapter 3. Free radical reactions with norbornadiene have, on the contrary, shown that products issued from 1,2-vinyl migration are completely absent.[234] This was the case in the reaction between norbornadiene and S_{10}. No product from double bond participation could be detected in this reaction and the sole isolation of trithiolane **27** and of *bis*-sulfurated compound **42** constitutes a further indication as to the radical nature of the mechanism.

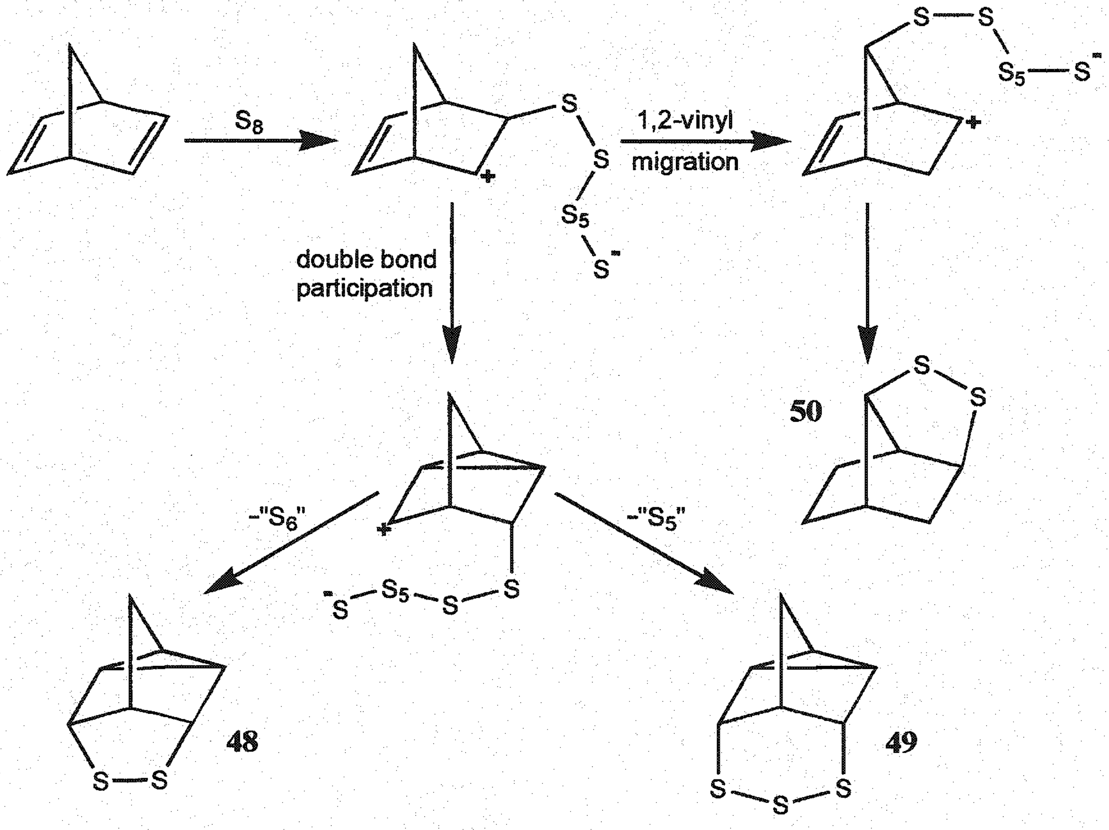

Figure 71. Ionic Mechanism Proposed by Bartlett and Ghosh for the Formation of Compounds **48**, **49** and **50**

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[234] Trecker, D. J. and Henry, J. P. *J. Am. Chem. Soc.*, **1963**, *85*, 3204.

4.3. Proposed Mechanisms

Based on the implication of sulfur radicals in the thermal decomposition of S_{10}, described above, mechanisms have been postulated in order to account for the formation of the different products isolated or detected in the course of this study.

It is thus proposed that the first step of the reaction between S_9, S_{10}, S_{12} or S_{20} and simple or conjugated alkenes is the homolytic cleavage of an S-S bond of the sulfur ring as shown in Figure 72 for S_{10}.

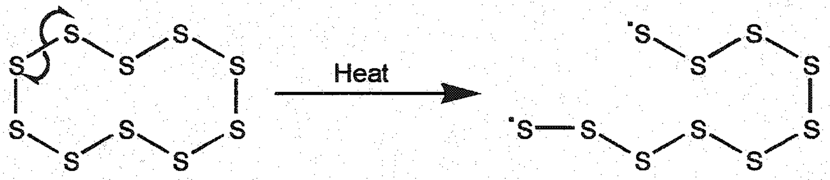
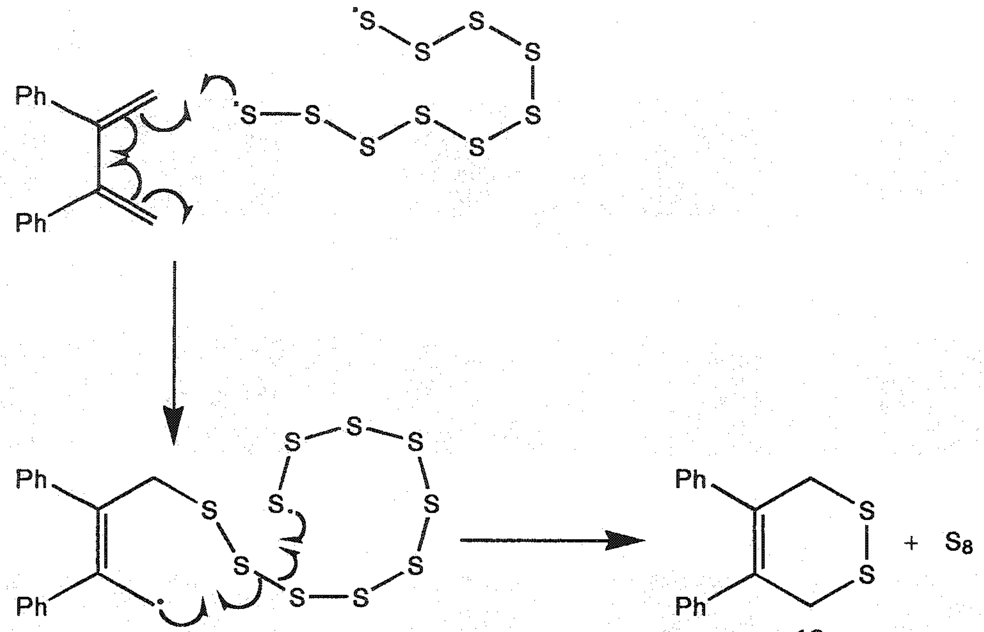


Figure 72. Homolytic Cleavage of an S-S Bond in S_{10}

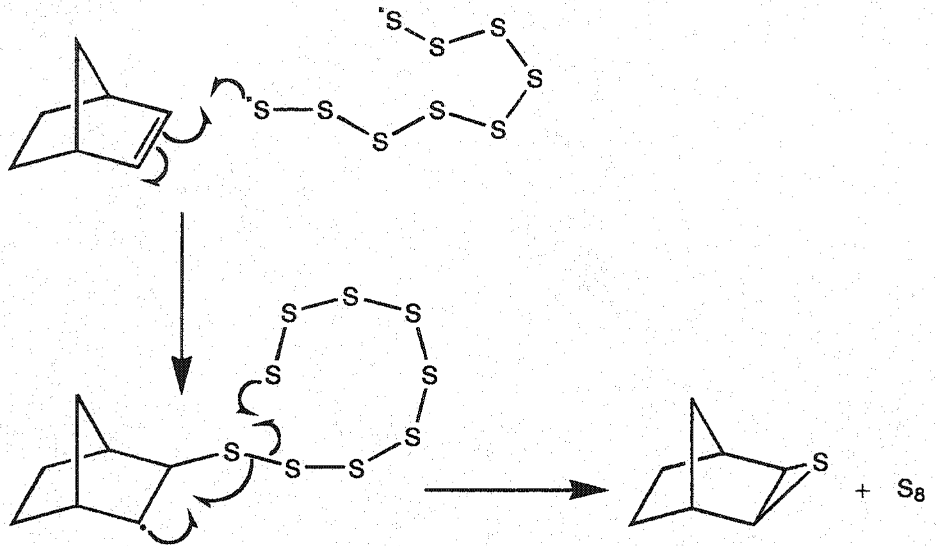
The resulting di-radical sulfur chain can then react with a simple alkene or a 1,3-diene as was already proposed.[167] This is shown in Figure 73 for 2,3-diphenyl-1,3-butadiene.



13a

Figure 73. Reaction of S_{10} Di-radical with 2,3-Diphenyl-1,3-butadiene

A key element of the proposed mechanism is the cyclo-elimination of S_8 during product formation in these reactions. This cyclo-elimination is supported by the high ratios of disulfide adducts **13a** and **13b** over their tetrasulfide analogues **35** and **36** obtained in the reaction of S_{10} with 1,3-dienes **12a** and **12b**. Reversibly, ratios **13a/35** and **13b/36** more in favor of tetrasulfides **35** and **36** could account for the generation of a discrete S_4 chain by the same cyclo-elimination process in reactions of S_{12} and S_{20} with 1,3-dienes **12a** and **12b**. This process is now even further supported by the formation of *exo*-norbornane episulfide (**69**) during the reaction of norbornene with S_9. A mechanism accounting for the formation of episulfide **69** is shown in Figure 74.



69

Figure 74. Formation of Episulfide **69** from Norbornene and S_9

A similar mechanism has already been proposed for the formation of trithiolane **19** from the reaction of S_{10} with norbornene.[167] *Cyclo*-decasulfur S_{10}, which can be considered as a net 2-sulfur atom donor in this case, is first suggested to react with norbornene to form 1,2-dithietane **17** as an intermediate. Further sulfuration of this intermediate with any form of sulfur present in the reaction mixture ("Sulfur") can then result in the formation of the more stable trithiolane **19**, which was isolated as the unique product. This mechanism is shown in Figure 75.

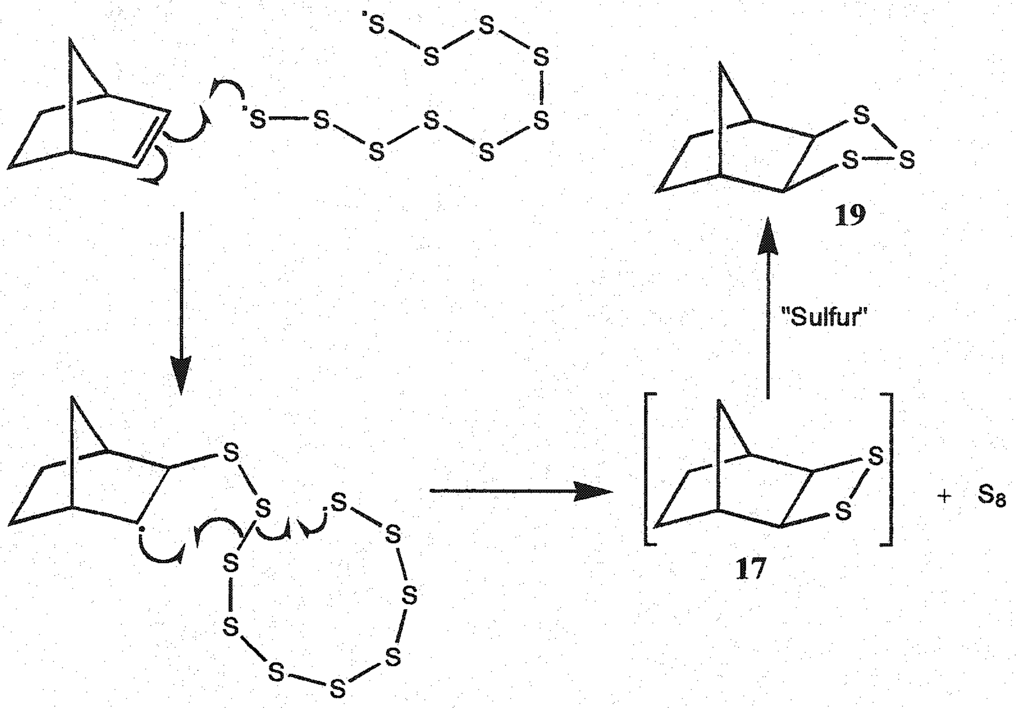


Figure 75. Formation of Trithiolane **19** from S_{10} and Norbornene

The cyclo-elimination process of S_8 is thus a main driving force in the reaction of sulfur allotropes with simple alkenes or 1,3-dienes. This process can be easily compared to the depolymerization of polymeric sulfur (S_μ) to produce S_8. The difference here lies in the fact that the first step of sulfur chains polymerization has simply been intercepted by the olefins.

Nevertheless, S_8 cyclo-elimination does not appear as the only governing factor to account for the formation of the different products isolated in the course of this study. The two radical species **94** and **95**, which are envisaged as intermediates during these reactions, can also attack the adjacent sulfur chain at different positions. The presence of small amounts of tetrasulfide adducts **35** and **36** in the reaction of S_{10} with 1,3-dienes **12a** and **12b** or the formation of trithiolane **19** in the reaction of S_9 with norbornene can thus be explained (see Figure 76 and 77, respectively). As a reminder, tetrasulfides **35** and disulfide **13a** as well as trithiolane **19** and episulfide **69** were shown not to be in equilibrium with each other as it was discussed in previous Chapters (see Figure 29 and 54).

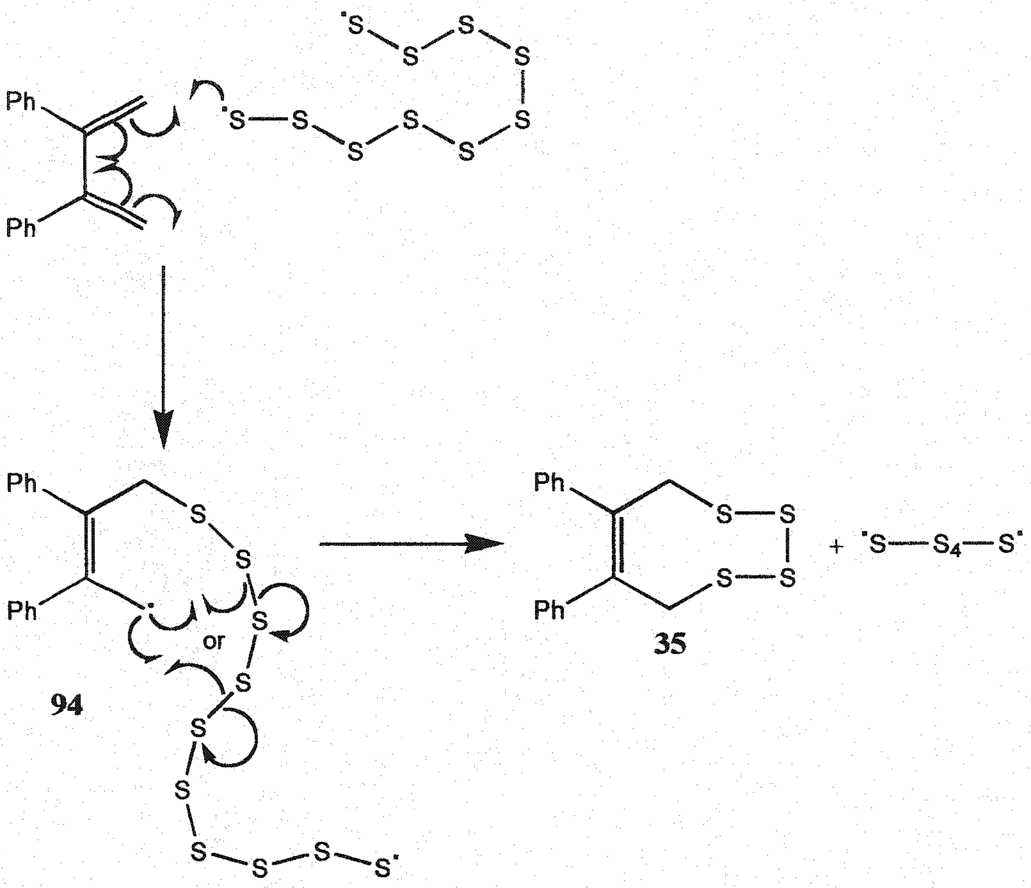


Figure 76. Formation of Tetrasulfide **35** from 1,3-Diene **12a** and S_{10}

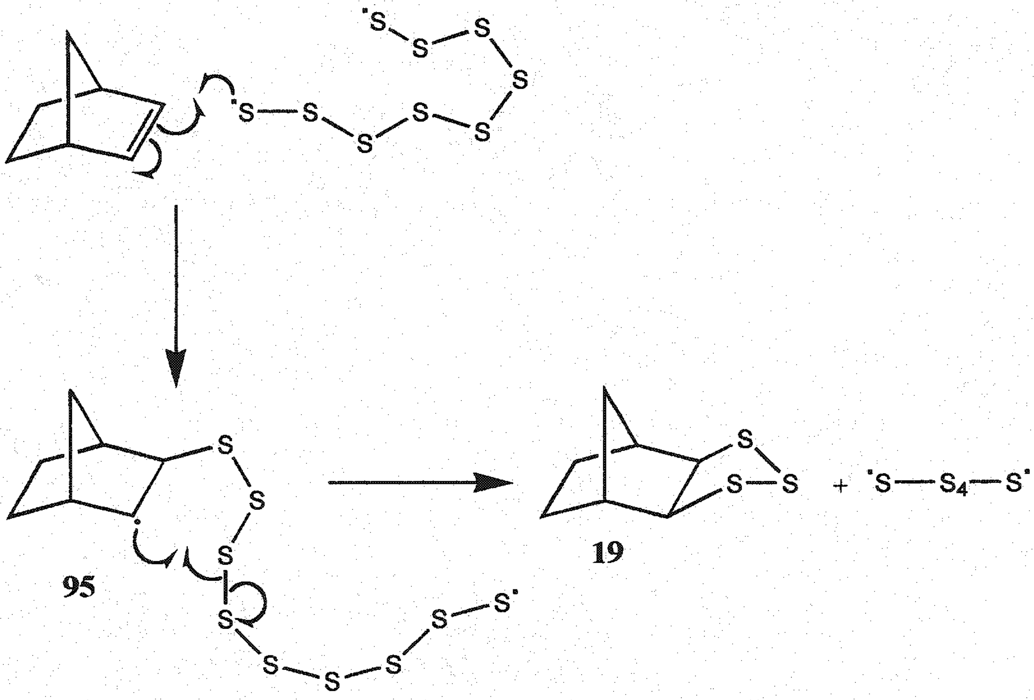


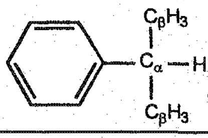
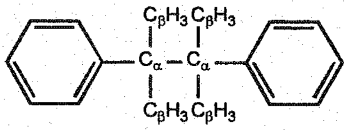
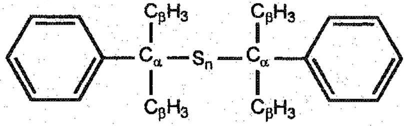
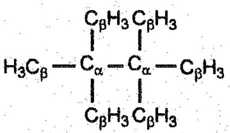
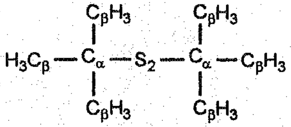
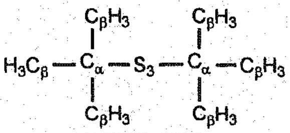
Figure 77. Formation of Trithiolane **19** from Norbornene and S_9

The mechanism shown in Figure 76 also offers the possibility of the formation of disulfide adduct **13a**. This mechanism resembles the one proposed by Harpp and Rys in the sulfuration reaction of 1,3-dienes with S_8 in polar solvents, which was already described (Figure 44).[163]

Finally, a fully ionic mechanism can also be envisaged for the reactions implicating S_9, S_{10}, S_{12} and S_{20}. Most of the mechanisms proposed would be very similar except for the initial S-S bond cleavage, which would simply be heterolytic, catalyzed or not by trace impurities.

4.4. Conclusion

The above mechanistic study has clearly implicated sulfur radicals in the decomposition reaction of S_{10} and in its reaction with olefins even at low temperatures. An extension of this behavior to other metastable sulfur rings such as S_9, S_{12} and S_{20} can be postulated. In the course of this study, it has been seen that S_{10} acts as the 2-sulfur atom donor that was anticipated. S_9 has shown the ability to deliver a single sulfur atom under certain conditions. As for S_{12} and S_{20}, their aptitude to deliver discrete S_4 units has been proposed.

Compound		NMR Data[a]		
		α	β	aryl
 **91**	^{1}H	2.90 (m, 1H)	1.25 (d, 6H)	7.23 (m, 5H)
	^{13}C	34.18	24.02	148.83, 128.34, 126.42, 125.79
 **92**	^{1}H	-	1.29 (s, 12H)	7.10 (m, 10H)
	^{13}C[b]	43.68	25.21	146.89, 128.65, 126.66, 125.52
 **93**	^{1}H	-	1.82 (s), 1.815 (s), 1.81 (s), 1.80 (s), 1.785 (s), 1.76 (s)	7.40 (m)
	^{13}C	54.68, 54.64, 54.55, 54.46, 54.365, 54.09	29.01, 28.94	143.61-143.95, 126.73-128.54
	^{1}H[c]	-	0.86	-
	^{13}C[c]	35.03	25.74	-
	^{1}H[d]	-	1.28 (s, 18H)	-
	^{13}C[d]	45.97	30.56	-
	^{1}H[d]	-	1.36 (s, 18H)	-
	^{13}C[d]	48.91	29.88	-

[a] $CDCl_3$; δ in ppm. [b] Ref. 231; CCl_4/TMS. [c] Ref. 232. [d] Ref. 170.

Table 30. NMR Data for Compounds **91**, **92**, **93** and Selected Di-*tert*-butyl Polysulfides

CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

The reaction between *cyclo*-decasulfur (S_{10}) and a variety of simple or conjugated alkenes has been investigated for the first time, products isolated and identified. The parameters of a model reaction between 2,3-diphenyl-1,3-butadiene and S_{10} have been optimized. A selectivity as high 9.5:1 in favor of the corresponding disulfide adduct 4,5-diphenyl-3,6-dihydro-1,2-dithiin *vs.* its tetrasulfide counterpart 6,7-diphenyl-5,8-dihydro-1,2,3,4-tetrathiin has been observed. The sulfuration reactions with S_{10} have the advantage of being efficient without the use of harsh reagents such as bases or nucleophiles and to proceed at relatively low temperatures. The only residual product from S_{10} decomposition is elemental sulfur (S_8).

The reaction of norbornadiene with S_{10} has allowed the isolation of the new *bis*-sulfurated compound *exo*-3,4,5-*exo*-9,10,11-hexathiatetracyclo[5.5.1.$0^{2,6}$.$0^{8,12}$]tridecane. A new compound coming from the dimerization of norborn-5-ene-2,3-dithiol has also been synthesized. The structure of both these new materials has been confirmed by single crystal X-ray diffraction.

The reaction between S_{10} and simple or conjugated alkenes has also been extended to *cyclo*-nonasulfur (S_9), *cyclo*-dodecasulfur (S_{12}) and *cyclo*-eicosasulfur (S_{20}). All these allotropes have shown to react with 2,3-diphenyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene and norbornene. Products have been identified and yields calculated. The sulfuration of norbornene with S_9 produced almost equimolar amounts of trithiolane *exo*-3,4,5-trithiatricyclo[5.2.1.$0^{2,6}$]decane and of episulfide *exo*-2,3-epithionorbornane. *Cyclo*-dodecasulfur (S_{12}) and to a lesser extent *cyclo*-eicosasulfur (S_{20}) have show an increased selectivity towards the production of tetrasulfide adducts when reacted with 1,3-dienes.

The results obtained from the trapping reactions of S_9, S_{10}, S_{12} and S_{20} with simple or conjugated olefins have been compared to standard sulfuration methods involving elemental sulfur (S_8) and diatomic sulfur (S_2) precursors. The sulfuration efficiencies of these sulfur allotropes have also been estimated with regards to selected olefins. Under the conditions of this study, S_{10} was *45 times* more efficient than S_{20} and *22 times* more efficient than S_{12} at sulfurating 2,3-diphenyl-1,3-butadiene. The same calculations for S_9 showed that this allotrope was *11* and *5 times* more efficient than S_{20} and S_{12}, respectively.

The reaction between S_{10} and 2,3-diphenyl-1,3-butadiene, as well as the thermal decomposition of S_{10}, have been investigated for the presence of sulfur radical intermediates. The rate of the reaction between S_{10} and 2,3-diphenyl-1,3-butadiene was shown to be affected by standard radical scavengers such as BHT or TEMPO. Products from the thermal decomposition reaction of S_{10} in cumene have also been isolated and indicate the presence of sulfur radicals.

Mechanisms have been proposed, which account for the formation of the products identified in the trapping reactions of the herein studied sulfur allotropes with alkenes. *Cyclo*-decasulfur (S_{10}) appears to act as a 2-sulfur atom donor, *cyclo*-nonasulfur (S_9) can act as a one-sulfur atom donor and *cyclo*-dodecasulfur (S_{12}) and *cyclo*-eicosasulfur (S_{20}) seem to have the ability to deliver longer sulfur chains.

CHAPTER 5. EXPERIMENTAL

5.1. General Procedures

The commercially available reagents were obtained from Aldrich Chemical Company. They were used directly without further purification or purified as indicated.

Pure sulfur dichloride (SCl_2) was obtained by double flame distillation of technical grade SCl_2 (90%) on phosphorus pentachloride (PCl_5) according to the procedure of Fieser and Fieser.[235] The red fraction boiling at 58-60°C was collected and used straight away. Sulfuryl chloride (SO_2Cl_2) was distilled and used immediately. The fraction boiling at 68-70°C was collected.

Carbon disulfide (CS_2) used in the reactions involving sulfur allotropes was HPLC grade. The use of HPLC grade CS_2 avoided having to distill this very flammable and toxic solvent. In some occasions, freshly opened reagent grade CS_2 was used in the synthesis of S_{10} without any apparent decrease in the yield of the reaction or the purity of the thus prepared sulfur allotrope. Methylene chloride (CH_2Cl_2) was rigorously dried by distillation from phosphorus pentoxide (P_2O_5). Tetrahydrofuran (THF) was distilled from the blue sodium- or potassium-benzophenone ketal. Anhydrous diethyl ether ($C_2H_5OC_2H_5$) was stored over 3Å molecular sieves. High boiling point aromatic solvents such as chlorobenzene, xylenes or cumene were dried over 4Å molecular sieves.

Thin Layer Chromatography (TLC) was performed on 0.25 mm Merck silica plates (60F-254) with polyester backing and visualized under UV light and/or by dipping in a solution of ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) (10 g) and ceric ammonium sulfate ($(NH_4)_4Ce(SO_4)_4$) (4 g) in 10% v/v aqueous sulfuric acid (H_2SO_4) (400 mL). Column chromatography was carried out using Silicycle silica gel 60F-254 (230-400

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[235] Fieser, L. F. and Fieser, M. *Reagents for Organic Synthesis*, John Wiley and Sons, Pub., New-York, **1967**, *1*, 1121.

mesh). Flash column chromatography conditions were used in most cases.[236] For the isolation of some products issued from the decomposition of S_{10} in the presence of dienes or alkenes, a dry pack technique was used in order to load the sample on the column chromatography. Crude material (250 to 500 mg) was dissolved in an adequate solvent and adsorbed on 1 to 2 g of silica gel by evaporation of the solvent under vacuum with a rotary evaporator. Further drying could be achieved on higher vacuum. The crude compound thus adsorbed on silica gel was then loaded on top of the column chromatography.

^{1}H-NMR spectra were recorded at 200 MHz on Varian XL-200, Varian Gemini-200 or Varian Mercury-200 spectrometers, or at 300 MHz on Varian XL-300 or Varian Mercury-300 spectrometers. ^{13}C-NMR spectra were obtained on the same instruments at 50.3 MHz or 75.4 MHz. Deuterated chloroform ($CDCl_3$) was used as a solvent to record these spectra in most cases unless otherwise indicated. ^{1}H- and ^{13}C-NMR chemical shifts are reported in parts per million, δ (ppm) relative to tetramethylsilane (TMS) or to the NMR solvent peak as a reference. The spectra are reported as: Shift, multiplicity and integration, respectively. The following abbreviations are used for the multiplicity assignments: "s" for singlet, "d" for doublet, "t" for triplet, "q" for quartet, "m" for multiplet and "b" for broad. The yields of products for the small-scale reactions between various sulfur allotropes (S_9, S_{10}, S_{12} and S_{20}) and 1,3-dienes or simple alkenes were estimated by comparison with an internal standard. 9-Methylanthracene or 1,3,5-tri-*tert*-butylbenzene were used as internal standards as they were inert to the reaction. The ^{1}H-NMR spectra were recorded with a relaxation delay (d_1) of 5 seconds at the end of the pulse sequence. This delay ensured a more accurate integration for the different protons and thus a better estimate on the yields.

Melting points (Mp.) were recorded on Gallenkamp K 8500 melting point apparatus using open end capillaries and are uncorrected.

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[236] Still, W. C.; Kahn, M. and Mitra, A. *J. Org. Chem.*, **1978**, *43*, 2923.

Low resolution electron impact (EI), chemical ionization (CI) or fast atom bombardment (FAB) mass spectra were recorded using a Kratos MS 25RFA instrument equipped with a 70 eV ionizing energy source. Mr. Nadim Saadé performed the analyses. High resolution mass spectra were carried out on a ZAB HS instrument at the Biomedical Mass Spectrometry Unit of McGill University by Dr. O. Mamer.

Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra for unknown compound **43** were recorded on a Kratos Kompact MALDI-III TOF instrument. A maximum laser output of 6 mW is generated at a wavelength of 337 nm (N_2 laser light, 3 ns pulse width, 100 μm diameter spot). The MALDI instrument was operated in a positive reflectron mode. The best results were obtained by direct inlet of the sample. These analyses were carried out in the laboratory of Dr. Hay in the Chemistry Department at McGill University.

The elemental analysis for *bis*-sulfurated compound **42** was performed in the laboratories of Guelph Chemical Laboratories Ltd. in Guelph, Ontario.

The X-ray crystallography for *bis*-sulfurated compound **43** was determined by Dr. Anne-Marie Lebuis of the Chemistry Department at McGill University. The structure was solved using SHELXS-96 program. The X-ray crystallography for dimer compound **64** was determined by Dr. Francine Bélanger-Gariépy of the Chemistry Departement at the University of Montreal. The structure was solved and refined using SHELXS-97 and SHELXL-96 programs. The data acquisition for both structures was performed on an Enraf Nonius CAD-4 diffractometer in the Chemistry Department of the University of Montreal.

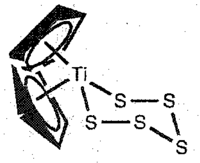
The FT-Raman spectra were recorded on a Bruker Model IFS-88 spectrometer with the aid of a Bruker FRA-106 Raman module equipped with an air cooled, 300 mW Nd:YAG laser operating in the near IR region at 1064 nm. The laser did not seem to affect the quality of the sulfur allotrope samples during the acquisition times that were needed in order to get a spectrum. No decomposition was observed even at high laser power. Data are reported in wavenumbers (cm^{-1}). Some intensity of the Raman bands are reported as follows: w, weak; vw, very weak; m, medium; s, strong; vs, very strong; sh, shoulder.

High Pressure Liquid Chromatography was performed on an Hewlett Packard 1100 Series instrument operated with an HP ChemStation module. The column used for the separation of sulfur allotropes was an HP Hypersil BDS-C18 reverse phase column with a particle size of 5 µm. The internal diameter of the column was 4.6 mm for a total length of 25 mm. Examples of chromatograms obtained with this instrument for sufur allotropes are shown in Appendix.

All air sensitive reactions were carried out under an inert nitrogen (N_2) atmosphere. For all water sensitive reactions, the glassware was either previously dried overnight in an oven at 140°C and cooled down in a dessicator containing Drierite or flame dried and cooled under a nitrogen stream. The glassware used for the synthesis of all sulfur allotropes as well as for their trapping reactions with 1,3-dienes or simple olefins was previously left for a few hours in a *ca.* 1M hydrochloric acid (HCl) bath. It was then rinsed under water and dried in an oven as described above.

5.2. Chapter 2

Synthesis of bis(π-cyclopentadienyl)titanium(IV) pentasulfide (28)



28

Shaver and McCall's procedure:[115c]

Titanocene dichloride Cp_2TiCl_2 (3.735 g, 15 mmol) was dissolved in 375 mL of freshly distilled THF and stirred under a nitrogen atmosphere. The solution was then transferred *via* a double ended needle into a 500 mL round bottom flask containing a previously prepared solution of S_8 (2.41 g, 9.4 mmol) in 30 mL of a commercially available 1M solution of SuperHydride $LiEt_3BH$ (30 mmol) in THF. The mixture was stirred for 12 hr under a gentle nitrogen stream. THF was then removed under reduced pressure with a rotary evaporator. The solid residue was extracted with 350 mL of CH_2Cl_2. Filtration of the mixture through Celite and removal of CH_2Cl_2 yielded a dark red solid that was purified by column chromatography according to the procedure below. Overall yield was 88%.

Steudel's procedure:[115d]

Extreme Caution! This procedure requires the use of H_2S gas, which is deadly at *ca.* 10 ppm in the atmosphere, and thus needs to be handled very carefully. The experimentator should be informed on the hazards of this gas prior to proceeding with the reaction. All steps of this reaction must be carried out inside a fume-hood and in a well-ventilated environment.

S_8 (80.0 g, 0.31 mol) was placed in a 3 L 3-neck round bottom flask along with 220 mL of a 29.5% by weight solution of NH_3 in water (3.81 mol). H_2S gas was then gently bubbled for about 1.5 hr within the solution and stirring was maintained. All S_8 slowly dissolved into the solution, which turned dark red. Of the remaining two necks of the flask, one was simply closed with a rubber septum while the last one was connected to a series of 3 consecutive bubbling bottles filled with solutions of 2M KOH, 1M KOH and bleach, respectively. The gas lines and the reaction flask were then purged for about 15-20 min with a nitrogen flow in order to get rid of remaining H_2S. At this stage, the traps were disconnected and their solution containing neutralized H_2S emptied in a bleach bath inside the fume-hood. Water (150 mL), $CHCl_3$ (1.5 L) and Cp_2TiCl_2 (50.0 g, 0.20 mol) were then successively added to the flask and vigorous stirring under a gentle nitrogen stream was maintained for at least 20 hr. An extra 500 mL of water was then added to the dark-brown mixture before being transferred into a 4 L extraction funnel. The $CHCl_3$ phase was separated and the remaining aqueous phase extracted with 500 mL portions of $CHCl_3$ until the extracts were very faint. The organic phase was then divided into two portions and each half was further washed with 3x500 mL portions of water. $CHCl_3$ was then evaporated under reduced pressure and crude **28** was obtained as a smelly dark brown solid. Purification by column chromatography according to the procedure described below afforded pure **28** in overall 88% yield.

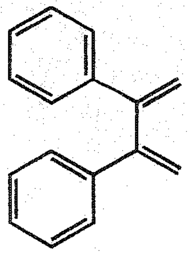
Purification of **28**:

Crude **28** (10.0 g) was placed into a 500 mL round bottom flask and dissolved with stirring over 3-4 hr in 300 mL of CS_2. Silica gel (30 g) was then added and the mixture stirred for 5 min. CS_2 was removed under reduced pressure with a rotary evaporator until the silica looked dry. The thus adsorbed crude **28** was then loaded on a 9 cm diameter chromatography column packed with 15 cm silica gel and eluted with chloroform. The column was then flushed with chloroform and the whole red fraction corresponding to pure **28** collected in one pot. $CHCl_3$ was evaporated, the remaining dark red solid was dried under high vacuum for several hours and 8.8 g of pure **28** were obtained.
28: Mp. 184-186°C (lit. 196-198°C,[115c] *ca.* 190°C[115d]) **^{1}H-NMR** ($CDCl_3$) δ: 6.33(s, 5H), 6.05(s, 5H) ppm.

Synthesis of S_{10}

Pure titanocene pentasulfide (**28**) (8.0 g, 23.6 mmol) was placed in a dry 500 mL flask previously washed in an acid bath and dissolved in 270 mL of HPLC grade CS_2. The mixture was stirred at 0°C in the dark under a nitrogen flow for at least 1 hr in order to ensure complete dissolution of **28**. To this mixture was added dropwise, within *ca.* 20 min *via* a double ended needle under nitrogen, a solution of 1.9 mL of freshly distilled sulfuryl chloride SO_2Cl_2 (23.6 mmol) in 22 mL of CS_2. The mixture was stirred for a further 2 hr in the dark under a nitrogen flow at 0°C before being placed for 4-5 hr in the freezer at -40°C in order to ensure complete precipitation of Cp_2TiCl_2. Rapid filtration on a Buchner funnel afforded a yellow orange solution that was concentrated down to 120 mL under reduced pressure with a rotary evaporator. CH_2Cl_2 (240 mL) was added to the CS_2 phase and the thus yellow turbid solution was passed through a coarse size fritted funnel. The filtrate was then placed at –40°C in the dark for 2 days. Filtration afforded a yellow residue that was extracted with aliquots of CS_2 until a very pale yellow practically insoluble solid was obtained. This solid was dried at room temperature and afforded S_{20} (189 mg) in 5% yield. The CS_2 extracts were gently concentrated on a hot plate and n-pentane was added until turbidity. Crystallization at –40°C in the dark for two days afforded pure S_{10} (1.33 g) in 35% yield (lit. 35%,[113] 38%[124a]) as bright yellow crystals.

Synthesis of 2,3-Diphenyl-1,3-butadiene (12a)



12a

Magnesium turnings (1.465 g, 60.3 mmol) were added to a 100 mL 3-neck round bottom flask which had been previously flame dried and allowed to cool under a nitrogen stream. Anhydrous diethyl ether (30 mL) was added to the flask and vigorous stirring was started. A reflux condenser and a flame dried addition funnel were connected to the flask and α–bromostyrene (7.9 mL, 90%, 54.6 mmol) was added to the addition funnel. A few drops of α-bromostyrene were added on the magnesium turnings until the reaction was initiated and reflux spontaneously started. Occasionally, the magnesium turnings were crushed with a glass rod in order to liberate some clean surfaces of magnesium. The remaining α-bromostyrene was diluted with an extra 10 mL of anhydrous diethyl ether and dropwise addition of the solution completed. Reflux was then maintained for 1 hr upon completion of the addition. The mixture was allowed to cool down to room temperature and the thus formed Grignard was added *via* a double ended needle under nitrogen to a 500 mL round bottom flask containing a vigorously stirred solution of dichlorobis(triphenylphosphine)nickel(II) ($(PPh_3)_2NiCl_2$) (3.59 g, 5.49 mmol) and α-bromostyrene (6.3 mL, 90%, 43.7 mmol) in 50 mL of anhydrous diethyl ether at 0°C. The mixture was stirred at 0°C for 30 min, warmed to room temperature and stirred overnight. The mixture was then cooled again on ice and 150 mL of a 1.2M HCl solution were added very slowly. The organic phase was separated from the aqueous phase in a separatory funnel and the aqueous phase was further extracted with 4x50 mL of diethyl ether. The combined organic extracts were washed with a saturated sodium bicarbonate ($NaHCO_3$) solution (50 mL) and dried over magnesium sulfate ($MgSO_4$). The solvent was evaporated under reduced pressure with a rotary evaporator and an amber oil was produced. The crude product was purified by elution with hexanes on a silica gel flash column chromatography. It afforded pure **12a** (4.51 g) as a waxy white solid in 50% yield.

12a: Mp. 52-54°C (lit.[237] 46-47°C) **^{1}H-NMR** ($CDCl_3$) δ: 7.2-7.4 (m, 10H), 5.54 (d, 2H), 5.31 (d, 2H) ppm. **^{13}C-NMR** (CDCl3) δ: 149.91, 140.25, 128.21, 127.99, 127.55, 116.39 ppm.

General Procedure for the Small Scale Reaction of S_{10} with 2,3-Diphenyl-1,3-butadiene (12a) in the Presence of an Internal Standard

Freshly chromatographed **12a** (21.0 mg, 0.102 mmol) was placed in a 3-neck 25 mL round bottom flask and dissolved in 2.5 mL (xylenes) or 10 mL (chlorobenzene, toluene or benzene) of a selected solvent along with either 9-methylanthracene (30.0 mg, 0.156 mmol) or 1,3,5-tri-*tert*-butylbenzene (45.0 mg, 0.183 mmol). The latter were used as internal standards. The mixture was placed under a nitrogen atmosphere and was then either refluxed with a heating mantle (for chlorobenzene, toluene or benzene) or maintained at 120°C with the help of an oil bath (for xylenes). Freshly recrystallized S_{10} (33.7 mg, 0.105 mmol) was dissolved in CS_2 and the solution concentrated to *ca.* 500 μL on a warm sand bath. The S_{10}/CS_2 solution was then injected on top of the hot diene solution with a syringe over *ca.* 30 sec. An extra 100 μL of CS_2 was used to rinse the flask that contained S_{10} and was subsequently added to the solution. Heating was maintained for 2-6 hr. The solution was sampled at desired times and solvent evaporated

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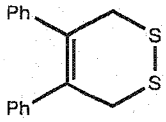
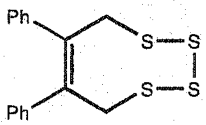
[237] Dodson, R. M.; Srinivasan, V.; Sharma, K. S. and Sauers, R. F. *J. Org. Chem.*, **1972**, *37*, 2367.

under reduced pressure with a rotary evaporator. Yields of the expected products were estimated by ^{1}H-NMR comparison with the internal standard.

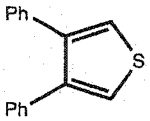
Large Scale Reaction of S_{10} with 2,3-Diphenyl-1,3-butadiene (12a)



13a



35



37

Freshly chromatographed **12a** (210.0 mg, 1.0 mmol) was dissolved in 25 mL of xylenes and maintained at 120°C with an oil bath under a nitrogen flow. Freshly recrystallized S_{10} (337.0 mg, 1.0 mmol) was dissolved in CS_2 and the solution concentrated to *ca.* 5 mL on a warm sand bath. The S_{10}/CS_2 solution was then injected on top of the hot diene solution with a syringe over *ca.* 30 sec. An extra 1 mL of CS_2 was used to rinse the flask which contained S_{10} and was subsequently added to the hot solution. Heating was maintained for 2 hr. The solvent was then evaporated and the residue triturated repeatedly with 3x3 mL of diethyl ether or hexanes and then with smaller portions of CS_2 until no product was detected by TLC. Products were separated on a silica gel chromatographic column using a dry pack in order to load the sample. Typical eluants were 2% diethy ether in hexanes or 20-40% $CHCl_3$ in hexanes. Compounds **13a** and **35** were obtained as a mixture in an overall 42% yield. The ratio **13a/35** was determined by ^{1}H-NMR. Yields for **13a** and **35** calculated from this ratio were 38% and 4%, respectively. 3,4-Diphenylthiophene (**37**) was also isolated in 3% yield.

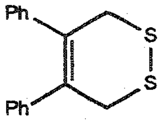
13a: **^{1}H-NMR** ($CDCl_3$) δ: 6.96-7.12 (m, 10H), 3.67 (s, 4H) ppm. **^{13}C-NMR** ($CDCl_3$) δ: 142.50, 134.67, 129.19, 127.89, 126.57, 34.59 ppm.

35: **^{1}H-NMR** ($CDCl_3$) δ: 7.06-7.14 (m, 10H), 4.07 (s, 4H) ppm. **^{13}C-NMR** ($CDCl_3$) δ: 140.90, 138.03, 129.55, 127.72, 126.88, 42.95.

37: Mp. 110-112°C (lit.[168] 112-113°C). **^{1}H-NMR** ($CDCl_3$) δ: 7.32 (s, 2H), 7.18-7.28 (m, 10H) ppm; **^{13}C-NMR** ($CDCl_3$) δ: 141.71, 136.49, 128.99, 128.12, 126.85, 124.02 ppm. **MS** (EI, 70 eV, 100°C) m/z (relative intensity): 238 (M^+) (6), 237 (22), 236 (100), 235

(68), 234 (28), 221 (14), 203 (5), 202 (11), 191 (5), 189 (7), 118 (7), 117 (13), 110 (6), 104 (9).

Reaction of a Mixture of Disulfide 13a and Tetrasulfide 35 with Triphenylphosphine

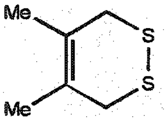


13a

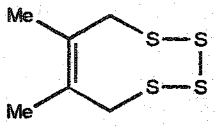
A 9.5:1 mixture of disulfide **13a** and tetrasulfide **35** (253.0 mg, 0.83 mmol/0.083 mmol) and excess triphenylphosphine (110.0 mg, 0.419 mmol) were dissolved in 20 mL of diethyl ether and stirred for 24 hr at room temperature. S_8 (20.0 mg, 0.078 mmol) was then added to the reaction mixture which was further stirred for 3 hr. Evaporation of the solvent followed by chromatographic separation of the residue in 2% diethyl ether in hexanes afforded 250 mg of almost pure disulfide **13a**. Ratio of disulfide **13a**/tetrasulfide **34** went up to 60:1 which showed an 85% efficiency for the reaction.

13a: Mp. 99-100°C (lit. 101-102°C[237]). **^{1}H-NMR**: See data above. **^{13}C-NMR**: See data above. **MS** (EI, 70 eV, 100°C) m/z (relative intensity): 270 (M^+) (7), 236 (5), 207 (14), 206 (86), 205 (100), 204 (12), 203 (13), 202 (11), 191 (26), 178 (11), 165 (7), 129 (11), 128 (15), 115 (12), 103 (9), 102 (7), 101 (8), 91 (36), 89 (11), 77 (14).

Reaction of S_{10} with 2,3-Dimethyl-1,3-butadiene (12b)



13b



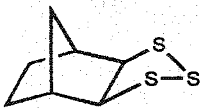
36

Commercially available **12b** (120 μL, 1.0 mmol) was combined with 100 mL of toluene and refluxed under a nitrogen flow. Freshly recrystallized S_{10} (337.0 mg, 1.0 mmol) was dissolved in CS_2 and the solution concentrated to *ca.* 5 mL on a warm sand bath. The S_{10}/CS_2 solution was then injected on top of the hot diene solution with a syringe over *ca.* 30 sec. An extra 1 mL of CS_2 was used to rinse the flask which contained S_{10} and was subsequently added to the hot solution. Heating was maintained for 3 hr. The solvent was then evaporated and the residue triturated repeatedly with 3x3 mL of diethyl ether or hexanes and then with smaller portions of CS_2 until no product was detected by TLC. Products were separated on a silica gel chromatographic column using a dry pack in order to load the sample. The composition of the eluant was 2% diethyl ether in hexanes. Compounds **13b** and **36** were obtained as a mixture in an overall 42% yield. The ratio **13b/36** was determined by ^{1}H-NMR. Yields for **13b** and **36** calculated from this ratio were 36% and 6%, respectively.

13b: ^{1}**H-NMR** ($CDCl_3$) δ: 3.18 (s, 4H), 1.73 (s, 6H) ppm. ^{13}**C-NMR** ($CDCl_3$) δ: 124.50, 34.62, 21.43 ppm.

36: ^{1}**H-NMR** ($CDCl_3$) δ: 3.62 (s, 4H), 1.77 (s, 6H) ppm. ^{13}**C-NMR** ($CDCl_3$) δ: 129.59, 43.14, 18.76 ppm.

Reaction of S_{10} with Norbornene (16)



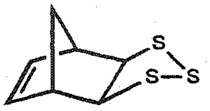
19

Commercially available norbornene (**16**) (96.0 mg, 1.0 mmol) was dissolved in 100 mL of toluene and refluxed under a nitrogen flow. Freshly recrystallized S_{10} (337.0 mg, 1.0 mmol) was dissolved in carbon disulfide and the solution concentrated to *ca.* 5 mL on a warm sand bath. The S_{10}/CS_2 solution was then injected on top of the refluxing olefin solution with a syringe over *ca.* 30 sec. An extra 1 mL of CS_2 was used to rinse the flask which contained S_{10} and was subsequently added to the refluxing solution. Reflux was maintained for 3 hr. The solvent was then evaporated and the residue triturated repeatedly with 3x3 mL of diethyl ether and then with smaller portions of CS_2 until no product was detected by TLC. Flash silica gel chromatographic column using a dry pack in order to load the sample and hexanes as the eluant allowed the isolation of 165 mg (85%) of pure trithiolane **19** as a yellow oil.

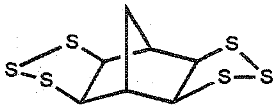
19: ^{1}**H-NMR** ($CDCl_3$) δ: 3.61 (d, J=2.0 Hz, 2H), 2.43 (m, 2H), 1.89 (dt, J_1=10.0 Hz, J_2=2.0 Hz, 1H), 1.70 (m, 2H), 1.24 (m, 2H), 1.03 (dt, J_1=10.0 Hz, J_2=2.0 Hz, 1H) ppm.

^{13}**C-NMR** ($CDCl_3$) δ: 69.68, 40.66, 32.21, 27.49 ppm. **MS** (EI, 70 eV, 100°C) m/z (relative intensity): 190 (M^{+}) (100), 126 (46), 125 (31), 98 (19), 97 (35), 93 (60), 92(24), 91 (45), 79 (26), 77 (31), 67 (21), 66 (65), 65 (24), 64 (28).

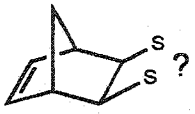
Reaction of S_{10} with Norbornadiene (26)



27



42



43

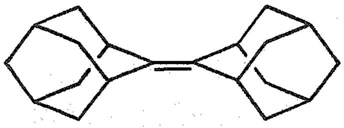
Commercially available norbornadiene (**26**) (110 μL, 1.0 mmol) was dissolved in 100 mL of toluene and refluxed under a nitrogen flow. Freshly recrystallized S_{10} (337.0 mg, 1.0 mmol) was dissolved in carbon disulfide and the solution concentrated to *ca.* 5 mL on a warm sand bath. The S_{10}/CS_2 solution was then injected on top of the refluxing olefin solution with a syringe over *ca.* 30 sec. An extra 1 mL of CS_2 was used to rinse the flask which contained S_{10} and was subsequently added to the refluxing solution. Reflux was maintained for 3 hr. The solvent was then evaporated and the residue triturated repeatedly with 3x3 mL of diethyl ether and then with smaller portions of CS_2 until no product was detected by TLC. Separation of the products was carried out by flash silica gel column chromatography using a dry pack in order to load the sample. Column was first eluted with hexanes and then with 2% diethyl ether in hexanes. Trithiolane **27** (112.5 mg, 59%) was isolated as a yellow oil and *bis*-sulfurated compound **42** (50.3 mg, 17%) was also obtained as an off-white solid. Unknown compound **43** was also isolated as a white solid (9.1 mg).

27: ^{1}**H-NMR** ($CDCl_3$) δ: 6.36 (t, J=1.8 Hz, 2H), 4.03 (d, J=1.8 Hz, 2H), 2.89 (m, 2H), 2.45 (d, J=9.4 Hz, 2H), 1.70 (dt, J_1=9.4 Hz, J_2=1.8 Hz, 2H) ppm. ^{13}**C-NMR** ($CDCl_3$) δ: 139.40, 70.85, 46.30, 43.18 ppm. **MS** (EI, 70 eV, 150°C) m/z (relative intensity): 188 (M^{+}) (11), 124 (36), 123 (37), 122 (36), 97 (22), 92 (45), 91 (100), 79 (13), 77 (8), 66 (30), 65 (16), 64 (7).

42: This material decomposes over a range starting at 180°C; it is likely that polymerization takes place. ^{1}**H-NMR** ($CDCl_3$) δ: 3.83 (bs, 4H), 2.63 (t, J=1.5 Hz, 2H) 1.98 (bs, 2H) ppm. ^{13}**C-NMR** ($CDCl_3$) δ: 68.63, 45.61, 28.18 ppm. **MS** (EI, 70 eV, 150°C) m/z (relative intensity): 284 ($M^{+\cdot}$) (51), 220 (14), 156 (14), 125 (11), 124 (100), 123 (89), 122 (25), 121 (18), 97 (52), 92 (33), 91 (94), 79 (23), 78 (13), 77 (16), 76 (26), 66 (26), 65 (16), 44 (15). **HRMS**: Calculated for $C_7H_8S_6$ 283.8950; found 283.8951. It gave a satisfactory carbon and hydrogen analysis albeit the sulfur percentage was low by 2.4%: Calculated for $C_7H_8S_6$ C, 29.55; H, 2.83; S, 67.62; found C, 29.96; H, 2.88; S, 65.22.

43: Mp. 87-89°C. **^{1}H-NMR** ($CDCl_3$) δ: 6.07 (t, J=1.7 Hz, 2H), 4.66 (m, 2H), 3.17 (m, 2H), 2.18 (d, J=9.0 Hz, 1H), 2.06 (dt, J_1=9.0 Hz, J_2=2.0 Hz, 1H) ppm. **^{13}C-NMR** ($CDCl_3$) δ: 135.48, 70.72, 56.75, 46.37 ppm. **MALDI-TOF-MS** m/z (relative intensity): 155 (100).

Synthesis of Adamantyledeneadamantane (44)



44

Adamantyledeneadamantane (**44**) was prepared by the procedure of McMurry.[238] Potassium metal (3.84 g, 98.0 mmol) was added to a stirred slurry of $TiCl_3$ (4.30 g, 28.0 mmol) in 150 mL of dry THF under a mild nitrogen flow at room temperature. After refluxing for 40 min, the black mixture was cooled and a solution of adamantanone (1.05 g, 7.0 mmol) in 10 mL of THF was added and the mixture was refluxed for another 16 hr. The reaction mixture was then cooled to room temperature and filtered under an inert atmosphere. The filter cake, which is pyrophoric in contact with air, was carefully quenched in *iso*-propanol. Removal of the solvent from the organic phase under reduced pressure and column chromatography of the residue on silica gel with hexanes afforded 1.3 g (70%) of adamantyledeneadamantane (**44**). Mp. 182-184°C (lit.[238] 183-185°C).

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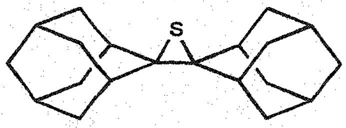
[238] McMurry, J. E.; Fleming, M. P.; Kees, K. L. and Krepski, L. R. *J. Org. Chem.*, **1978**, *43*, 3255.

Reaction of S_{10} with Adamantyledeneadamantane



45

Adamantyledeneadamantane (**44**) (241.0 mg, 0.9 mmol) was dissolved in 100 mL of toluene and refluxed under a nitrogen flow. Freshly recrystallized S_{10} (337.0 mg, 1.0 mmol) was dissolved in carbon disulfide and the solution concentrated to *ca.* 5 mL on a warm sand bath. The S_{10}/CS_2 solution was then injected on top of the refluxing olefin solution with a syringe over 30 sec. An extra 1 mL of CS_2 was used to rinse the flask which contained S_{10} and was subsequently added to the refluxing solution. Reflux was maintained for 3 hr. The solvent was then evaporated and the residue triturated repeatedly with 3x3 mL of hexanes and then with smaller portions of CS_2 until no product was detected by TLC. The crude reaction mixture was separated on a silica gel chromatographic column using a dry pack in order to load the sample. During the course of the separation, the eluant composition was switched from hexanes to 3% diethyl ether in hexanes. Adamantyledeneadamantane thiirane (**45**) (109 mg) was isolated as an off white solid in 40% yield. Mp. 144-146°C (lit. 142-143°C,[239] 153-154°C[198]).

45: ^{1}**H-NMR** ($CDCl_3$) δ: 1.80-2.08 (m, 14H) ppm. ^{13}**C-NMR** ($CDCl_3$) δ: 71.70, 40.04, 39.05, 38.86, 38.23, 35.43, 28.30, 27.71 ppm.

Reduction of Trithiolane 27 with Lithium Aluminium Hydride

63

Trithiolane **27** (80.0 mg, 0.425 mmol) was dissolved in 25 mL of dry diethyl ether and cooled to 0°C under a nitrogen atmosphere. To this solution was added dropwise a solution of $LiAlH_4$ (26.0 mg, 0.685 mmol) in 3 mL of diethyl ether. The reaction mixture slowly warmed to room temperature and was further stirred overnight before being

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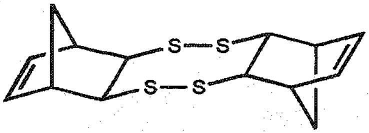
[239] Abu-Youssef, I. A., Ph.D. Thesis, McGill University, **1995**.

cooled again on ice and quenched by careful addition of *ca.* 25 mL of a 5% HCl solution. The organic phase was then extracted with 3x20 mL of diethyl ether and further washed with 2x20 mL of water and 20 mL of a saturated NaCl solution. Purification by flash column chromatography in CS_2 yielded 32.6 mg (48%) of norborn-5-ene-2,3-dithiol (**63**) as a clear smelly oil.

63: ^{1}**H-NMR** ($CDCl_3$) δ: 6.12 (t, J=2.0 Hz, 2H), 3.07 (dt, J_1=4.8 Hz, J_2=2.0 Hz, 2H), 2.77 (m, 2H), 1.97 (dm, J=9.2 Hz, 1H), 1.89 (dd, J_1=4.6 Hz, J_2=2.0 Hz, 2H), 1.53 (dt, J_1=9.2 Hz, J_2=2.0 Hz, 1H) ppm. ^{13}**C-NMR** ($CDCl_3$) δ: 136.29, 53.15, 43.53, 42.72 ppm.

Reaction of Norborn-5-ene-2,3-dithiol (63) with Iodine in the Presence of Pyridine



64

Pyridine (14 µL, 0.173 mmol) was diluted in 25 mL of dry $CHCl_3$ and cooled to 0°C under a nitrogen atmosphere. To this solution were added simultaneously with an automated delivery system over 5 hr, two solutions of dithiol **63** (13.5 mg, 0.086 mmol) and iodine (21.7 mg, 0.085 mmol) in 5 mL of dry $CHCl_3$. Upon completion of the addition, the pale yellow reaction mixture was stirred under N_2 at room temperature for another 12 hr. Excess iodine was then quenched by addition of aliquots of a *ca.* 10% $Na_2S_2O_3$ solution in water until no more yellow coloration could be seen. The organic phase was then washed with 3x30 mL of water and 30 mL of a saturated NaCl solution and dried over magnesium sulfate. Purification by flash column chromatography with 30% $CHCl_3$ in hexanes as an eluant afforded 11.3 mg (84%) of pure dimer compound **64**. Dimer **64** decomposes slowly over a wide range starting at 160°C and is fully decomposed at 250°C.

64: ^{1}**H-NMR** ($CDCl_3$) δ: 6.20 (t, J=1.8 Hz, 2H), 3.46 (d, J=1.5 Hz, 2H), 2.86 (m, 2H), 1.58 (dbs, J=9.3 Hz, 2H), 1.37 (dt, J_1=9.3 Hz, J_2=1.8 Hz, 2H) ppm. ^{13}**C-NMR** ($CDCl_3$) δ: 137.62, 57.00, 49.27, 44.79 ppm. **MS** (EI, 70 eV, 200°C) m/z (relative intensity): 312

($M^{+\cdot}$) (60), 188 (40), 156 (32), 124 (25), 123 (40), 122 (100), 97 (14), 92 (14), 91 (49), 79 (11), 66 (30), 65 (14), 45 (12).

Preparation of Polymeric Sulfur (S_μ)

S_8 (3.0 g, 11.7 mmol) was placed in a stainless steel cup and heated with a sand bath. The sulfur melt was stabilized at 250°C for 20 min and then quenched in a water bath. The yellow solid was aged for 15 hr at room temperature and crushed in a mortar. 1.8 gr of the crushed material were then extracted in 30 mL of CS_2 at room temperature for 7 hr in the absence of light. The slurry mixture was filtered on a Buchner funnel and the light yellow sulfur residue dried for one hour in the dark. Polymeric sulfur (0.36 g) was obtained in 20% yield and its identity confirmed by FT-Raman spectroscopy.[148]

5.3. Chapter 3

Synthesis of S_6

Pure titanocene pentasulfide (**28**) (10.0 g, 29.6 mmol) was placed in a dry 1000 mL flask previously washed in an acid bath and dissolved in 500 mL of HPLC grade CS_2. The mixture was stirred at 0°C in the dark under a nitrogen flow for at least 1 hr in order to ensure complete dissolution. To this mixture was added dropwise, within *ca.* 45 min *via* a double ended needle, a solution of 1.9 mL of freshly distilled SCl_2 (29.6 mmol) in 200 mL of HPLC grade CS_2. The mixture was stirred for an extra 1 hr in the dark under a nitrogen flow at 0°C upon completion of the addition before being placed for 4-5 hr in the freezer at -40°C in order to ensure complete precipitation of Cp_2TiCl_2. Rapid filtration on a Buchner funnel afforded an orange solution. Solvent was evaporated under reduced pressure with a rotary evaporator. The solid residue was extracted with aliquots of CS_2 until a very pale yellow practically insoluble solid was obtained. This solid was dried at room temperature and afforded 520 mg of S_{12} (9% yield, lit.[113] 11%). The CS_2 extracts were gently concentrated on a hot plate and n-pentane was added till turbidity.

Crystallization at –40°C in the dark for two days afforded 4.6 g of S_6 (81% yield, lit.[113] 87%).

Synthesis of S_4Cl_2 by Chlorination of S_6

Cyclo-hexasulfur S_6 (4.57 g, 23.8 mmol) was placed in a dry 500 mL round bottom flask and dissolved in 180 mL of HPLC grade CS_2. A fresh solution of Cl_2 in CCl_4 was then prepared. 70 mL of CCl_4 were measured in a 100 mL graduated cylinder and dry Cl_2 gas was bubbled in the solvent until a 5.06 g (71.4 mmol) weight gain of the solution was obtained. The Cl_2/CCl_4 solution was then transferred *via* a double ended needle to the previously prepared S_6 solution. The mixture was then stirred under a nitrogen flow for 5 hr at room temperature. The solvent was evaporated under reduced pressure with a rotary evaporator and the residue was extracted with *ca.* 50 mL of n-pentane. The pentane extracts were passed through a pipette equipped with a cotton bowl in order to get rid of all solid residues. Pentane was then evaporated under reduced pressure (*ca.* 15 mm Hg) with a rotary evaporator and the flask was further kept for 20 min on the rotary evaporator with the temperature of the bath maintained at 40°C. The flask was then even left for 5 min under higher vacuum on an oil pump while being simultaneously warmed with a water bath at *ca.* 40°C in order to ensure complete evaporation of residual S_2Cl_2. Dichlorotetrasulfane (S_4Cl_2) (2.18 g, 46% yield) was obtained as an orange smelly oil.

Synthesis of S_9

Pure titanocene pentasulfide (**28**) (3.7 g, 10.9 mmol) was dissolved in 130 mL of HPLC grade CS_2 and cooled down to 0°C over 0.5 hr under a nitrogen atmosphere and in the dark. A solution of 2.18 g of S_4Cl_2 (11.0 mmol) in 20 mL of HPLC grade CS_2 was then added dropwise under nitrogen within 20 min *via* a double ended needle. The solution was further stirred for 0.5 hr in the dark at 0°C under nitrogen. The mixture was then placed in the freezer at -40°C for 4-5 hr in order to ensure complete precipitation of Cp_2TiCl_2. The filtrate obtained upon filtration on Buchner, was concentrated down to *ca.* 30 mL and again placed in the freezer at -40°C overnight in order to precipitate any remaining Cp_2TiCl_2. The supernatant was pipetted into a 125 mL Erlenmeyer flask and *ca.* 19 mL of diethyl ether were added. The flask was left in the freezer at -40°C overnight. Some polymeric sulfur precipitated out, the filtrate was pipetted out, another *ca.* 19 mL of diethyl ether were added and the solution kept at -40°C for another 2 days. A precipitate of crude S_9 (826 mg, 26%) formed and upon recrystallization in CS_2/pentane afforded pure S_9 (672 mg, 21%; lit. 18%,[111] 30%,[123a] 38%[123b]) as bright yellow crystals. Mp. 61-63°C (lit.[111] 63-65°C).

Synthesis of S_{12} and S_{20}

Both S_{12} and S_{20} were obtained as side products of the synthesis of S_6 and S_{10}, respectively, from titanocene pentasulfide (**28**). These procedures have been described earlier in this Section.

Extraction of S_{12} from Sulfur Melts

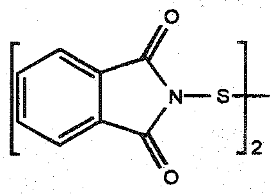
The procedure followed the one of Steudel.[100a] S_8 (400.0 g, 1.56 mol) was placed in a 500 mL beaker and heated for 5-10 min in an oil bath at *ca.* 200°C. The sulfur melt was then allowed to cool to 140°C within 15 min before being quenched in 2 L of liquid nitrogen. The solid residue was then extracted with 250 mL of CS_2 for 1 hr at room temperature. The extracts were then placed in the freezer at -40°C for one day and then rapidly filtered on a Buchner funnel. The precipitate of S_8 and $S_{12}\bullet CS_2$ was warmed to room temperature, vigorously shaken with 50 mL of CS_2 and the solution rapidly decanted off; the suspended colorless powdery $S_{12}\bullet CS_2$ was thus carried over with the solution and separated from the large S_8 crystals. The $S_{12}\bullet CS_2$ were recovered by filtration on a Buchner funnel and the filtrate returned to the $S_8/S_{12}\bullet CS_2$. The extraction procedure was repeated three times. The crude product was dissolved in 250 mL of CS_2 and placed in the freezer at -40°C overnight. Filtration and prolonged drying on a Buchner funnel afforded 320 mg (0.08%, lit.[100a] 0.2%) of S_{12} as a pale yellow solid. Mp. 145-147°C (lit.[100a] 146-148°C).

General Procedure for the Trapping Reaction of S_9, S_{12} and S_{20} with 2,3-Diphenyl-1,3-butadiene (12a), 2,3-Dimethyl-1,3-butadiene (12b) and Norbornene (16)

The procedure followed the one of the small scale model reaction between S_{10} and 1,3-diene **12a** previously described in this Section.

Pure olefin **12a**, **12b** or **16** (0.102 mmol) was placed in a 3-neck 25 mL round bottom flask and dissolved in 10 mL of chlorobenzene or toluene along with 9-methylanthracene (30.0 mg, 0.156 mmol). The latter was used as an internal standard. The mixture was placed under a nitrogen atmosphere and was refluxed with a heating mantle. Freshly recrystallized S_9 (30.3 mg, 0.105 mmol) was dissolved in CS_2 and the solution concentrated to *ca.* 500 μL on a warm sand bath. The S_9/CS_2 solution was then injected on top of the hot olefin solution with a syringe over *ca.* 30 sec. An extra 100 μL of CS_2 was used to rinse the flask that contained S_9 and was subsequently added to the solution. In the case of S_{12} (40.4 mg, 0.105 mmol) and S_{20} (67.3 mg, 0.105 mmol) their low solubility in CS_2 did not allow for their addition as a solution and they were simply combined with the olefin prior to heating. Reflux was maintained for 3-15 hr. The solution was sampled at desired times and solvent evaporated under reduced pressure with a rotary evaporator. Yields of the expected products were estimated by ^{1}H-NMR comparison with the internal standard.

Synthesis of NN'-Dithiobis(phthalimide) (71)

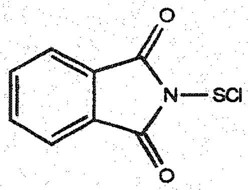


71

Phthalimide potassium salt (**70**) (36.65 g, 197.9 mmol) was placed in a 500 mL round bottom flask and combined with 200 mL of CH_2Cl_2. The suspension was vigorously stirred at 0°C for 0.5 hr and a solution of 7.7 mL of S_2Cl_2 (98%, 96.3 mmol) was then added within 10 minutes. The reaction mixture was stirred for an additional 0.5 hr at 0°C, the solvent evaporated, the solid filtered and dried on a Buchner funnel.

Recrystallization in $CHCl_3$ afforded 23.7 g (70%) of the desired disulfide **71**. Mp. 226-228°C (lit.[207] 229-230°C).

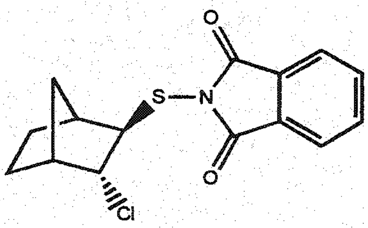
Synthesis of Phthalimido-N-sulfenyl chloride (72)



72

NN'-Dithiobis(phthalimide) (**71**) (20.0 g, 56.1 mmol) was dissolved in 130 mL of $CHCl_3$ in a 3-neck 250 mL round bottom flask equipped with a reflux condenser and the temperature maintained at 50-60°C with an oil bath. Chlorine gas was bubbled through the mixture for 2 hr after which the reaction became completely homogeneous. The third neck of the flask was connected to a series of two consecutive bubbling bottles filled with a 1M KOH solution and water, respectively, in order to ensure complete neutralization of unreacted chlorine gas. After completion of the reaction, nitrogen gas was passed through the reaction mixture for 15 min in order to remove excess chlorine gas. $CHCl_3$ was evaporated, the solid residue filtered on Buchner, washed with some petroleum ether and dried for 5 minutes. This gave 21.6 g (90%) of phthalimido-N-sulfenyl chloride (**72**) as a yellow solid. Compound **72** was kept in the freezer at -40°C. Mp 115-116°C (lit.[207] 115-117°C).

Synthesis of *endo*-3-Chloro-*exo*-2-(phthalimido-N-thio)bicyclo[2.2.1]heptane (73)

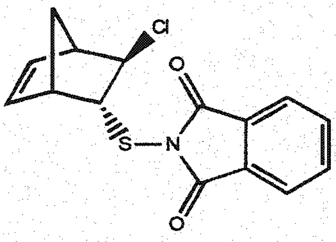


73

A solution of norbornene (533.0 mg, 5.7 mmol) in 10 mL of dry CH_2Cl_2 was prepared and stirred under a mild nitrogen flow. A yellow solution of phthalimido-N-sulfenyl chloride (**72**) (1.0 g, 4.7 mmol) in 3 mL of dry CH_2Cl_2 was then added dropwise under nitrogen *via* a double ended needle. The mixture was subsequently stirred under nitrogen overnight for 12 hr. Evaporation of the solvent under reduced pressure gave the desired adduct **73** in quantitative yield.

73: Mp. 109-111°C (lit.[207] 113°C). ^{1}**H-NMR** ($CDCl_3$) δ: 7.7-8.0 (m, 4H), 4.22 (m, 1H), 3.17 (m, 1H), 2.48 (m, 1H), 2.47 (m, 1H), 1.20-1.92 (m, 6H) ppm.

Synthesis of *exo*-3-Chloro-*endo*-2-(phthalimido-N-thio)bicyclo[2.2.1]hept-5-ene (76)

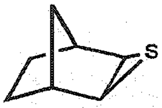


76

Norbornadiene (3.03 mL, 28.0 mmol) was mixed with 40 mL of dry CH_2Cl_2 in a pre-dried 100 mL round bottom flask, stirred under a nitrogen atmosphere and cooled down to -78°C for 30 min. A solution of 4.0 g of phthalimido-N-sulfenyl chloride (**72**) (18.7 mmol) in 10 mL of dry CH_2Cl_2 was prepared. It was then added over 10 min under nitrogen *via* a double ended needle to the cold norbornadiene solution and the whole mixture was stirred at -78°C under nitrogen for a further 3 hr. The white precipitate that formed was filtered and the volume of the solvent was decreased under reduced pressure on a rotary evaporator. The solution was then transferred to a 50 mL Erlenmeyer flask and gently heated on a hot plate. The volume of hot CH_2Cl_2 was reduced to a minimum amount and some methanol was added until the solution turned turbid. It was placed in the freezer at -40°C for 24 hr. Filtration on a Buchner funnel of the off white crystals that formed (3.8 g, 67% yield) and recrystallization in benzene/methanol afforded 3.2 g (55% yield) of pure white crystals of *exo*-3-chloro-*endo*-2-(phthalimido-N-thio)bicyclo[2.2.1]hept-5-ene (**76**).

76: Mp. 159-160°C. ^{1}**H-NMR** ($CDCl_3$) δ: 7.7-8.0 (m, 4H), 6.2-6.4 (m, 2H), 3.86 (t, J=2.4 Hz, 1H), 3.59 (t, J=2.8 Hz, 1H), 3.09 (m, 1H), 3.01 (m, 1H), 1.90 (d-bs, J=9.3 Hz, 2H), 1.76 (dq, J_1=9.0 Hz, J_2=2.0 Hz, 2H) ppm. ^{13}**C-NMR** ($CDCl_3$) δ: 168.07, 136.51, 135.81, 134.66, 131.87, 123.96, 63.66, 62.09, 52.13, 46.90, 46.36 ppm. **MS** (EI, 70 eV, 200°C) m/z (relative intensity): 305 (M^{+}) (4), 270 (8), 241 (38), 240 (16), 239 (100), 206 (4), 205 (6), 204 (19), 160 (7), 158 (16), 153 (14), 149 (7), 148 (37), 147 (20), 136 (12), 130 (14), 129 (36), 123 (15), 112 (12), 104 (21), 92 (22), 91 (31), 77 (27), 76 (22), 66 (25).

Synthesis of *exo*-2,3-Epithionorbornane (69)

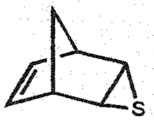


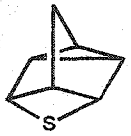
69

Lithium aluminum hydride (252.0 mg, 6.6 mmol) was combined with 10 mL of dry THF in a 50 mL dry round bottom flask. The suspension was stirred under a nitrogen atmosphere and cooled to -78°C for 30 min. A solution of 1.07 g of *endo*-3-chloro-*exo*-2-(phthalimido-N-thio)bicyclo[2.2.1]heptane (**73**) (3.5 mmol) in 5 mL of dry THF was then added dropwise to this mixture under nitrogen *via* a double ended needle over 15 min. The mixture was then stirred for a further 15 min at -78°C before being slowly warmed back to room temperature. The reaction mixture was then quenched by successive dropwise addition of 250 μL of water, 250 μL of a 15% KOH solution and 3x250 μL of water. The white granular precipitate that formed upon stirring was collected on a Buchner funnel, the solution dried over $MgSO_4$ and the solvent evaporated. Column chromatography of the residue in 10% $CHCl_3$ in hexanes afforded 225 mg (51%) of *exo*-2,3-epithionorbornane (**69**) as a colorless smelly oil.

69: **^{1}H-NMR** ($CDCl_3$) δ: 2.68 (s, 2H), 2.39 (bs, 2H), 1.54-1.62 (m, 2H), 1.47 (dt, J_1=10.5 Hz, J_2=2.4 Hz, 1H), 1.16-1.23 (m, 2H), 0.60 (d, J=9.9 Hz, 1H) ppm. **^{13}C-NMR** ($CDCl_3$) δ: 37.43, 37.22, 27.34, 27.30 ppm.

Reaction of *exo*-3-Chloro-*endo*-2-(phthalimido-N-thio)bicyclo[2.2.1]hept-5-ene (76) with Lithium Aluminum Hydride


77


78

Lithium aluminum hydride (211.0 mg, 5.6 mmol) was combined with 10 mL of dry THF in a 50 mL dry round bottom flask. The suspension was stirred under a nitrogen atmosphere and cooled to -78°C for 30 min. A solution of 1.0 g of *exo*-3-chloro-*endo*-2-(phthalimido-N-thio)bicyclo[2.2.1]hept-5-ene (**76**) (3.3 mmol) in 5 mL of dry THF was then added dropwise to this mixture under nitrogen *via* a double ended needle over 15 min. Stirring was subsequently maintained for 15 min at -78°C before the reaction was slowly warmed back to room temperature. The reaction mixture was then quenched by successive dropwise addition of 220 μL of water, 220 μL of a 15% KOH solution and 3x220 μL of water. The white granular precipitate that formed upon stirring was collected on a Buchner funnel, the solution dried over $MgSO_4$ and the solvent evaporated. Separation of the crude mixture by flash column chromatography eluted with 10% $CHCl_3$ in hexanes afforded *endo*-epithionorborn-5-ene (**77**) (64.3 mg, 16%) and nortricyclene **78** (28.5 mg, 7%) as clear smelly oils.

77: ^{1}**H-NMR** ($CDCl_3$) δ: 5.74 (t, J=2.1 Hz, 2H), 3.30 (t, J=1.7 Hz, 2H), 3.02 (bs, 2H), 2.13 (d, J=8.1 Hz, 1H), 2.04 (d, J=7.5 Hz, 1H) ppm. ^{13}**C-NMR** ($CDCl_3$) δ: 130.32, 62.39, 43.73, 32.84 ppm. **MS** (EI, 70 eV, 100°C) m/z (relative intensity): 124 ($M^{+\cdot}$) (94), 123 (84), 97 (70), 92 (14), 91 (100), 79 (57), 78 (23), 77 (31), 66 (22), 65 (20), 58 (18), 51 (12), 45 (25), 39 (26).

78: ^{1}**H-NMR** ($CDCl_3$) δ: 3.53 (bs, 2H), 3.12 (bs, 1H), 2.26 (m, 1H), 2.21 (m, 2H), 1.42 (t, J=1.5 Hz, 2H) ppm. ^{13}**C-NMR** ($CDCl_3$) δ: 56.26, 55.68, 37.95, 35.07, 28.43 ppm. **MS** (EI, 70 eV, 100°C) m/z (relative intensity): 124 ($M^{+\cdot}$) (100), 123 (96), 97 (81), 92 (15), 91 (98), 79 (65), 78 (28), 77 (36), 66 (30), 65 (26), 58 (12), 51 (11), 45 (25), 39 (20).

5.4. Chapter 4

General Procedure for the Trapping Reaction of S_{10} with 2,3-Diphenyl-1,3-butadiene (12a) in the Presence of a Radical Scavenger

The procedure followed the one described in the small scale model reaction between S_{10} (33.7 mg, 0.105 mmol) and 1,3-diene **12a** (21.0 mg, 0.102 mmol). The reactions with BHT (92.0 mg, 0.417 mmol) and TEMPO (33.0 mg, 0.211 mmol) were carried out in refluxing toluene (10 mL) and chlorobenzene (10 mL), respectively. Carbon disulfide (500 μL + 100 μL) was used as usual in order to inject S_{10} on the refluxing diene. Cumene was also used as a radical scavenger. In this case, cumene (2.5 mL) was directly used as a solvent and the temperature of the mixture was maintained at *ca.* 130°C with an oil bath. Reactions were sampled at regular time intervals and the product yields calculated by comparison with 9-methylanthracene (30.0 mg, 0.156 mmol), which was used as an internal standard. Reaction times never exceeded 6 hr and reaction was stopped after 2 hr in the case of TEMPO and cumene.

Decomposition of S_{10} in Cumene

Cumene (50 mL) was heated at *ca.* 120°C and the temperature maintained by an oil bath in an open-air flask. S_{10} (400.0 mg, 1.25 mmol) was dissolved in 5 mL of CS_2 and added to the hot solution within *ca.* 30 seconds with a syringe. An extra 1 mL of CS_2 was used to rinse the flask that contained S_{10} and the rinses were also combined to cumene. Upon addition of S_{10}, the solution turned turbid but cleared up within 5 minutes. The reaction mixture was heated for 2 hr. A paper moistened in a lead acetate solution and maintained over the reaction mixture darkened as reaction progressed. Cumene was evaporated under reduced pressure and the residue triturated repeatedly with 2 mL portions of $CHCl_3$. A dry pack was then prepared between the extracts and 2 g of silica gel. Separation of the complex mixture was achieved by successive flash column chromatography in $CHCl_3$/hexanes as eluant systems. It afforded crude bicumyl (**92**) (12.9 mg) in 4% yield as well as 16.4 mg of a dark red mixture of bicumyl polysulfides

(**93**). Compound **92** was then further purified by chromatography in hexanes and afforded a white solid.

92: Mp. 107-108°C (lit.[240] 109-111°C). **^{1}H-NMR** ($CDCl_3$) δ: 7.10 (m, 10H), 1.29 (s, 12H) ppm. **MS** (CI (NH_3), 70 eV, 150°C) m/z (relative intensity): 119 ($M^{+\cdot}/2$), 91.

93: **^{1}H-NMR** ($CDCl_3$) δ: 7.40 (m), 1.82 (s), 1.815 (s), 1.81 (s), 1.80 (s), 1.785 (s), 1.76 (s) ppm. **^{13}C-NMR** ($CDCl_3$) δ: 143.61-143.95, 126.73-128.54, 54.68, 54.64, 54.55, 54.46, 54.365, 54.09, 29.01, 28.94 ppm. **MS** (CI (NH_3), 70 eV, 150°C) m/z (relative intensity): 246 (8), 214 (29), 182 (9), 149 (8), 119 (32), 118 (100), 117 (57), 116 (8), 115 (29), 103 (61), 91 (33), 78 (27), 77 (20), 64 (15).

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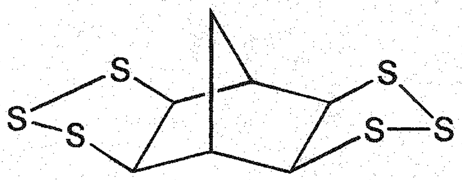
[240] Grovenstein, E.; Blanchard, E. P.; Gordon, D. A. and Stevenson, R. W. *J. Am. Chem. Soc.*, **1959**, *81*, 4842.

APPENDIX I. X-RAY STRUCTURES



Appendix I-1. X-Ray Structure Determination of *bis*-Sulfurated Compound **42**

Table XR-1. Crystal Data for the Structure Determination of **42**

Table XR-2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **42**

Table XR-3. Bond Distances and Angles for **42**

Table XR-4. Bond Angles for **42**

Table XR-5. Torsion Angles for **42**

Intensity data were collected at -50°C on an Enraf-Nonius diffractometer controlled by CAD-4 software using the $\omega/2\theta$ scan mode.

Table XR-1. Crystal Data for the Structure Determination of **42**

Chemical formula	$C_7H_8S_6$
Formula weight	284.49
Cell setting	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	
a = 6.805 (3) Å	α = 90°
b = 13.023 (5) Å	β = 100.68 (4)°
c = 12.241 (5) Å	γ = 90°
V (Å^3)	1066.0 (8)
Z	4
Density (calculated) (g·cm^{-3})	1.773
F (000)	584
Radiation	Cu Kα
λ (Å)	1.54056
μ (mm^{-1})	11.313
Crystal shape	Stick
Colour	Very pale yellow
Crystal dimension (mm)[a]	0.61 x 0.27 x 0.23
Absorption correction	none
Number of measured reflections	6775
Number of independent reflections	2027
Number of reflections with $I>2\sigma$ (I)	1838
R_{int}	0.044
θ max (°)	69.91
h, k, l ranges	$-8\leq h \leq 8$, $-15 \leq k \leq 15$, $-14 \leq h \leq 14$
Number of standard reflections	5
Frequency (min)	60
Intensity decay (%)	1.01
Refinement method	Full-matrix on F^2
For significant reflections	R = 0.0345, R_w = 0.0906, S = 1.078
Number of reflections used in refinement	2027
Number of parameters refined	150
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$ (e/Å^3)	0.429
$\Delta\rho_{min}$ (e/Å^3)	-0.477
Extinction correction	SHELXL-93 (Sheldrick, 1995)
Secondary extinction value	0.0038 (4)

[a] Cell dimensions were obtained from 25 reflections with θ angle in the range 20 to 25; [b] $R=\Sigma(F_o-F_c)/\Sigma(F_o)$; [c] $wR=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$; [d] $S=(\Sigma[w(F_o^2-F_c^2)^2]/(\#\text{ reflections} - \#\text{ parameters}))^{1/2}$.

	x	y	z	U_{eq}
S3	1.01930 (11)	0.64651 (5)	-0.30489	2.51 (2)
S4	0.99423 (13)	0.49457 (5)	-0.34716	3.22 (2)
S5	0.91382 (14)	0.45150 (5)	-0.19993	3.25 (2)
S9	0.45154 (11)	0.67519 (5)	0.03917 (5)	2.36 (2)
S10	0.32225 (11)	0.81602 (5)	-0.00199	2.57 (2)
S11	0.55787 (11)	0.86705 (5)	-0.06983 (5)	2.27 (2)
C1	0.7854 (4)	0.7327 (2)	-0.1688 (2)	1.76 (5)
C2	0.7773 (4)	0.6522 (2)	-0.2612 (2)	1.84 (5)
C6	0.7233 (4)	0.5508 (2)	-0.2042 (2)	1.88 (5)
C7	0.7098 (4)	0.5878 (2)	-0.0854 (2)	1.85 (6)
C8	0.5151 (4)	0.6509 (2)	-0.0975 (2)	1.83 (5)
C12	0.5686 (4)	0.7521 (2)	-0.1546 (2)	1.84 (5)
C13	0.8698 (4)	0.6708 (2)	-0.0241 (2)	1.94 (6)

Table XR-2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **42**

Bond lengths (Å)			
S3-C2	1.825 (3)	S3-S4	2.0443 (12)
S4-S5	2.0561 (13)	S5-C6	1.825 (3)
S9-C8	1.831 (3)	S9-S10	2.0561 (12)
S10-S11	2.0483 (13)	S11-C12	1.830 (3)
C1-C13	1.533 (3)	C1-C2	1.536 (3)
C1-C12	1.538 (4)	C1-H1	0.97 (3)
C2-C6	1.568 (3)	C2-H2	0.93 (3)
C6-C7	1.551 (3)	C6-H6	0.93 (3)
C7-C13	1.521 (4)	C7-C8	1.543 (4)
C7-H7	0.90 (3)	C8-C12	1.567 (3)
C8-H8	0.95 (3)	C12-H12	0.93 (3)
C13-H13A	0.91 (3)	C13-H13B	0.94 (3)

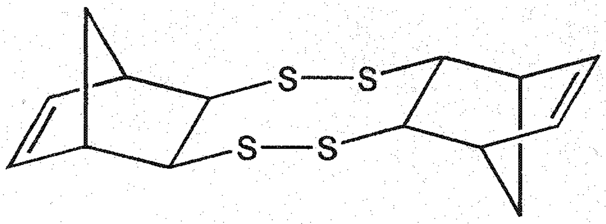
Table XR-3. Bond Lengths for **42**

Bond angles (deg)			
C2-S3-S4	94.36 (9)	S3-S4-S5	93.76 (4)
C6-S5-S4	94.83 (9)	C8-S9-S10	95.35 (9)
S11-S10-S9	93.28 (5)	C12-S11-S10	94.66 (10)
C13-C1-C2	102.3 (2)	C13-C1-C12	102.2 (2)
C2-C1-C12	106.9 (2)	C13-C1-H1	112 (2)
C2-C1-H1	114 (2)	C12-C1-H1	117 (2)
C1-C2-C6	103.1 (2)	C1-C2-S3	109.4 (2)
C6-C2-S3	113.3 (2)	C1-C2-H2	117 (2)
C6-C2-H2	110 (2)	S3-C2-H2	104 (2)
C7-C6-C2	102.4 (2)	C7-C6-S5	111.0 (2)
C2-C6-S5	112.7 (2)	C7-C6-H6	112 (2)
C2-C6-H6	108 (2)	S5-C6-H6	111 (2)
C13-C7-C8	102.3 (2)	C13-C7-C6	102.5 (2)
C8-C7-C6	106.0 (2)	C13-C7-H7	115 (2)
C8-C7-H7	116 (2)	C6-C7-H7	113 (2)
C7-C8-C12	102.9 (2)	C7-C8-S9	110.4 (2)
C12-C8-S9	112.1 (2)	C7-C8-H8	114 (2)
C12-C8-H8	110 (2)	S9-C8-H8	107 (2)
C1-C12-C8	102.7 (2)	C1-C12-S11	109.8 (2)
C8-C12-S11	113.4 (2)	C1-C12-H12	115 (2)
C8-C12-H12	112 (2)	S11-C12-H12	105 (2)
C7-C13-C1	94.9 (2)	C7-C13-H13A	114 (2)
C1-C13-H13A	111 (2)	C7-C13-H13B	115 (2)
C1-C13-H13B	111 (2)	H13B-C13-H13B	111 (2)

Table XR-4. Bond Angles for **42**

Torsion angles (deg)			
C2-S3-S4-S5	-49.05 (9)	C13-C7-C8-C12	34.3 (2)
S3-S4-S5-C6	48.51 (10)	C6-C7-C8-C12	-72.8 (2)
C8-S9-S10-S11	-48.81 (10)	C13-C7-C8-S9	-85.5 (2)
S9-S10-S11-C12	48.82 (9)	C6-C7-C8-S9	167.4 (2)
C13-C1-C2-C6	34.9 (3)	S10-S9-C8-C7	147.5 (2)
C12-C1-C2-C6	-72.1 (2)	S10-S9-C8-C12	33.3 (2)
C13-C1-C2-S3	-85.9 (2)	C13-C1-C12-C8	-35.1 (2)
C12-C1-C2-S3	167.1 (2)	C2-C1-C12-C8	71.9 (2)
S4-S3-C2-C1	149.7 (2)	C13-C1-C12-S11	85.8 (2)
S4-S3-C2-C6	35.3 (2)	C2-C1-C12-S11	-167.1 (2)
C1-C2-C6-C7	-0.5 (3)	C7-C8-C12-C1	0.7 (2)
S3-C2-C6-C7	117.6 (2)	S9-C8-C12-C1	119.3 (2)
C1-C2-C6-S5	-119.8 (2)	C7-C8-C12-S11	-117.7 (2)
S3-C2-C6-S5	-1.7 (2)	S9-C8-C12-S11	0.9 (3)
S4-S5-C6-C7	-146.8 (2)	S10-S11-C12-C1	-149.0 (2)
S4-S5-C6-C2	-32.6 9 (2)	S10-S11-C12-C8	-34.8 (2)
C2-C6-C7-C13	-34.3 (3)	C8-C7-C13-C1	-54.9 (2)
S5-C6-C7-C13	86.2 (2)	C6-C7-C13-C1	54.8 (2)
C2-C6-C7-C8	72.6 (2)	C2-C1-C13-C7	-55.2 (2)
S5-C6-C7-C8	-166.9 (2)	C12-C1-C13-C7	55.4 (2)

Table XR-5. Torsion Angles for **42**



Appendix I-2. X-Ray Structure Determination of Dimer Compound **64**

Intensity data were collected at room temperature on an Enraf-Nonius diffractometer controlled by CAD-4 software using the $\omega/2\theta$ scan mode.

Table XR-6. Crystal Data for the Structure Determination of **64**

Chemical formula	$(C_7H_8S_2)_2$
Formula weight	312.51
Cell setting	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a = 6.598 (2) Å	α = 80.98 (3)°
b = 7.108 (2) Å	β = 74.13 (3)°
c = 8.893 (3) Å	γ = 62.73 (3)°
V (Å^3)	356.34 (19)
Z	2
Density (calculated) (g·cm^{-3})	1.4563
Radiation	Cu Kα
λ (Å)	1.54056
μ (mm^{-1})	5.935
Crystal shape	Plate
Colour	Colourless
Crystal dimension (mm)[a]	0.48 x 0.25 x 0.02
Absorption correction	Integration ABSORP in *NRCVAX* T_{min}=0.2055, T_{max}=0.8488
Number of measured reflections	13204
Number of independent reflections	1351
Number of reflections with I>2σ (I)	1168
R_{int}	0.069
θ max (°)	69.80
h, k, l ranges	$-8 \leq h \leq 8$, $-8 \leq k \leq 8$, $-10 \leq h \leq 10$
Number of standard reflections	5
Frequency (min)	60
Intensity decay (%)	No decay, variation 2.2%
Refinement method	Full-matrix on F^2
For significant reflections	R = 0.0706, R_w = 0.2933, S = 1.353
Number of reflections used in refinement	1351
Number of parameters refined	83
$(\Delta/\sigma)_{max}$	0.000
$\Delta\rho_{max}$ (e/Å^3)	0.684
$\Delta\rho_{min}$ (e/Å^3)	-0.426
Extinction correction	SHELXL-96 (Sheldrick, 1996)
Extinction coefficient	0.081 (19)

[a] Cell dimensions were obtained from 25 reflections with θ angle in the range 20 to 25; [b] $R=\Sigma(F_o-F_c)/\Sigma(F_o)$; [c] $wR=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$; [d] $S=(\Sigma[w(F_o^2-F_c^2)^2]/(\#\text{ reflections} - \#\text{ parameters}))^{1/2}$.

	x	y	z	U_{eq}
S1	0.6645 (2)	0.6532 (2)	1.10439 (17)	0.0630 (7)
S2	0.7692 (2)	0.5965 (2)	0.87186 (16)	0.0622 (7)
C1	0.9392 (9)	0.2582 (9)	0.6923 (6)	0.0582 (14)
H1	0.8011	0.3470	0.6495	0.0770
C2	0.9258 (9)	0.3109 (9)	0.8606 (6)	0.0539 (13)
H2	0.8367	0.2462	0.9383	0.065
C3	1.1905 (9)	0.1937 (9)	0.8701 (6)	0.0542 (13)
H3	1.2107	0.0797	0.9509	0.065
C4	1.3158 (9)	0.0952 (9)	0.7053 (7)	0.0599 (14)
H4	1.4850	0.0517	0.6735	0.072
C5	1.2395 (12)	-0.0741 (10)	0.7048 (8)	0.0700 (16)
H5	1.3319	-0.2195	0.7090	0.084
C6	1.0157 (11)	0.0224 (10)	0.6971 (7)	0.0654 (15)
H6	0.9230	-0.0435	0.6951	0.078
C7	1.1682 (10)	0.2688 (10)	0.6020 (6)	0.0639 (15)
H7A	1.2133	0.2301	0.4939	0.077
H7B	1.1659	0.4049	0.6080	0.077

Table XR-7. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **64**

Bond lengths (Å)			
S1-C3^{i}	1.817 (6)	C3-S1^{i}	1.817 (6)
S1-S2	2.035 (2)	C3-H3	0.9800
S2-C2	1.812 (6)	C4-C5	1.503 (9)
C1-C6	1.510 (8)	C4-C7	1.533 (8)
C1-C7	1.535 (8)	C4-H4	0.9800
C1-C2	1.569 (7)	C5-C6	1.330 (9)
C1-H1	0.9800	C5-H5	0.9300
C2-C3	1.574 (7)	C6-H6	0.9300
C2-H2	0.9800	C7-H7A	0.9700
C3-C4	1.565 (7)	C7-H7B	0.9700

Table XR-8. Bond Lengths for **64**

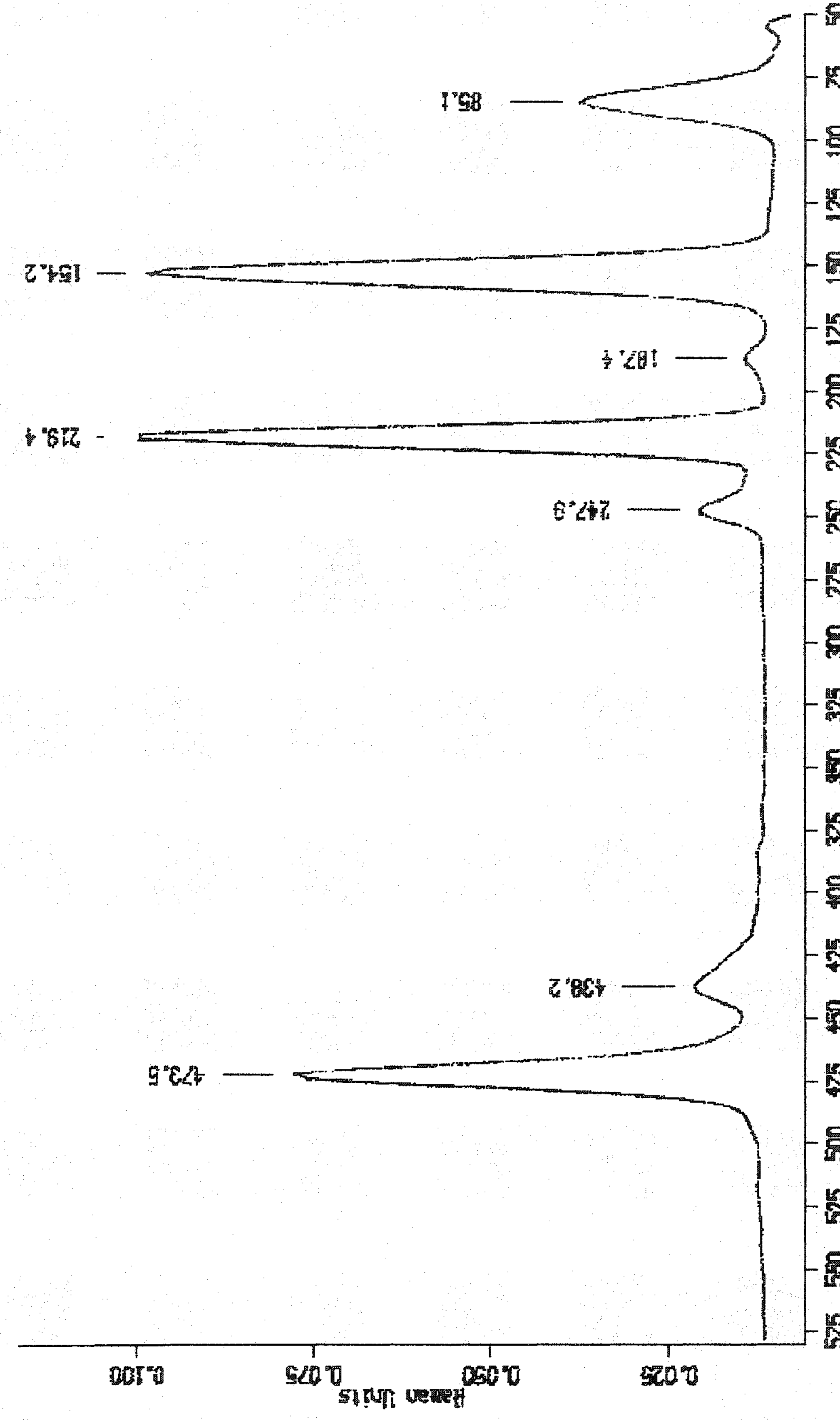
Bond angles (deg)			
C3^i-S1-S2	104.78 (19)	S1^i-C3-H3	109.4
C2-S2-S1	105.20 (18)	C5-C4-C7	100.9 (5)
C6-C1-C7	100.5 (5)	C5-C4-C3	105.2 (5)
C6-C1-C2	105.7 (5)	C7-C4-C3	101.0 (4)
C7-C1-C2	100.6 (4)	C5-C4-H4	115.9
C6-C1-H1	116.0	C7-C4-H4	115.9
C7-C1-H1	116.0	C3-C4-H4	115.9
C2-C1-H1	116.0	C6-C5-C4	107.4 (5)
C1-C2-C3	102.1 (4)	C6-C5-H5	126.3
C1-C2-S2	106.3 (4)	C4-C5-H5	126.3
C3-C2-S2	120.1 (4)	C5-C6-C1	107.6 (6)
C1-C2-H2	109.2	C5-C6-H6	126.2
C3-C2-H2	109.2	C1-C6-H6	126.2
S2-C2-H2	109.2	C4-C7-C1	93.7 (4)
C4-C3-C2	102.4 (4)	C4-C7-H7A	113.0
C4-C3-S1^i	106.4 (4)	C1-C7-H7A	113.0
C2-C3-S1^i	119.4 (4)	C4-C7-H7B	113.0
C4-C3-H3	109.4	C1-C7-H7B	113.0
C2-C3-H3	109.4	H7A-C7-H7B	110.4

Table XR-9. Bond Angles for **64**

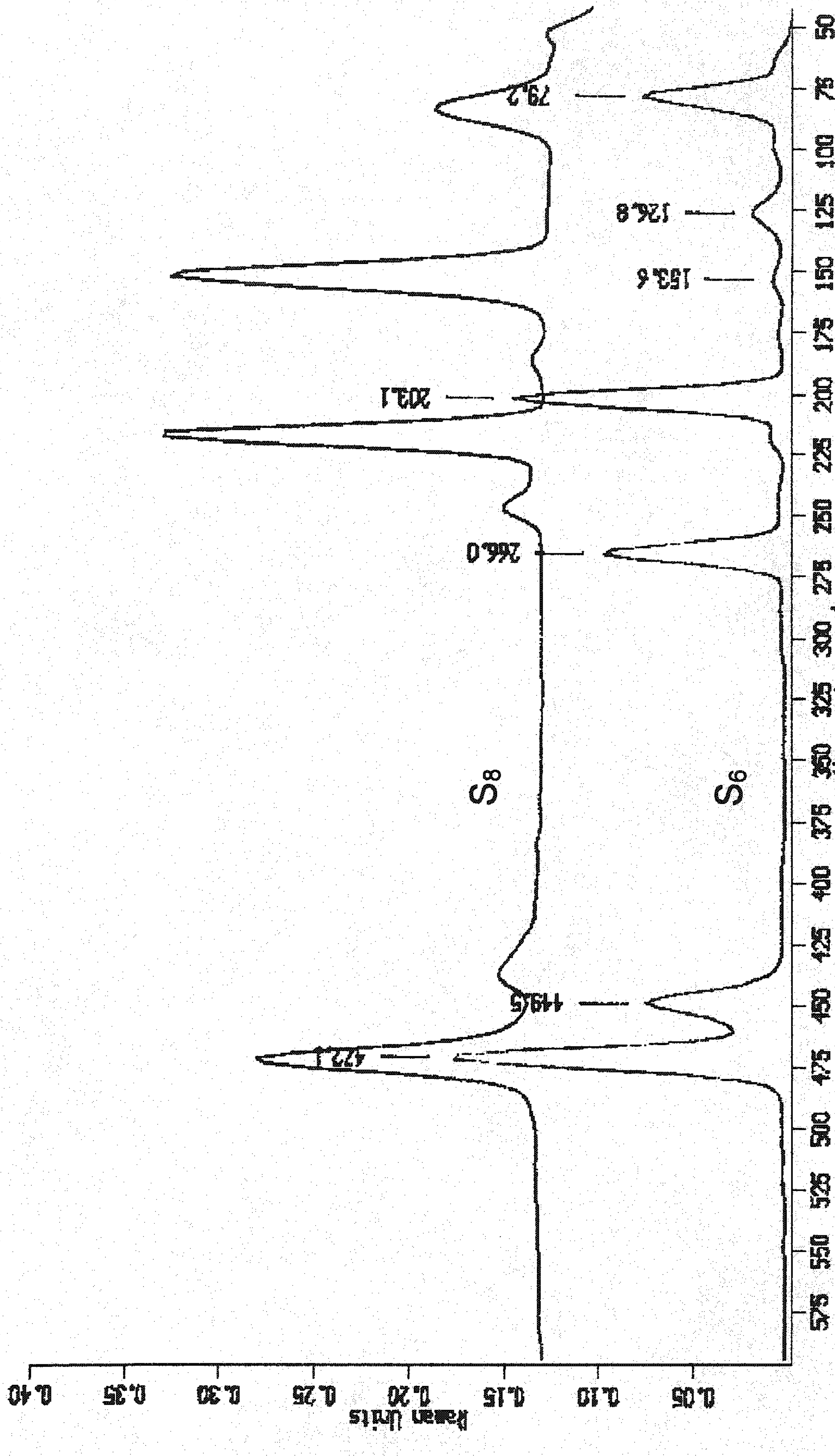
Torsion angles (deg)			
C3^{i}-S1-S2-C2	118.2 (2)	S1^{i}-C3-C4-C5	165.2 (4)
C6-C1-C2-C3	66.7 (5)	C2-C3-C4-C7	36.0 (5)
C7-C1-C2-C3	-37.5 (5)	S1^{i}-C3-C4-C7	-90.1 (4)
C6-C1-C2-S2	-166.7 (4)	C7-C4-C5-C6	-33.1 (6)
C7-C1-C2-S2	89.1 (4)	C3-C4-C5-C6	71.6 (6)
S1-S2-C2-C1	162.5 (3)	C4-C5-C6-C1	0.1 (7)
S1-S2-C2-C3	-82.5 (4)	C7-C1-C6-C5	32.9 (6)
C1-C2-C3-C4	1.0 (5)	C2-C1-C6-C5	-71.3 (6)
S2-C2-C3-C4	-116.2 (4)	C5-C4-C7-C1	49.5 (5)
C1-C2-C3-S1^{i}	118.1 (4)	C3-C4-C7-C1	-58.5 (5)
S2-C2-C3-S1^{i}	1.0 (6)	C6-C1-C7-C4	-49.2 (5)
S2-C3-C4-C5	-68.7 (5)	C2-C1-C7-C4	59.1 (5)

Table XR-10. Torsion Angles for **64**

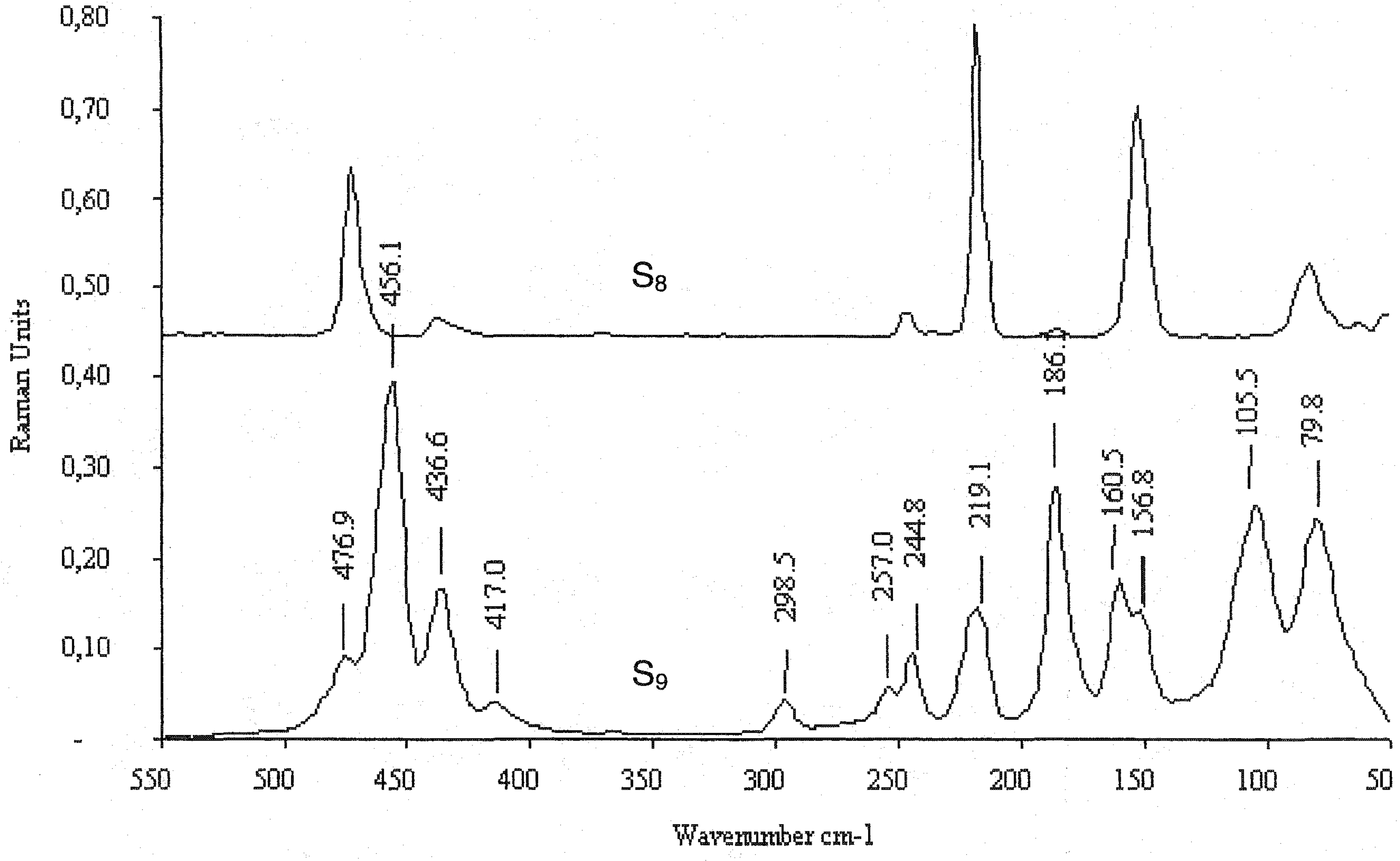
APPENDIX II. RAMAN SPECTRA



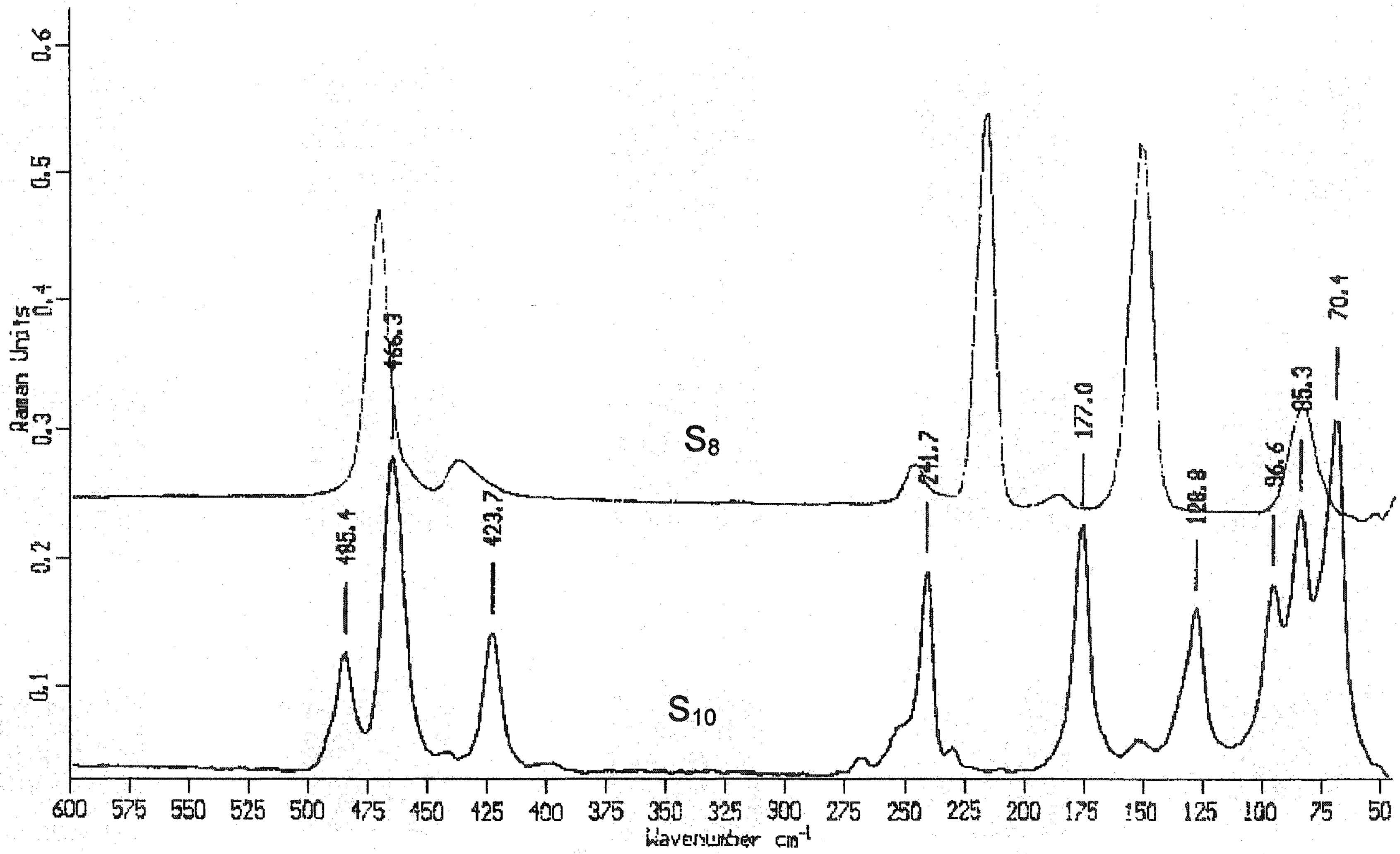
Appendix II-1. Raman Spectrum of S_8



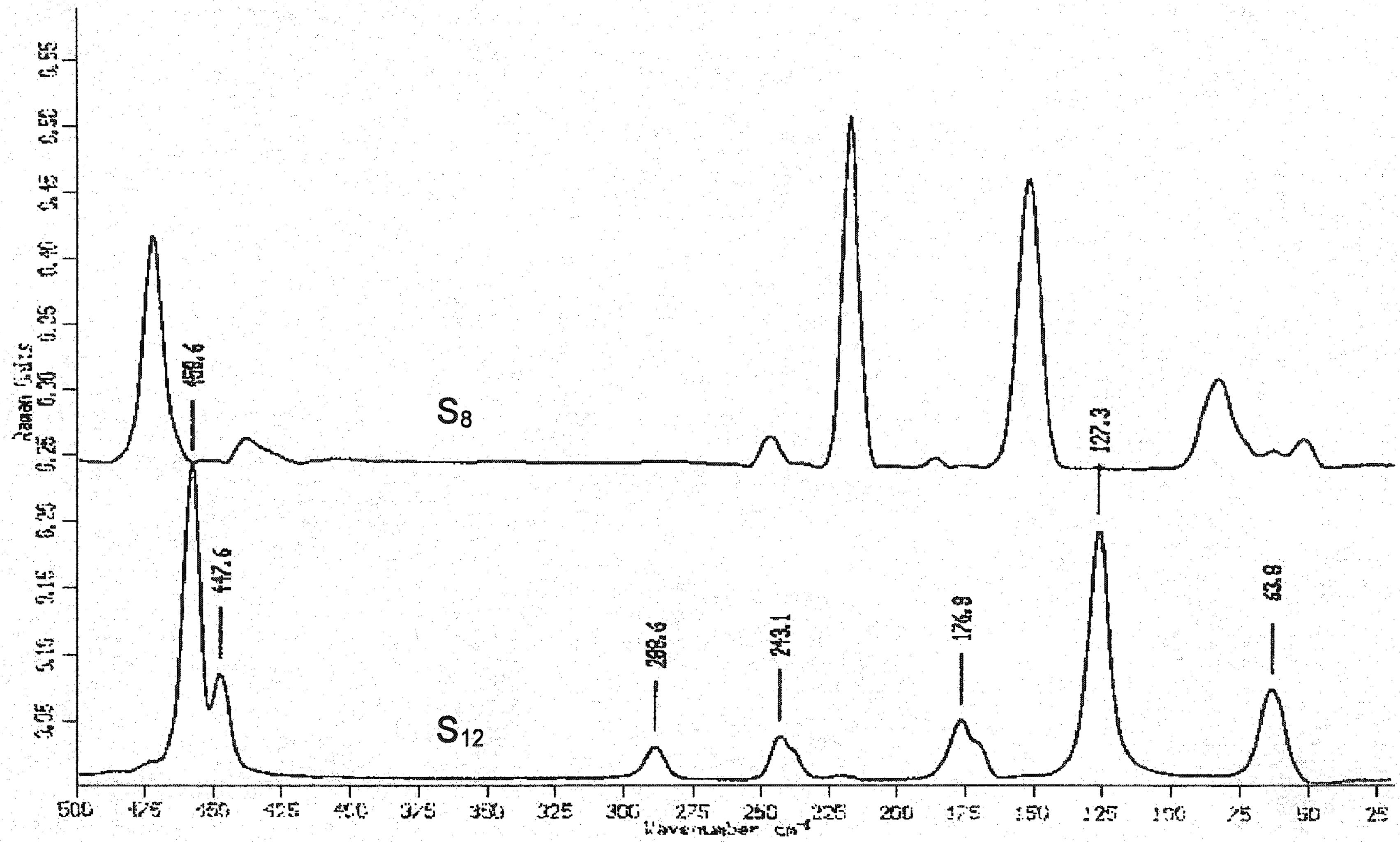
Appendix II-2. Raman Spectrum of S_6



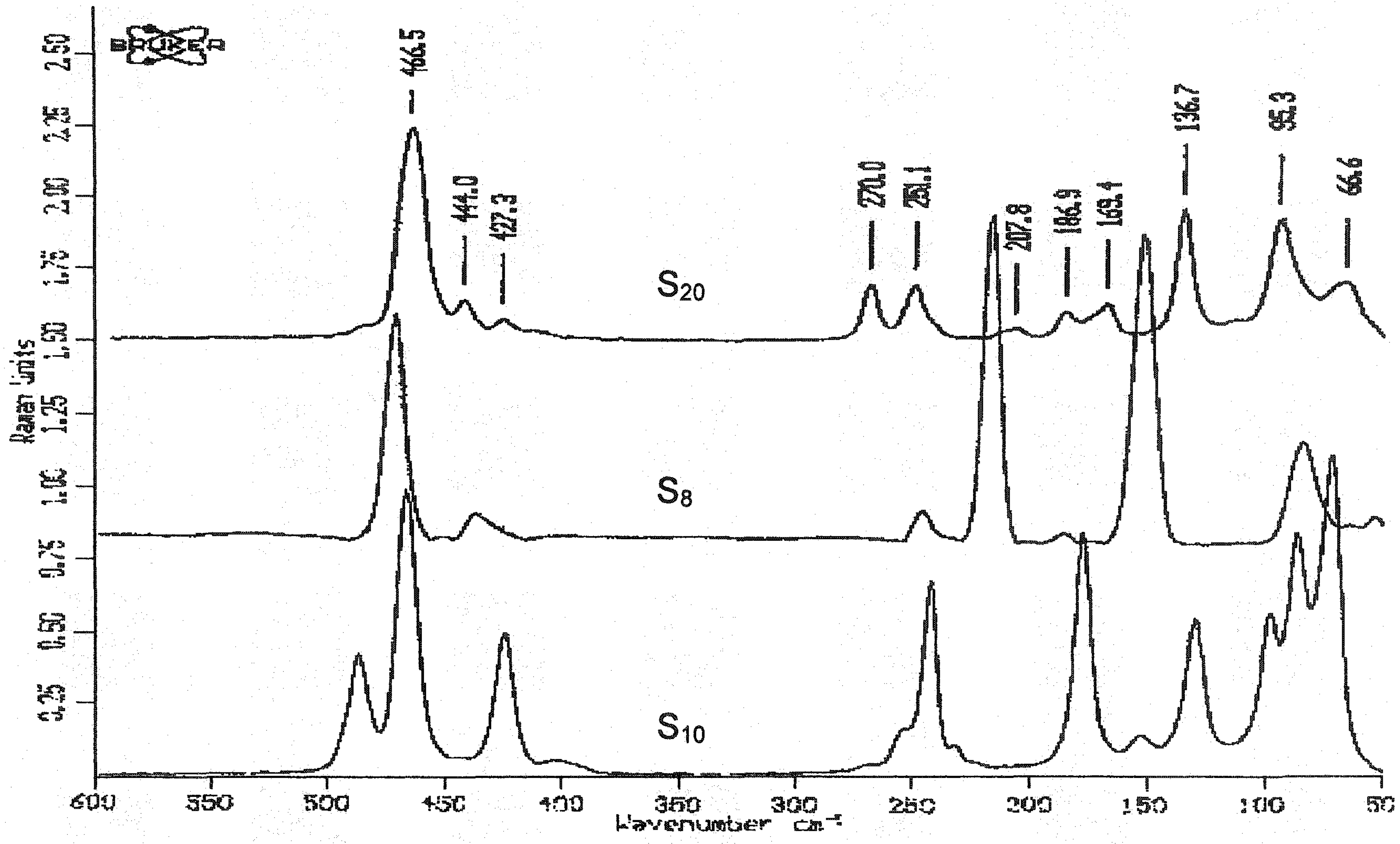
Appendix II-3. Raman Spectrum of α-S_9



Appendix II-4. Raman Spectrum of S $_{10}$

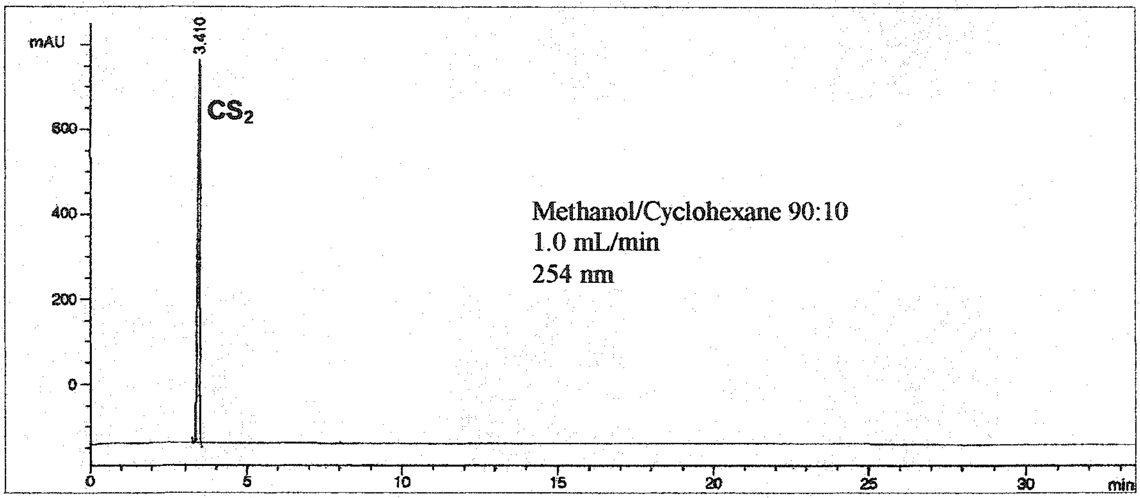


Appendix II-5. Raman Spectrum of S $_{12}$



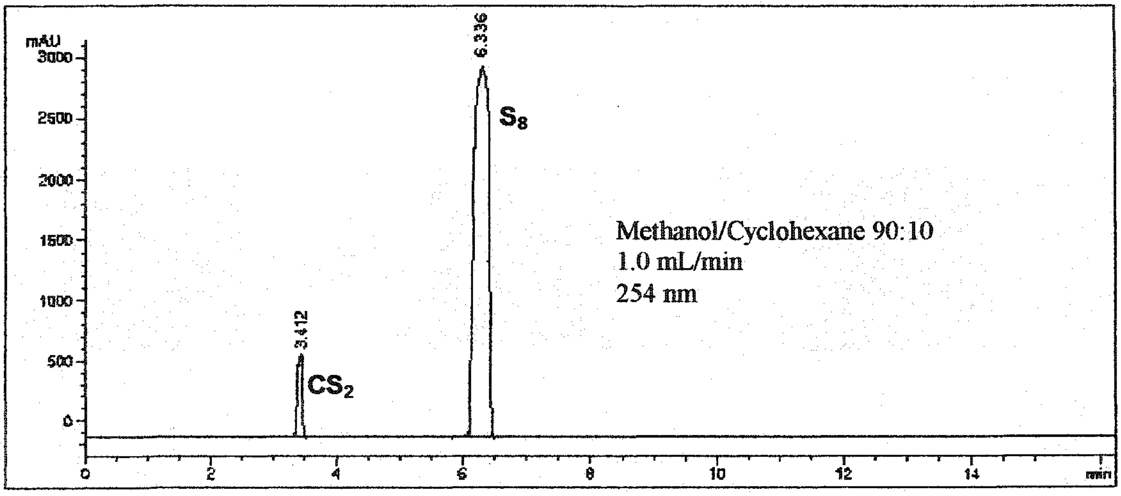
Appendix II-6. Raman Spectrum of S_{20}

APPENDIX III. HPLC SPECTRA



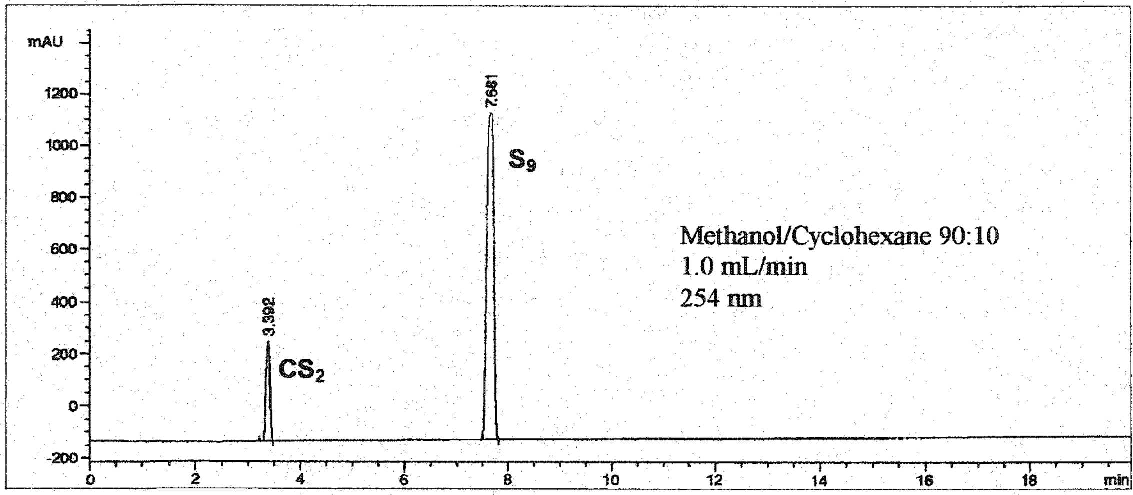
Methanol/Cyclohexane 90:10
1.0 mL/min
254 nm

Appendix III-1. HPLC Spectrum of CS_2

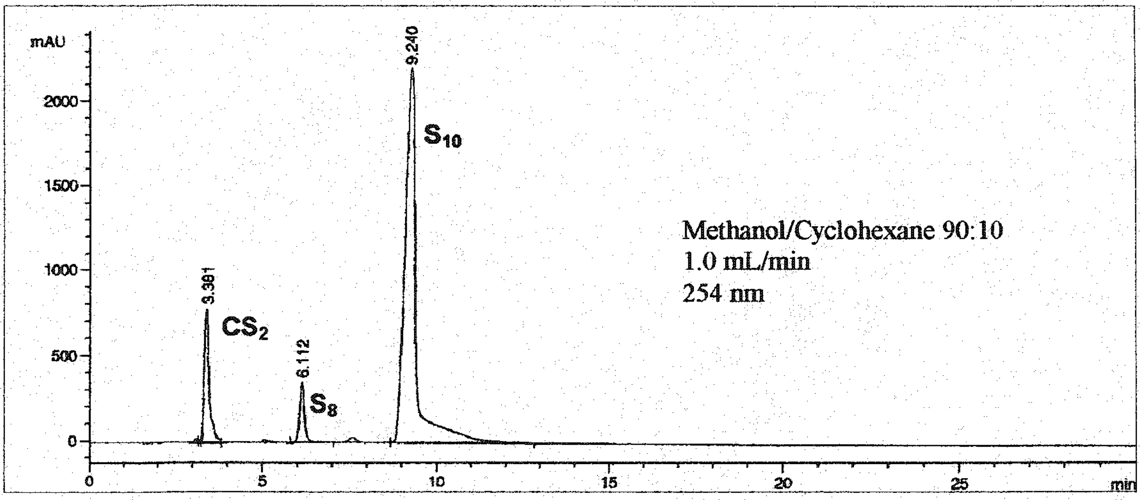


Methanol/Cyclohexane 90:10
1.0 mL/min
254 nm

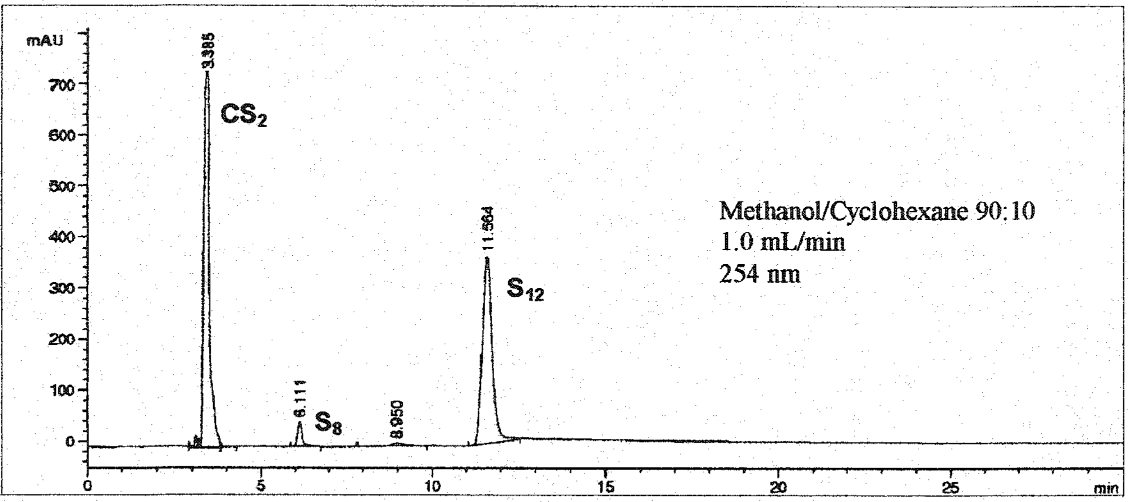
Appendix III-2. HPLC Spectrum of S_8



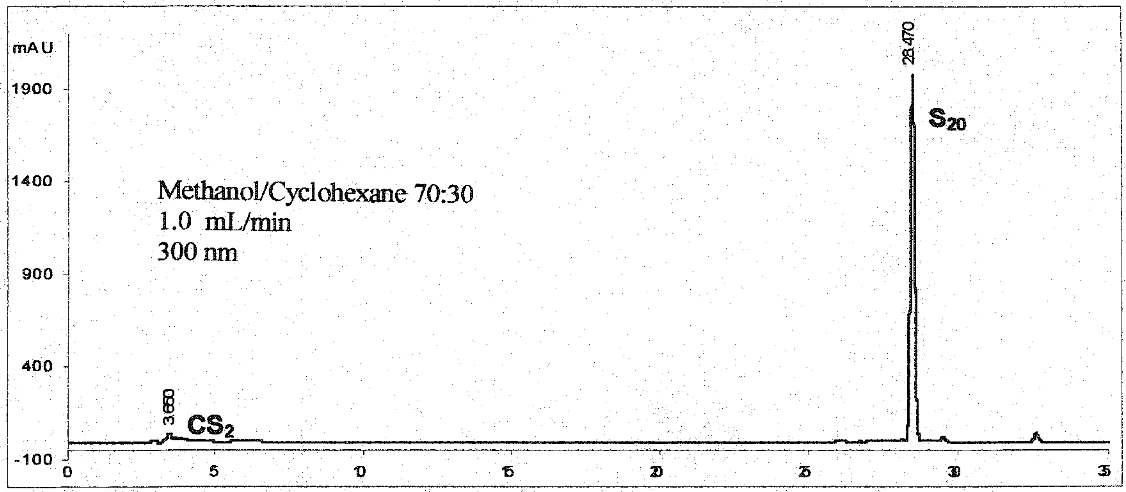
Appendix III-3. HPLC Spectrum of S_9



Appendix III-4. HPLC Spectrum of S_{10}



Appendix III-5. HPLC Spectrum of S$_{12}$



Appendix III-6. HPLC Spectrum of S$_{20}$