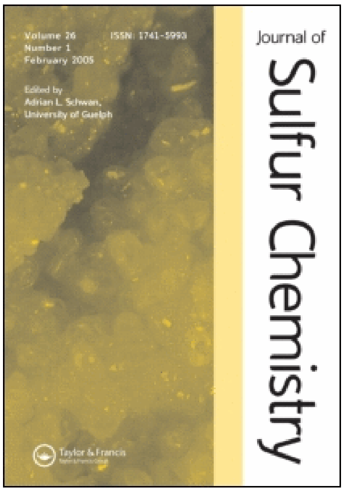

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The organic chemistry of diatomic sulfur

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REVIEW ARTICLE

The organic chemistry of diatomic sulfur†

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This review summarizes work on the generation and trapping of diatomic sulfur (S_2) as well as 2- and 4-sulfur transfer.

Keywords: Sulfur extrusion; Diatomic sulfur; Sulfur transfer reagent; Elemental sulfur; Sulfuration; Desulfurization; Concatenation; Thiirane; Dithietane; Dithiin; Allotrope; Cheletropic loss; Thiosulfenyl chloride; Dithiosulfenyl chloride; Polychalcogenide

1. Introduction

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

In nature it is found in combinations such as galena, cinnabar, celestite, sphalerite and iron pyrites [2]. The most important commercial use of sulfur is in the preparation of sulfuric acid [3]. Sulfur can have positive oxidation states [4–6]; these are possible because of its 3p and vacant d-orbitals which can give rise to $p\pi$-$d\pi$ overlaps. A number of papers in the literature have reviewed the bond strengths and angles of sulfur compounds [7–17]. Due to their wide occurrence in organic compounds and their significance in biological systems [18], interest in improving the methods of synthesis of organosulfur compounds is a very active research area. Numerous reviews [9–20] have summarized the great utility of organosulfur intermediates in the synthesis of a variety of organic compounds. Recently, the chemistry of organic polysulfanes R-S_n-R ($n > 2$) has been reviewed by Steudel [21]. This review paper presents in chronological order, the research developments of diatomic sulfur chemistry from generation to trapping.

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†Dedicated to Professor David N. Harpp for his 70th birthday.

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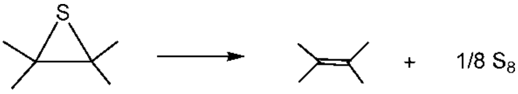


SCHEME 1

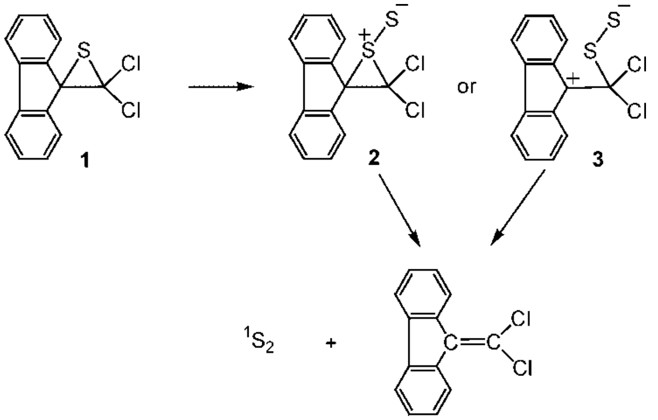
2. Sulfur extrusion

Sulfur extrusion means the loss of a sulfur atom from a molecule. Raney Nickel desulfurization [22, 23] and the Ramburg-Backlund rearrangement [24, 25] are very well-known sulfur extrusion processes. There are many examples in the literature demonstrating elemental sulfur as one of the products of a chemical reaction [26]. The sulfur that is lost is often inappropriately represented as S, [S], S°, or S_1. as opposed to S_8.

The mechanism by which sulfur is eliminated in these reactions is not well-understood. Extrusion of elemental sulfur is observed under many conditions: thermal, photochemical, as well as base and solvent-induced reactions. For example, Stark, Duke [27] and Loudon [28] examined extrusions in stable aromatic systems. Radl [29] reported extrusions which resulted in the formation of five-membered ring heterocycles. Guziec and Sanfilippo [30] studied other examples of the extrusion of sulfur, selenium, and tellurium. Moreover, a review on thermal decomposition of sulfur compounds including thiiranes, was published by Harpp and Williams [26].

In several cases, sulfur extrusion is proposed to proceed by means of a cheletropic loss of a singlet sulfur atom leading to the formation of elemental sulfur (S_8). However, the formation energy of singlet atomic sulfur is very high (about 66.3 kcal/mole) [31, 32], making this pathway of losing sulfur an unlikely event. Instead, a lower energy intermediate (S_2), or longer-chain fragments [33] have been proposed.

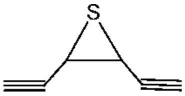
In many examples of sulfur extrusion, thiiranes, the sulfur analogue of oxiranes, are the proposed intermediates. They can undergo reactions similar to those of oxiranes such as nucleophilic ring opening [34] and olefin formation with phosphorus nucleophiles [35]. However, thiiranes can lose sulfur whereas oxiranes do not lose oxygen. There are also many instances where thiiranes can lose sulfur (scheme 1) in decomposing directly to olefins and elemental sulfur [36–52].



SCHEME 2

The thermal decomposition of thiirane to an olefin and sulfur has been proposed to occur through simple cheletropic loss of one sulfur atom. However, Lutz and Biellmann [53] indicated that the loss of sulfur from the decomposition of **1** took place not by first-order kinetics but through a more complex mechanism, perhaps involving a bridged sulfur species. Such species as **2** or **3** were later proposed in a mechanistic study by Harpp and Chew [54–56] in which diatomic sulfur could be extruded as shown in scheme 2, or by a concatenation of sulfur atoms until S_8 was ejected (*vide infra*).

An earlier study of sulfur extrusion involved the pyrolysis [57] of *cis*- and *trans*-1,2-diethenyl thiiranes (**4**) and **5**, respectively, in which there was a competition between sulfur extrusion and the thermal synthesis of thienocyclobutadiene (**6**). When performed at 100°C, pyrolysis of the thiiranes yields only the corresponding desulfurized olefins **7** and **8**.



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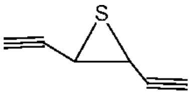

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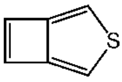

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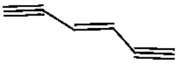
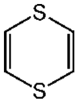


8

The mechanism of the above mentioned reaction is more complicated than a simple cheletropic loss of a sulfur atom. Thermal extrusion was thought to proceed through a loss of a sulfur atom from dithiins **9** and **10** to form thiophenes [58, 59] and from thiepins **11** to form stable aromatic systems [27, 28].



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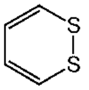

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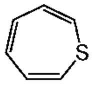

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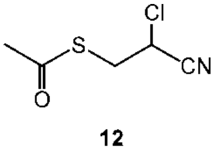
Mueller [60] was not able to trap sulfur in the reaction of α-chloro-β-(acetylthio)propionitrile (**12**) with alkenes in the presence of diethylamine. He proposed a thiirane intermediate which spontaneously produced sulfur. Also, Field and co-workers [61] were unsuccessful in trapping sulfur in the oxidation of phosphothiolate **13** by a peroxy acid.



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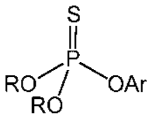
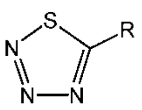


13

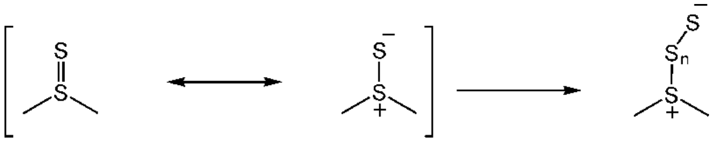
Moreover, photolysis of 5-substituted-1,2,3,4-thiatriazoles **14** in the presence of olefins did not yield the corresponding thiirane. However, under the same conditions, the photolysis of isothiocyanates **15** [62] appears to deliver a sulfur atom as they formed thiiranes.



14

R—N=C=S

15



16 **17**

SCHEME 3

The photolysis results were not surprising, since sulfur atoms are usually prepared by the photolysis of carbonyl sulfide (COS) [63, 64].

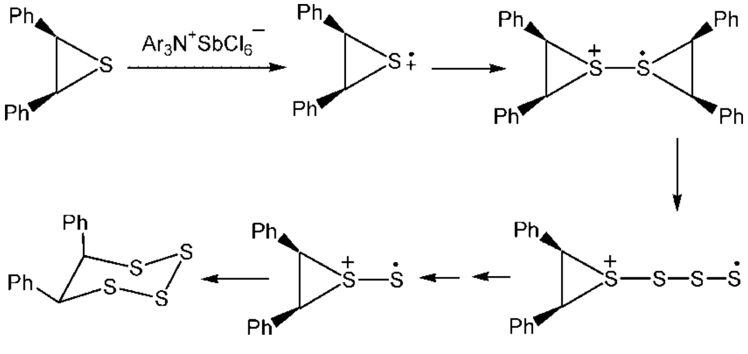
3. Concatenation of sulfur atoms

One of the most attractive mechanisms in sulfur extrusion reactions was first proposed by Foss in 1950 [65, 66]. The initial step involves the combination of two sulfur species followed by a transfer of a sulfur atom forming a thiosulfoxide-type intermediate **16** which then reacts with another molecule until the sulfur chain **17** is six or eight atoms long and could cyclize to S_6 or S_8 (scheme 3).

The concatenation mechanism of a thiosulfoxide to generate a sulfur atom has been extensively discussed in literature [54–56, 67–70]. Davis [71] proposed a similar mechanism to interpret the formation of elemental sulfur in acidified solutions of thiosulfate. Moreover, Kamata and co-workers [72] isolated a tetrathiane in the reaction of *cis*-and *trans*-2,3-diphenylthiirane with a catalytic amount of tris(*p*-bromophenyl)aminium hexachloroantimonate in methylene chloride. The proposed mechanism portrays the formation of the thiirane cation radical which abstracts a sulfur atom from another thiirane cation radical to produce cation radical **18** with a concomitant release of stilbene. A further linkage of two sulfur atoms gave intermediate **19** which cyclized affording the tetrathiane **20** (scheme 4).

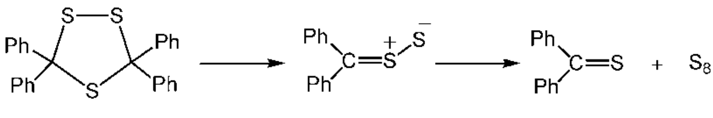
Huisgen and Rapp [73] suggested that in the thermal decomposition of trithiolane **21**, a thiobenzophenone-S-sulfide **(22)** is formed which undergoes an abstraction of a sulfur atom and leads to the formation of S_8 and blue thiobenzophenone (scheme 5).

Gleiter and co-workers [74] studied the loss of sulfur atoms from thiepins and concluded that the extrusion of sulfur proceeds *via* rearrangement to a thiirane intermediate **23** followed by linking of sulfur atoms to give intermediate **24** which would eventually lose elemental



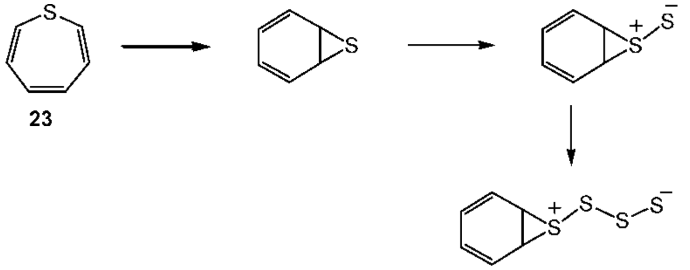
20 **19** **18**

SCHEME 4



21 **22**

SCHEME 5

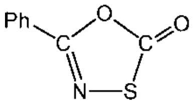


23 **24**

SCHEME 6

sulfur. The extrusion of S_2 or S_8 would be an energetically more favourable pathway than expulsion of other species of sulfur (scheme 6).

Concatenation was also proposed to account for the formation of elemental sulfur in the decomposition of heterocycle **25** [75], when phosphothiolate **13** was oxidized with a peroxy acid [61] and when dipyridol[1,2-a:1',2'-c]imidazolium-11-thiolate (**26**) was refluxed with hydrobromic acid [86].



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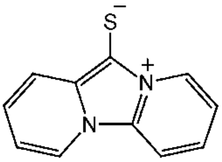
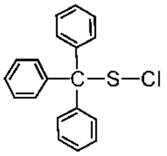


26

Harpp and Williams [77] investigated an interesting reaction of triphenylmethanesulfenyl chloride (**27**) where its sulfur atom is extruded quantitatively and catalytically by a reaction with thioketones; α -chlorodisulfide adducts such as **28** were isolated.



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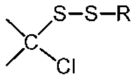
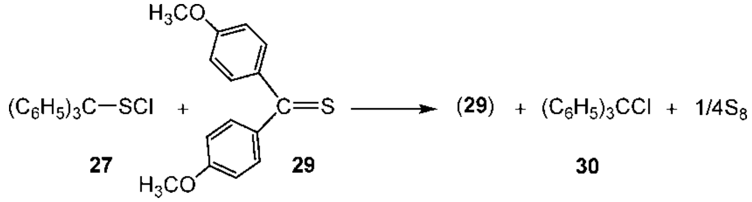


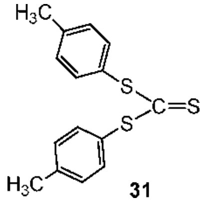
28

It was discovered that a yellow precipitate was immediately observed when **27** and 4,4'-dimethoxybenzothiophenone (**29**) were mixed in chloroform at room temperature. The precipitate was identified as sulfur and was isolated in near quantitative yield as expected for the conversion of **27** to chlorotriphenylmethane (**30**). Analysis of the reaction mixture using ^{13}C-NMR demonstrated the presence of the starting thioketone **29** and **30**. The proposed reaction sequence is displayed below (scheme 7).



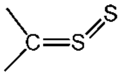
SCHEME 7

In another investigation, the same authors [77] found that the reaction of sulfenyl chloride **27** and bis(4-tolyl)trithiocarbonate **(31)** resulted in the precipitation of a quantitative amount of sulfur from the reaction mixture for the conversion of **27** to **30**.



31

It was proposed that intermediates **32** and **33** were formed in this process. They were not isolated by Harpp in 1991 [77] or by Senning who proposed them as reactive intermediates in 1986 [78]. In 1994, Nakayama and co-workers isolated the first dithirane **34** [79] and clearly demonstrated its structure.



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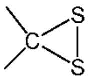

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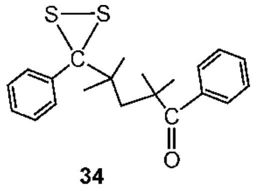
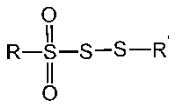


34

Harpp and co-workers [80] found that when some of sulfenylthiosulfenates **35** are placed in polar solvents, sulfur appears to be "spontaneously" extruded. The mechanism of the sulfur loss was described and appears to proceed by the concatenation of sulfur atoms.



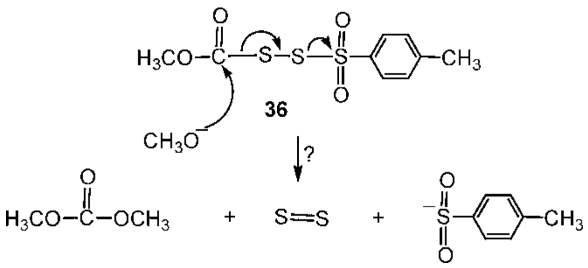
$R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-S-R'$

35

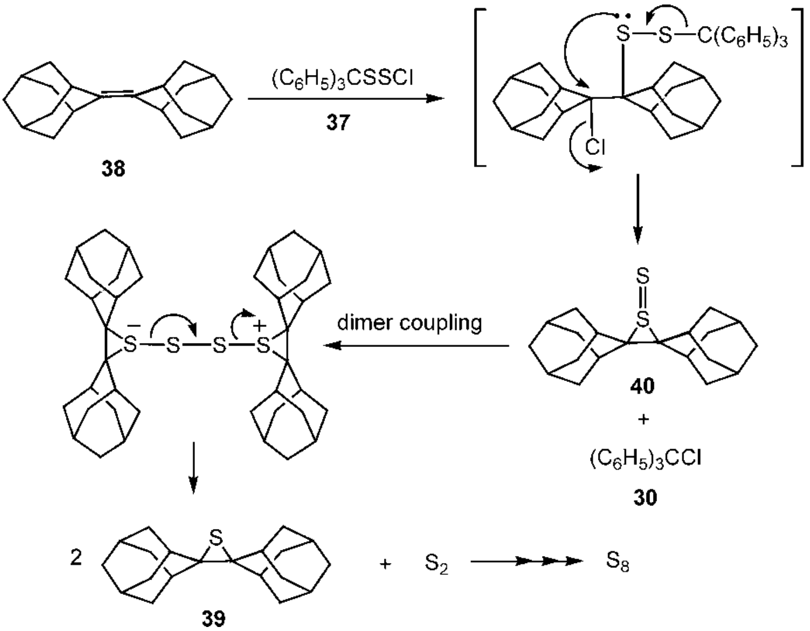
Adduct **36** in the presence of methoxide ion smoothly produced elemental sulfur [81]. The mechanism for the formation of sulfur was suggested to proceed through a concatenation of sulfur atoms and not through diatomic sulfur intermediate (scheme 8).

Abu-Yousef and Harpp [82–84] reported the reaction of thiosulfenyl chloride **37** with olefin **38** in which elemental sulfur was one of the products along with thiirane **39**. The likely mechanism for the formation of **39** and S_8 *via* the concatenation of intermediate **40** is as portrayed in scheme 9.

In addition, the same authors [83] suggested that the mechanism for the formation of thiirane **39** and elemental sulfur from the reaction of dithiosulfenyl chloride **41** and adamantylideneadamantane **(38)** could proceed *via* an intermediate **42** as shown in scheme 10.



SCHEME 8

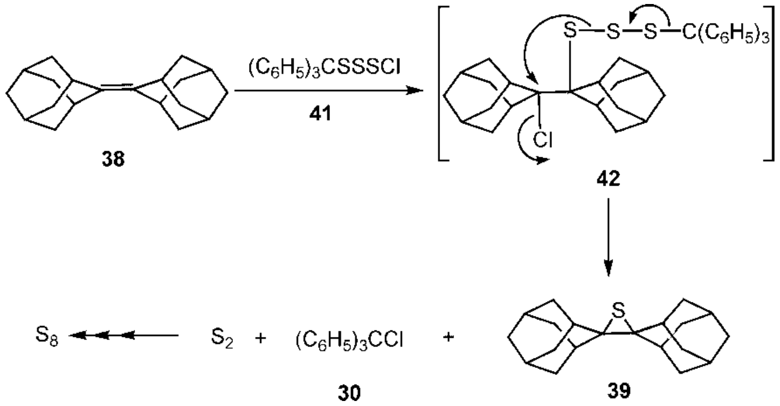


SCHEME 9

Of the possible mechanisms considered for the formation of sulfur in the many sulfur extrusion reactions reported above, it appears that both the loss of singlet diatomic sulfur and the concatenation of sulfur atoms to ultimately form elemental sulfur are the most reasonable pathways. The most likely mechanism for sulfur extrusion appears to be the concatenation of sulfur atoms to form a chain which would ultimately cyclize to form elemental sulfur [54–56]. Thus, singlet diatomic sulfur might not be formed as a distinct species in any of these reactions.

4. Diatomic sulfur precursors

Diatomic sulfur, S_2, is isovalent with O_2 and has a similar electronic structure. Singlet oxygen chemistry is well developed and has been extensively studied and reviewed [85–87]. The rapid development of singlet oxygen chemistry has initiated considerable interest in its analogous sulfur species, $^1S_2$.

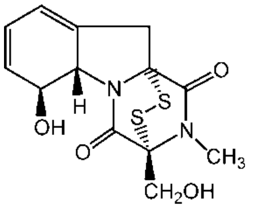


SCHEME 10

The properties and generation of S_2 are well-known [88–90] although not until 1984 in a fashion for use in rational synthesis (*vide infra*). Apparently it exists in either singlet $^1S_2$ or triplet $^3S_2$ forms quite analogous to the two states of diatomic oxygen [85, 87].

The singlet form of sulfur converts to the triplet state and finally to the stable S_8 ring [91]. The availability of diatomic sulfur *via* pyrolysis at high temperatures encouraged some researchers to explore the tempting possibility of its selective reactivity towards unsaturated compounds [91]. Diatomic sulfur has been known for about half a century [92], its electronic structure explored [93] and the dissociation energy determined to be 101.7 kcal/mol [94]. The formation, spectroscopy, photochemistry, and quantum chemistry of the $(S_2)(O_2)$ complex at very low temperature was reported by Neurock and co-workers [95]. It was shown that at high temperature, the gas is stable and the ground state of the molecule was determined to be in the triplet state [91].

Singlet oxygen is known to play an important role in many biological processes [85, 87]. Due to the importance of the disulfide functionality in many natural products such as the gliotoxin **43** [97], methods for the generation of singlet diatomic sulfur have gained prominence.



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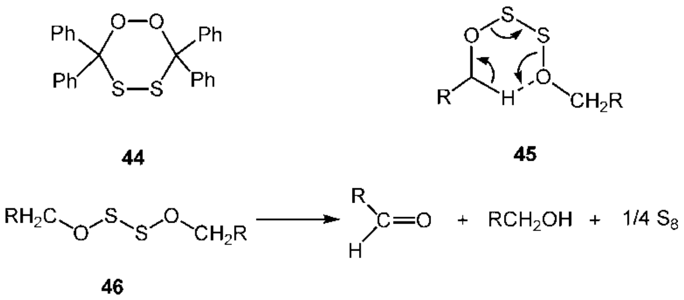
Diatomic sulfur, generated in a rational fashion, has been shown to be a useful synthetic tool for organic chemists. Its importance in synthetic organic chemistry and drug synthesis was reviewed by Steliou [96].

In 1928, Staudinger and Freudenberger [98] proposed a six-membered ring **44** as an intermediate in the photolytic decomposition of thioketones to give the corresponding ketones and elemental sulfur. This ring could undergo a cyclic reversion to form two molecules of ketone and S_2. A similar mechanism forming a six-membered ring intermediate **45** was inherent in a reaction studied by Thompson [99] involving the decomposition of dialkoxy disulfides **46** to the corresponding aldehyde, alcohol, and elemental sulfur (scheme 11).



SCHEME 11

A variety of methods for the formation of $^1S_2$ were discussed in 1991 by Steliou [100] and in 1997 by Harpp and co-workers [101]. Several unsuccessful approaches have been reported where no trapped products were identified [102–105].

Jahn and Schmidt [106] reported the first successful trapping of S_2 by diene **47** in 1975 through a photolysis reaction of thione ester **48**, portraying diatomic sulfur, S_2, as being lost with **49** as a probable intermediate (scheme 12). There were a variety of sulfurated products formed in the reaction and the yield of trapped disulfide adduct **50** was only 2%.

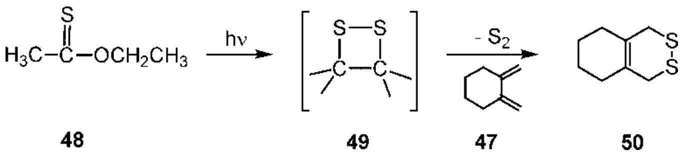
Reactions of activated elemental sulfur with dienes have been studied [107, 108]. These reactions resulted in the formation of several sulfurated products. The isolation of other sulfur-containing products in sulfur extrusion reactions suggested that sulfur may not be lost as S_2 only, but also in other forms of activated sulfur, the structures of which are unknown.

The first synthetically useful diatomic sulfur precursors were reported by Steliou [109] in 1984. S_2 was delivered and captured as a Diels-Alder adduct when an organometallic trisulfide **51** reacted with triphenylphosphine dibromide (**52**). Two intermediates were proposed in the reaction. A triphenylphosphine thioozonide intermediate **53** (such a structure would be similar to the oxygen analogue found in the reaction of PPh_3 with O_3) [110], as well as the six-membered species depicted as **54** (scheme 13).

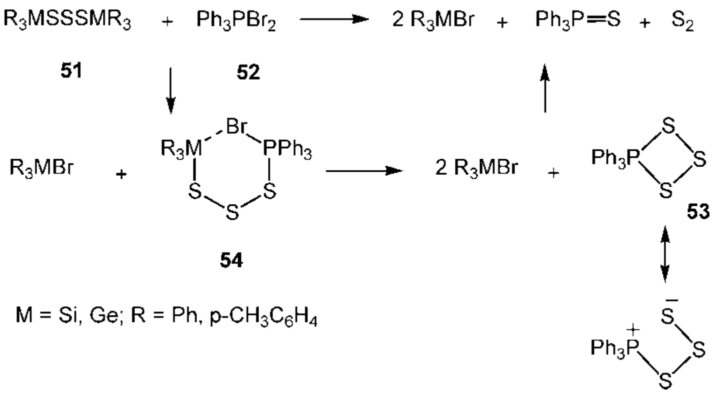
Two diatomic sulfur precursors were reported in 1987. Schmidt and Görl [111] showed that a tetrachalcogen **55** (5,5-dimethyl-1,2-dithia-3,7-diselenacycloheptane) undergoes thermal decomposition with ring contraction to diselenacyclopentane **56** transferring diatomic sulfur to 2,3-dimethyl-1,3-butadiene (**57**) and 2,3-diphenyl-1,3-butadiene (**58**) affording disulfide adduct **59** (1,2-dithia-4,5-dimethyl-4-cyclohexene) in *ca.* 48% isolated yield, and disulfide **60** (1,2-dithia-4,5-diphenyl-4-cyclohexene) in *ca.* 54% isolated yield, respectively (scheme 14).

A useful synthetic method that apparently generates S_2 was reported by Steliou and co-workers [112]. This method was based on a novel head-to-head dimerization of 2,2'-bis(thiobenzoyl)biphenyl (**61**) generated from 2,2'bis(benzoyl)biphenyl (**62**) in the presence of B_2S_3. A dithietane intermediate **63** that was postulated could spontaneously release S_2 and 9,10-diphenylphenanthrene (**64**) (scheme 15).

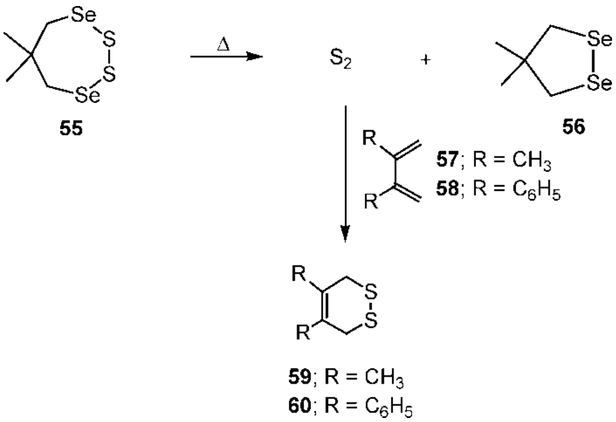
Diatomic sulfur is trapped when the above reaction is carried out in the presence of olefins; the cyclic disulfides were isolated in good yield.



SCHEME 12

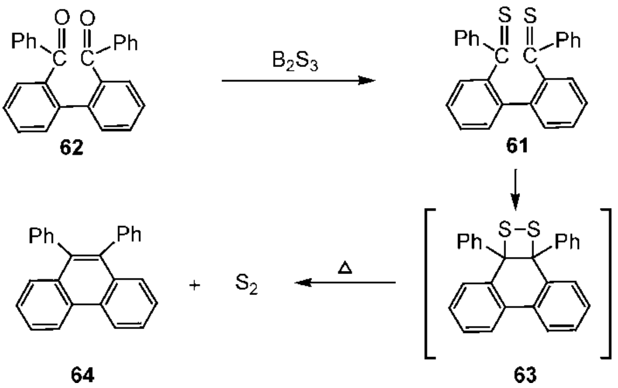


SCHEME 13

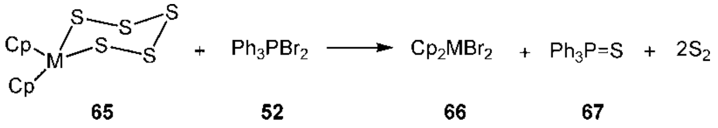


SCHEME 14

Harpp and McDonald [113] successfully generated a diatomic sulfur species in 1988. Their method is based on the pioneering work of Steliou [112] where reaction of an organometallic pentasulfides **65** with triphenylphosphine dibromide **(52)** gives organometallic dibromides **66**,



SCHEME 15

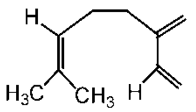


M = Ti, Zr, Hf; Cp = η^5-C_5H_5

SCHEME 16

triphenylphosphine sulfide (**67**), and diatomic sulfur that is trapped by 1,3-butadienes. The intermediate in the formation of S_2 could again be the thioozonide **53** (scheme 16).

Clearly, the generation of S_2 provides a logical one-step synthetic procedure for the preparation of cyclic disulfides *via* Diels-Alder addition to 1,3-dienes. For example, myrcene disulfide (**68**) was successfully prepared in 75% isolated yield from myrcene (**69**) by Steliou [112], as well as by Schmidt and Görl in an isolated yield of 40% [111].



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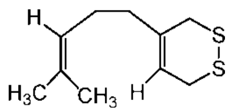
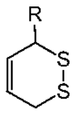


68

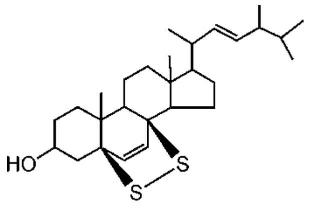
Some substituted 3,6-dihydro-1,2-dithiin derivatives **70** prepared by the S_2 methodology [112], proved to posses anti-HIV activity [98].



70

R = CH_2CO_2H, CH_2CH_2OH, CH_2CH_2OAc

This methodology conceivably could be used in the synthesis of bridged disulfides where the most difficult step in this synthesis is the formation of the S-S bond like in gliotoxin **43** [114, 115]. In a parallel reaction, attempts to prepare ergosterol endodisulfide **71** from ergosterol **72** using the S_2 methodology were not successful [116].



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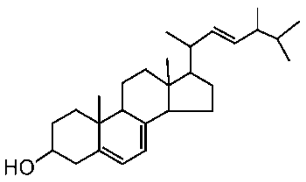
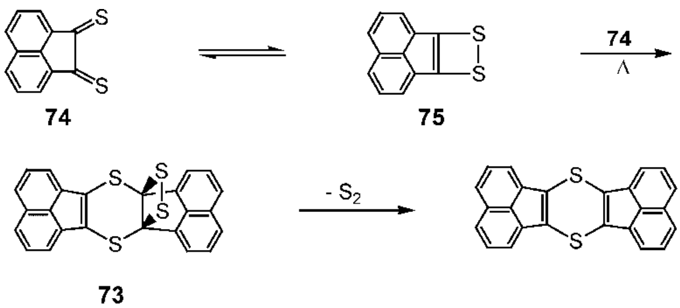


72

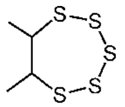
Interestingly, in 1985 Cava and co-workers [103] reported S_2 to be a by-product of the decomposition of 1,2-dithetane **73**, formed from a Diels-Alder addition of acenaphthenedithione **74** with its 1,2-dithiete tautomer **75** (scheme 17) but no supporting trapping evidence for its formation was presented.

Another pathway for the production of S_2 was reported by Ando and co-workers [117] where the thermal decomposition of anthracene endodisulfide **76** produces anthracene (**77**) and likely diatomic sulfur (scheme 18).



SCHEME 17

However, it was not clear whether the Diels-Alder adducts were isolated or detected; the yields were based on the amount of recovered product. Bartlett and Ghosh [105] attempted to trap diatomic sulfur in the conversion of pentathiepins **78** to trithiolanes **79** but were unsuccessful.



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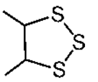
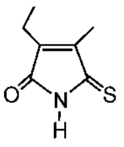


79

Nicolaou and co-workers [118] synthesized and isolated the first stable 1,2-dithietane, dithiatopazine **80**, an intermediate used in the total synthesis of brevotoxin B. When dithietane **80** was heated at 100 °C, [119] it smoothly extruded diatomic sulfur which was trapped with 2,3-diphenyl-1,3-butadiene (**58**) to give the cyclic disulfide adduct **60** in 25% isolated yield and the corresponding olefin **81** (scheme 19). The formation of S_2 may not be the sole mechanistic pathway as the cyclic tetrasulfide **82** (1,2,3,4-tetrathia-6,7-diphenyl-6-cyclooctene) was also isolated in 28% yield. These reactions were conducted in a ten-fold excess of **80**.



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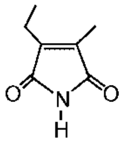

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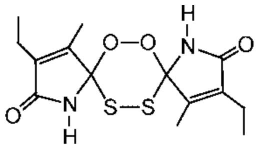
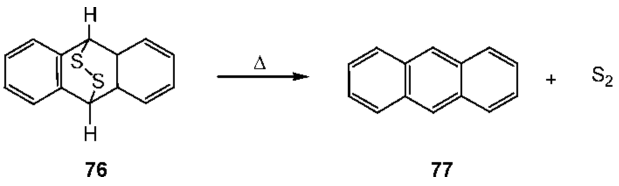
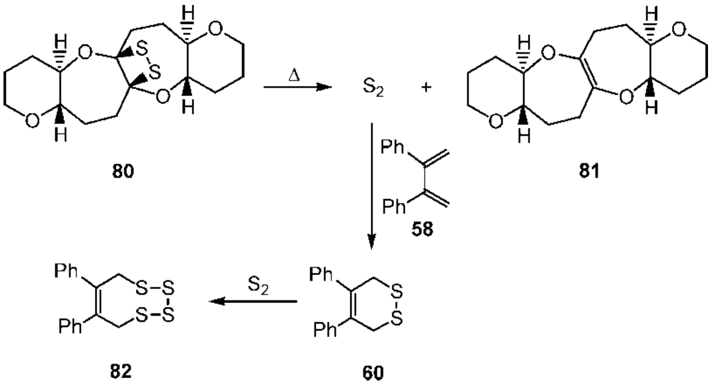


85

Rapoport and co-workers [120] observed the presence of an S_2 fragment in the conversion of the monothiomaleimide **83** to the oxygen analogue, maleimide **84**. The proposed six-membered intermediate **85** was similar to the one which was proposed by Staudinger and Freudenberger in air oxidation of thioketones in 1928 [98].



SCHEME 18

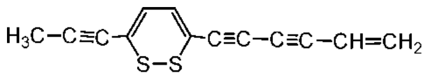


SCHEME 19

Evidence for the trapped diatomic sulfur unit was suggested by ^{1}H NMR but the yields were too low for isolation. S_2 was also identified by infrared [121] and photoelectron spectroscopy [122] as one of the products of the thermal decomposition of 1,2,3,4-thiatriazoles **86** (scheme 20).

The formation of S_2 was proposed from the dimerization of two dinitrogen sulfide (N_2S) molecules initially present in the thermal decomposition; the products were two molecules of nitrogen and one of S_2 (scheme 21).

Constabel and Towers [123] claimed that singlet sulfur is the toxic product of thiarubin A (**87**), a 1,2-dithiin, but there was no evidence for this claim. Their results showed that light enhanced conversion of **87** to the thiophene **88** caused toxic effects that were greater than those resulting from **87** or **88** alone. Their claim was based on the analogy that singlet oxygen is the toxic species generated from peroxides [124–126].



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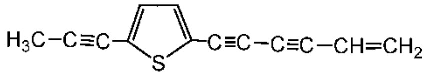
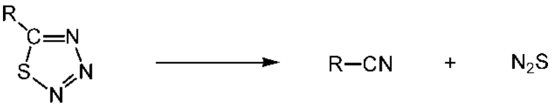


88

Thionosulfite **89** that can be prepared from the reaction of diol **90** with sulfur transfer reagent **91** was an interesting structure which could potentially deliver diatomic sulfur (scheme 22) [70].

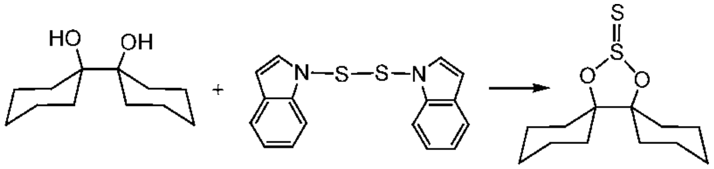


86

SCHEME 20

$$\overset{-}{N}=\overset{+}{N}=S \longrightarrow \overset{-}{N}=N-S-S-\overset{+}{N}\equiv N \longrightarrow 2\,N_2 + S_2$$

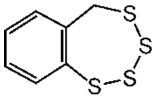
SCHEME 21



SCHEME 22

When **89** is heated above its melting point (100–101 °C) to *ca* 150 °C, an acidic gas (likely S_2O_2) is evolved along with the corresponding olefin **92** and elemental sulfur (scheme 23); no trapped products resulted by trapping efforts.

Sato and co-workers [127] discovered that many olefins could capture active sulfur species generated from cyclic 5H-benzo[f]-1,2,3,4-tetrathiepin (BTTP) **93** or 6H-benzo[g]-1,2,3,4,5-pentathiocin (BPTC) **94** at 120°C in DMSO to give [2 + 3], [4 + 2], or [6 + 3] cycloadducts in good isolated yields.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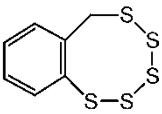
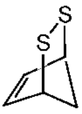

94

Sulfur transfer reagents such as cyclic 2,3-dithiabicyclo[2.2.1]hept-5-ene (**95**) [128, 129] hexahydro-5,8-epoxy-2,3-benzodithiin (**96**) [129], and 1,4-dihydro-2,3-benzodithiin (**97**) [129], have been prepared by oxidation of the corresponding dithiols. Pyrolysis of **95**, **96**, or **97** was studied by the same authors resulting in formation of diatomic sulfur (trapping) and the corresponding diene (chelotropic reversion process).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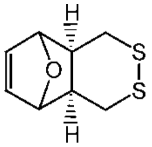
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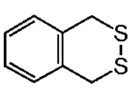
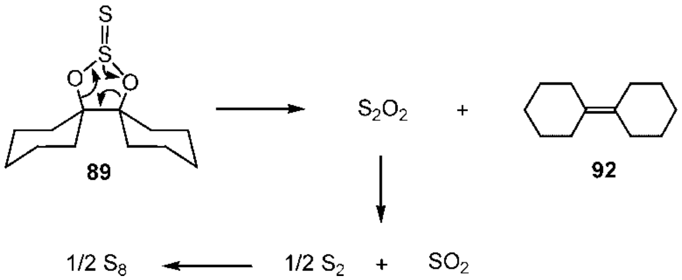
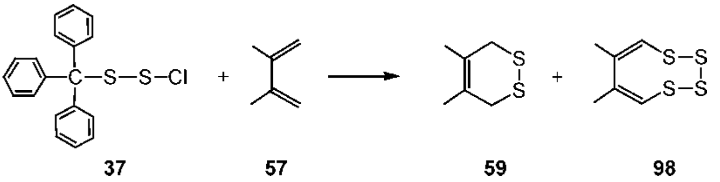

97

In 1991, Harpp and Williams [130] showed that the reaction of triphenylmethanethiosulfenyl chloride (**37**) with 2,3-dimethyl-1,3-butadiene (**57**) affords a 1,4-addition product which subsequently produces the cyclic disulfide **59** (1,2-dithia-4,5-dimethyl-4-cyclohexene) and the



SCHEME 23



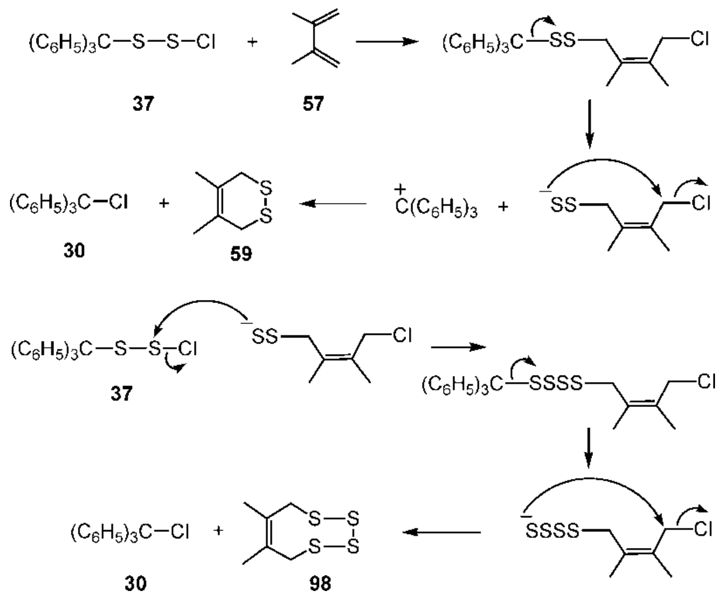
SCHEME 24

cyclic tetrasulfide **98** (1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene). The identity of **59** and **98** were confirmed by ^{1}H NMR and mass spectral data. The net effect of the latter transformation is to deliver a 2- and 4- sulfur fragment to the diene in 35 and 30% isolated yields, respectively. The overall reaction for the decomposition of disulfide **37** to form the two trapped adducts is shown in scheme 24.

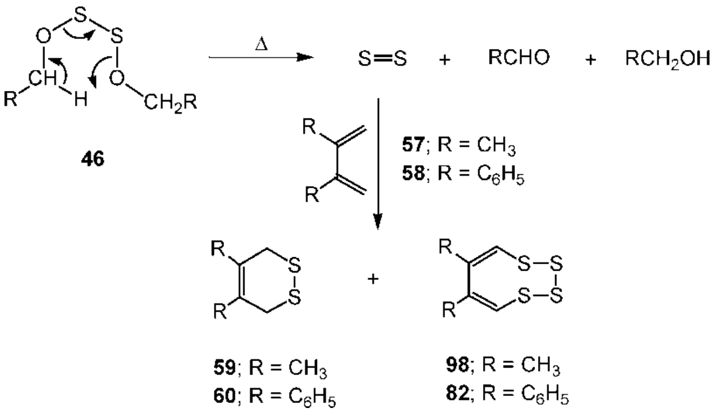
They demonstrated [130] that the mechanism involves a 1,4 addition of thiosulfenyl chloride **37** to the diene followed by a transfer of two sulfur units to the 1,3-butadiene along with concomitant formation of triphenylmethyl chloride (**30**) (scheme 25). Thus, while there is the appearance of diatomic sulfur transfer, it is much more likely the cyclic di- and tetrasulfides result as shown in scheme 25.

A significant breakthrough for the effective generation of diatomic sulfur involves the chemistry of alkoxydisulfides **46**. Harpp and co-workers [131] found that members of this class of compound decompose near 75°C to permit the transfer of diatomic sulfur to 1,3-butadienes **57** and **58** to give the corresponding cyclic disulfides **59** and **60**, respectively, in overall yields of *ca.* 75% after treatment of the tetrasulfide adducts **98** and **82** with triphenylphosphine (scheme 26).

Control experiments have shown that upon heating, only very small amounts of the disulfide adducts **59** and **60** are converted to the tetrasulfides **98** and **82**, respectively [132].

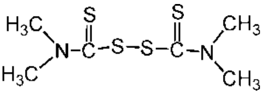


SCHEME 25



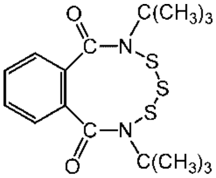
SCHEME 26

Chew and Harpp [133] also have been able to trap diatomic sulfur by 1,3-dienes from thiuram **99** but the yield was low.



99

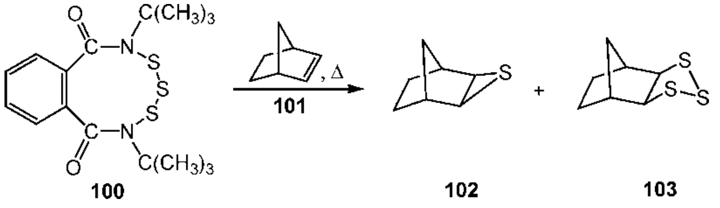
Thermolysis of benzotrithiadiazacyclononene **100** in the presence of 1,3-butadiene **57** generated only cyclic disulfide adduct **59** [134].



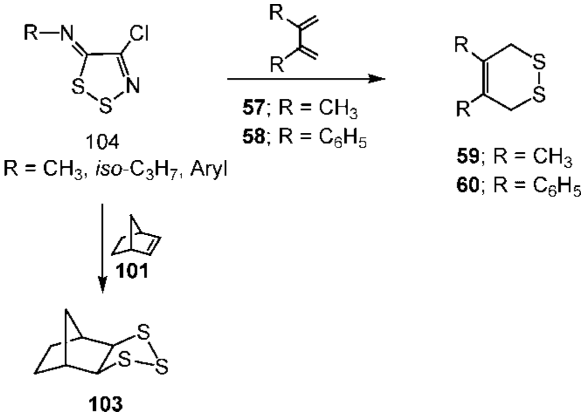
100

Two main sulfur adducts, episulfide **102** and trithiolane **103** were formed in moderate yield upon thermolysis of **100** in the presence of norbornene **101** (scheme 27) [134].

Diatomic sulfur was extruded from imino-1,2,3-dithiazole **104** at 150 °C and trapped with 1,3-dienes **57** and **58** to give disulfide adducts **59** (30%) and **60** (20%), respectively (scheme 28) [135, 136]. Under the same conditions, norbornene **101** gave trisulfide **103** in good yield (70%) as shown in scheme 28.



SCHEME 27



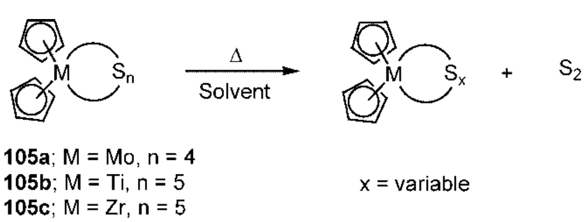
SCHEME 28

In another investigation, Rys and Harpp [137] discovered that metallocene polysulfides **105** decompose smoothly upon heating in DMSO, chlorobenzene or DMF to deliver diatomic sulfur in *ca.* 25–50% yields to various 1,3-dienes (scheme 29).

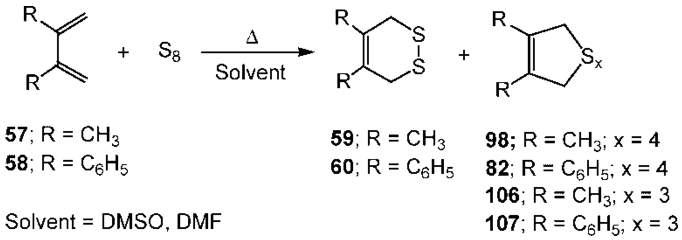
Disulfide adducts **59** and **60** along with polysulfides **82**, **98**, **106**, and **107** were formed upon thermal decomposition of elemental sulfur (S_8) in the presence of 1,3-dienes **57** and **58** (scheme 30). The final yield of disulfides **59** and **60** (after conversion of the polysulfides with triphenylphosphine) are in the range of 45% to over 70% depending on the nature of the diene. The best yield (*ca.* 72%) of disulfide adduct **60** was obtained using 2,3-diphenyl-1,3-butadiene (**58**) with DMSO at 125°C as a solvent [138].

The authors proposed a mechanism that directly implicates highly polar solvent, dimethyl sulfoxide (DMSO), in the opening of the sulfur ring as shown in scheme 31.

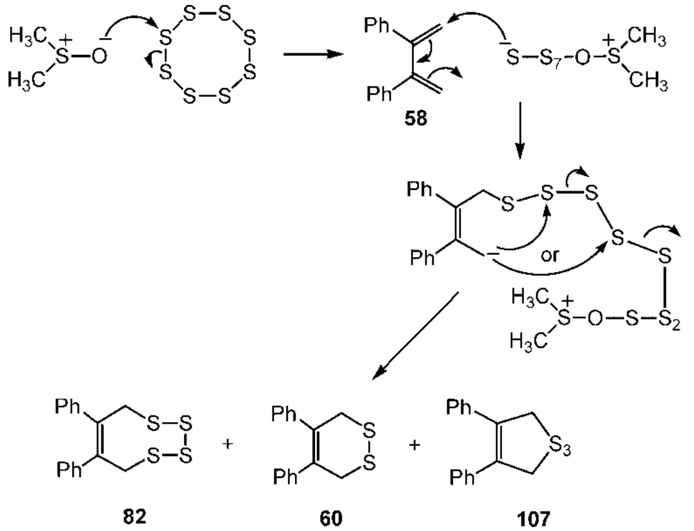
Whereas, diatomic sulfur was trapped by 2,3-dimethyl-1,3-butadiene (**57**) and 2,3-diphenyl-1,3-butadiene (**58**) upon thermal decomposition of elemental sulfur (S_8) in the presence



SCHEME 29



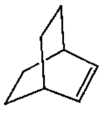
SCHEME 30



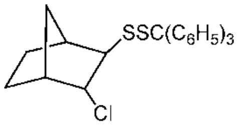
SCHEME 31

of sodium hydride [139]. The final yield of disulfide adducts **59** and **60** was 40 and 7%, respectively.

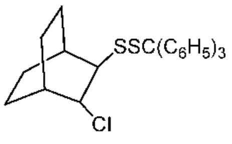
Abu-Yousef and Harpp [140] reported that the addition of equimolar amounts of triphenylmethanesulfenyl chloride **(27)** to various bicyclic alkenes (norbornene (**101**) and bicyclo[2.2.2]octene (**108**) leads, contrary to expectation, to β-chlorodisulfides **109** (*endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane) and **110** (*endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane), respectively, in good isolated yields. The prediction was that a *mono* β-chlorosulfide derivative would be formed.



108



109

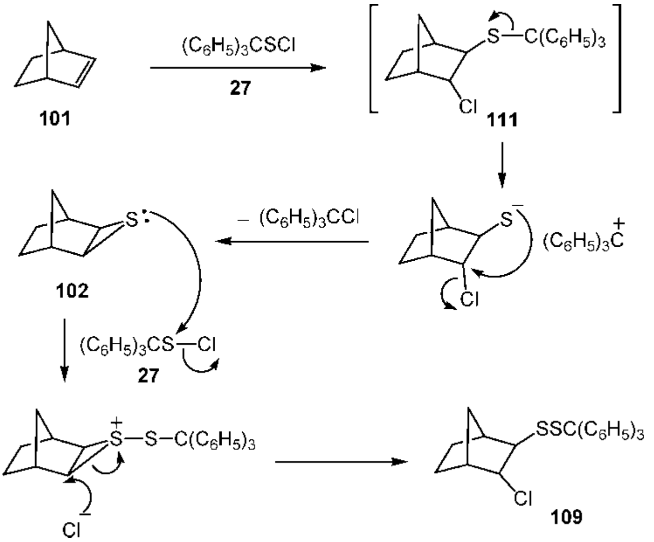


110

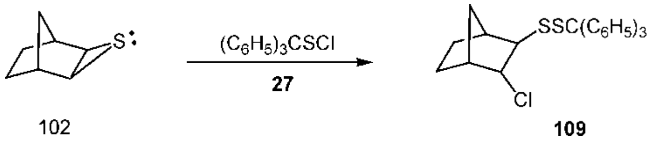
The identity of adducts **109** and **110** was confirmed by ^{1}H and ^{13}C NMR as well as combustion analysis. The X-ray crystallographic structure of **109** and **110** were also reported [140] showing the stereochemistry of the product. It revealed the regiochemistry of **109**; the symmetry of **110** permits only one enantiomeric pair of isomers. Elemental and X-ray analysis demonstrated that the addition products **109** and **110** contained two sulfur atoms rather than one. A plausible mechanism provides the explanation for the presence of the second sulfur atom indicated by the pathway *via* intermediate **111** as shown in scheme 32 [140, 141].

The formation of thiirane **102** was demonstrated as the first step in this reaction and the stereochemistry of addition has been determined by X-ray analysis. To confirm the likelihood of this mechanism, the *exo*-episulfide **102** was prepared and was treated with triphenylmethanesulfenyl chloride (**27**). Dithio **109** was isolated in 90% yield (scheme 33).

The same authors initiated a study of some of the chemistry of this type of addition for the preparation of a new series of di- and trisulfides hoping that these reagents can be used to develop a useful pathway to dithietanes **112** as potentially stable intermediates and/or diatomic sulfur precursors. Subsequent rearrangement of **112** in the presence of 1,3-butadiene **57** gave evidence for a diatomic sulfur transfer (**58**, **98**) as shown in scheme 34 [140, 141].



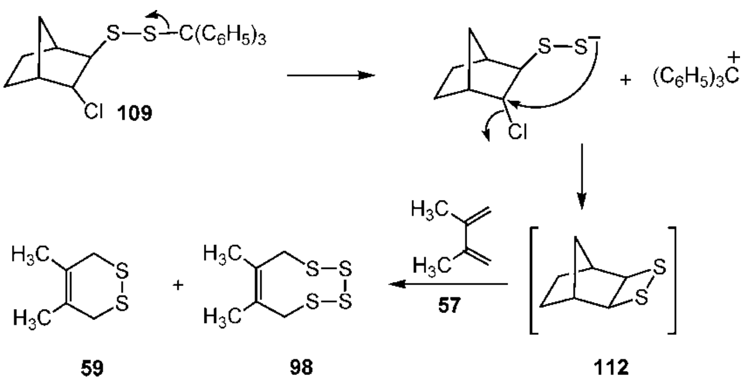
SCHEME 32



SCHEME 33

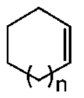
Triphenylmethanethiosulfenyl chloride (**37**) reacts nicely with bicyclic alkenes **101** and **108** to furnish excellent yields of β-chlorodisulfides **109** and **110** [140].

In addition, Abu-Yousef and Harpp [141–143] reported a new reaction of sulfenyl chlorides with various cyclic alkenes. Triphenylmethanethiosulfenyl chloride (**37**) has been found to react smoothly with cyclopentene (**113**) and cyclohexene (**114**) to give stable addition products

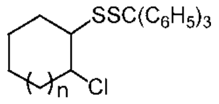


SCHEME 34

115 and **116**, respectively, in high isolated yields (*ca.* 95%).



113; n = 0
114; n = 1



115; n = 0
116; n = 1

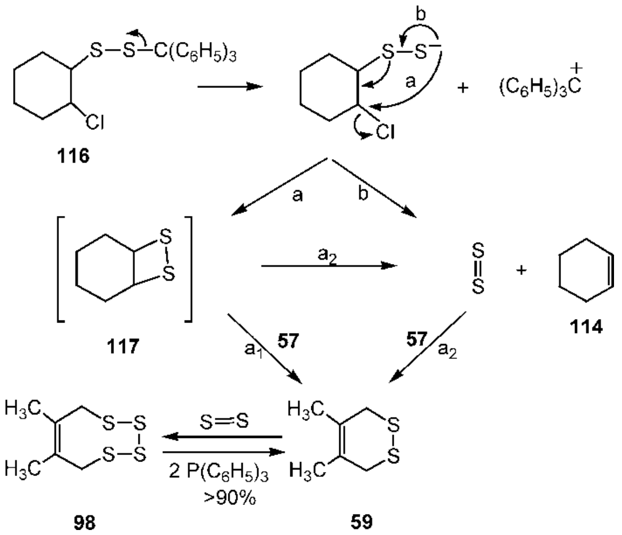
The proposed structures of compounds **115** and **116** were based on ^{1}H and ^{13}C NMR as well as by elemental analysis.

The same authors [141, 142] discovered that this new methodology is a good means to effect diatomic sulfur transfer. The addition products (**115**, **116** from **37**) were found to be useful in transferring sulfur to a diene trap *via* the dithietane intermediate **117**. When these adducts **115** and **116** were each warmed with 2,3-dimethyl-1,3-butadiene (**57**), in a variety of solvents, temperature, time, and concentration, they deliver diatomic sulfur-trapped derivatives in good overall yield (scheme 35).

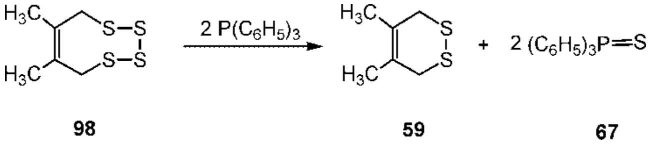
The possible dithietane intermediate **117** (scheme 35, path a) could either directly transfer its two sulfur atoms to the diene trap to form **59** (scheme 35, path a$_1$) or undergo a cycloreversion to give cyclohexene (**114**) and S$_2$ which is then trapped (scheme 35, path a$_2$). In addition, we found cyclohexene (**114**) in the crude mixture; it was difficult to rationalize the presence of this molecule except by the decomposition of dithietane intermediate **117** or by a concerted expulsion of S$_2$ from intermediate **117** as shown in scheme 35.

Moreover, the same authors found that cyclic tetrasulfide adduct **98** can be converted quantitatively to the disulfide adduct **59** and triphenylphosphine sulfide (**67**) by *in situ* treatment with triphenylphosphine (scheme 36).

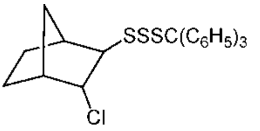
In the same manner, triphenylmethanedithiosulfenyl chloride (**41**) reacts with norbornene (**101**), cyclopentene (**113**) and cyclohexene (**114**) to give stable addition products **118**, **119** and **120**, respectively, in high isolated yields (*ca.* 93%) [141–143].



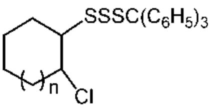
SCHEME 35



SCHEME 36



118



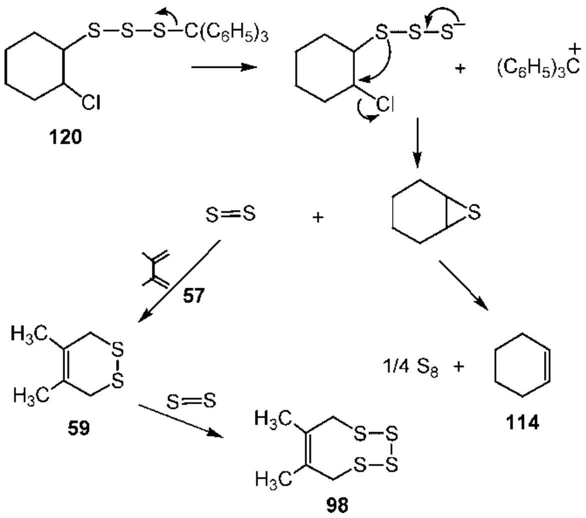
119; n = 0
120; n = 1

The X-ray structures of **119** and **120** were also reported [142]. When those adducts were warmed with diene **57**, they smoothly deliver the diatomic sulfur-trapped derivatives **98**; the mechanism was proposed as shown in scheme 37. As a result, this new methodology serves to transfer two-sulfur units to a diene in more than 50% overall isolated yield.

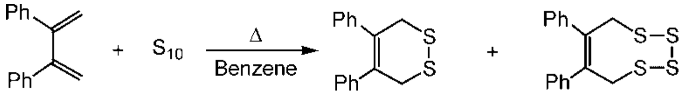
The chemistry of one of the sulfur allotropes was investigated by Leste-Lasserre and Harpp in 1999 [144]. When equimolar amounts of cyclodecasulfur (S_{10}) and 2,3-diphenyl-1,3-butadiene (**58**) are warmed under mild conditions, disulfide adduct **60** and tetrasulfide **82** were formed in 25 and 2% yield, respectively (scheme 38).

The authors proposed a radical mechanism for the sulfuration of conjugated dienes by S_{10} (scheme 39).

In another investigation, the same authors [145] studied the reaction of *bis*-benzimidazole (**121**) with diphenylhydrazine (**122**) in the presence of 1,3-dienes. They found diatomic sulfur is released and trapped with 2,3-diphenyl-1,3-butadiene (**58**) to give the corresponding disulfide adduct **60** (9%) and tetrasulfide **82** (8%) (scheme 40).

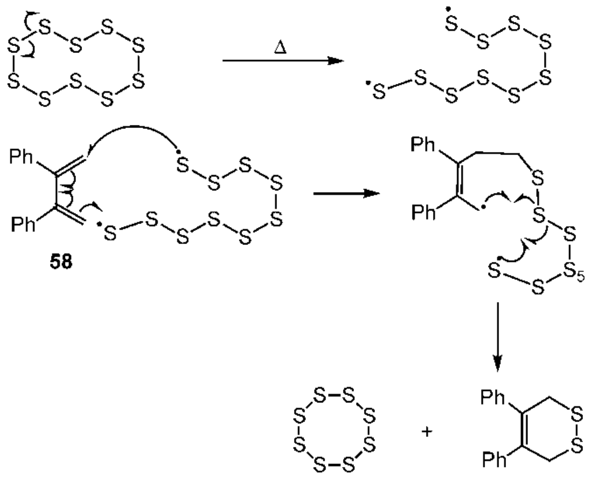


SCHEME 37



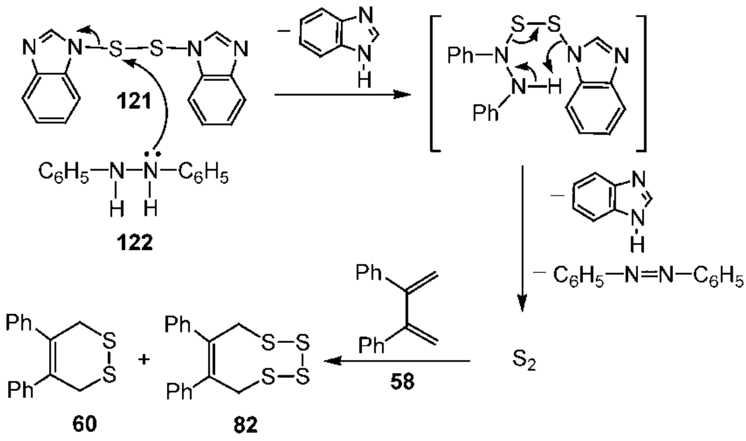
58 **60** **82**

SCHEME 38



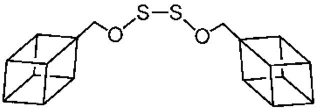
SCHEME 39

A novel diatomic sulfur route was recently reported by Harpp and co-workers in 2002 [146]. Aliphatic dialkoxy disulfides precursors **123** and **124** undergo thermal decomposition to expel S_2 under mild conditions. When disulfides **123** and **124** were subjected to 1,3-dienes **57** and **58**, cyclic disulfides **59** and **60** as well as tetrasulfide adducts **98** and **82** were formed, respectively,

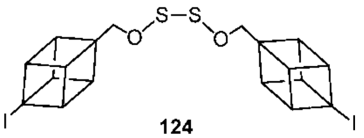


SCHEME 40

in good isolated yields.

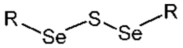


123

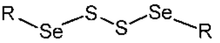


124

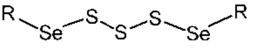
Recently, it was reported [147] the synthesis of various organic polychalcogenides **125–127** with a common structure of RSeS_xSeR in >90% isolated yield and high purity from the reaction of triphenylmethanesulfenyl chloride (**27**) and (its thio or dithio **41** homologue) with diselenides **128** in chloroform at room temperature.



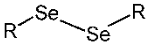
125a; R = C_6H_5
125b; R = $CH_2C_6H_5$
125c; R = CH_3



126a; R = C_6H_5
126b; R = $CH_2C_6H_5$
126c; R = CH_3
126d; R = CH_2-C_6H_4-NO_2-*p*



127a; R = C_6H_5
127b; R = $CH_2C_6H_5$
127c; R = CH_3



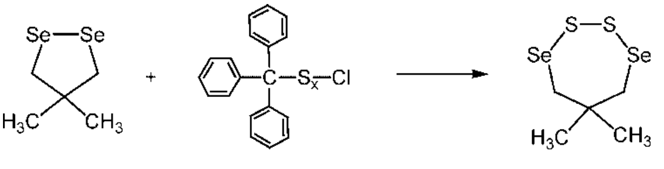
128

The identity of the polychalcogenide adducts **125–127** was confirmed by ^{1}H and ^{13}C NMR as well as by elemental analysis. The X-ray crystallographic structures of **126b** and **127b** were successfully completed [147]. Under the same conditions, 5,5-dimethyl-1,2-dithia-3,7-diselenacycloheptane (**55**) (originally used by Schmidt to transfer S_2 [111]) was synthesized in quantitative yield and high purity from the reaction of triphenylmethanethiosulfenyl chloride (**37**) with diselenide **56** and in 50% from its reaction with sulfenyl chloride **27** in chloroform at room temperature [147] (scheme 41).

The likely mechanism [147] for the insertion of two sulfur units into diselenide **128** *via* thiosulfenyl chloride **37** is described in scheme 42.

The mechanism of this sulfur insertion reaction is believed to be analogous to the one proposed in the reaction of disulfides (R-S-S-R) with thiosulfenyl chloride **37** and related sulfur transfer reagents [148].

Most recently, the same authors [149] found that when diselenatetrasulfides **126b** and **55** are warmed with 2,3-diphenyl-1,3-butadiene (**58**), they smoothly deliver diatomic sulfur-trapped derivatives, cyclic disulfide adduct **60** and tetrasulfide adduct **82** (scheme 43). Various concentrations were employed to optimize the yield of **60** and **82**. It was clear that the reaction

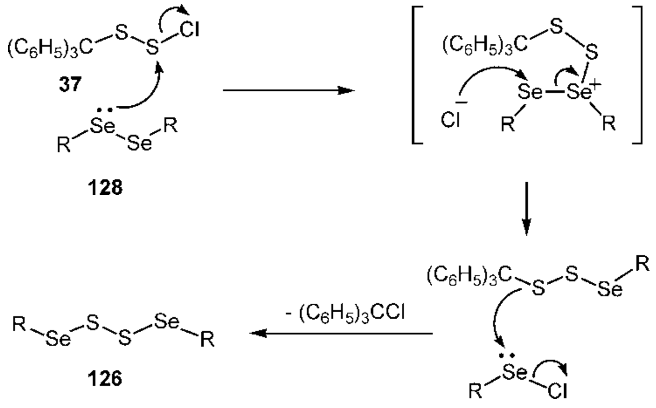


56

27; x = 1
37; x = 2

55 (100% from **37**)

SCHEME 41



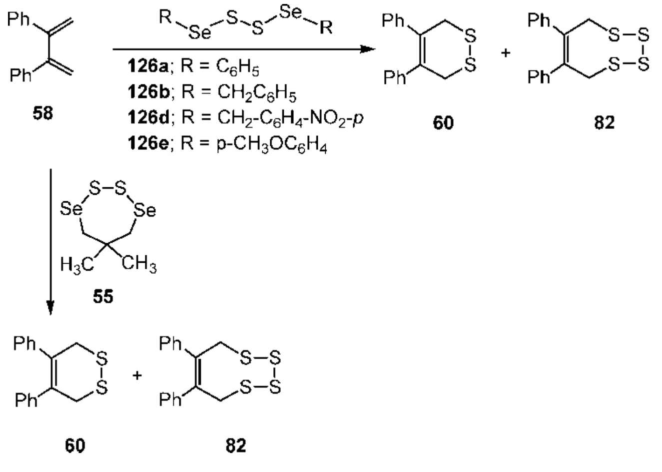
SCHEME 42

requires a 2-fold excess of diselenides **55** and **126b** to be efficient. The tetrasulfide adduct **82** is quantitatively converted to disulfide **60** with triphenylphosphine affording cyclic disulfides in more than 50% isolated yield.

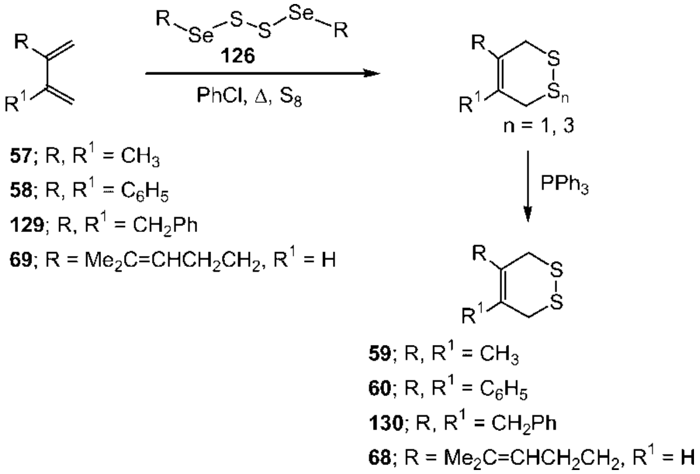
Contrary to previous claims [111], not only the cyclic diselenatetrasulfide **55** but also linear diselenatetrasulfides **126** transfer sulfur to dienes as shown in scheme 43. Interestingly, it was verified [149] that the sulfur-transferring properties of diselenatetrasulfides **126** are virtually identical to those of diselenides combined with elemental sulfur (S_8) (scheme 44). The efficiency of various diselenides in sulfur transfer reactions was tested with various dienes (**57**, **58**, **69**, and **129**) as shown in scheme 44. The sulfuration yields were in the 40–67% range with dienes containing aromatic groups showing the best results (including a new dibenzyl substituted disulfide **130**).

A plausible mechanism for the formation of disulfide adducts is probably as portrayed in scheme 45.

The sulfuration appears to be a thermally controlled homolytic process. This would imply a cleavage of the diselenides to form reactive radicals (R^1—Se$^\cdot$) as reported by Ogawa [150, 151] and Chu [152]. Other radicals do not seem to form as no R'S_xR' products are observed. In path A, sulfur is transferred to dienes to form the expected sulfuration products. In path B,



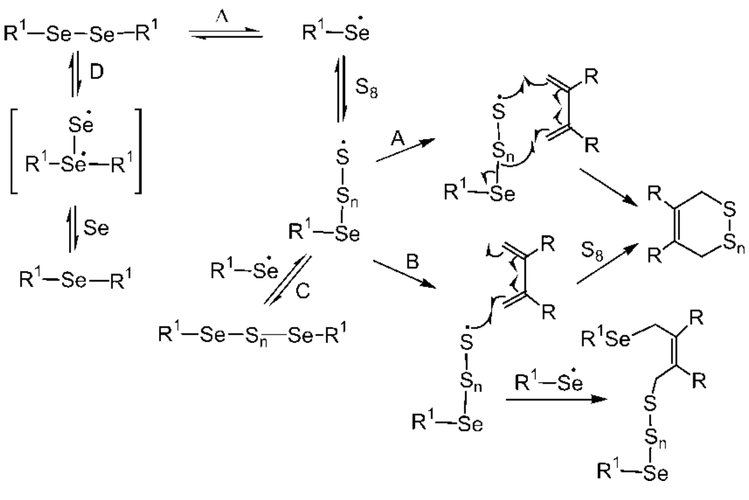
SCHEME 43



SCHEME 44

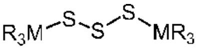
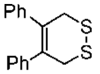
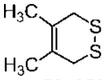
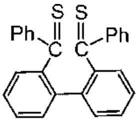
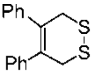
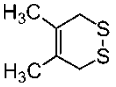
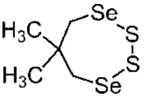
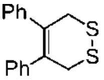
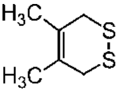
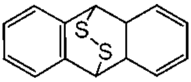
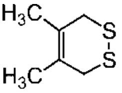
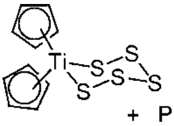
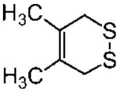
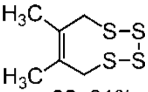
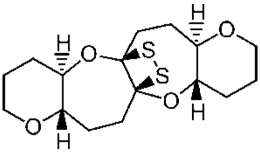
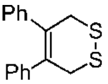
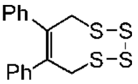
unsymmetric addition results in the formation of a mixed adduct similar to what was reported by Ogawa and co-workers [151]. This path seems to be redirected to the formation of sulfur transfer products when massive amounts of elemental sulfur are added. Finally, in path C, the sulfur radical species reversibly converts to diselenapolysulfides. It is by following this path that diselenatetrasulfides convert to radical sulfur species. Benzylic diselenides tend to lose selenium upon heating (scheme 45, path D). It seems that this process is not a prerequisite in sulfuration as even diselendes that do not deselenize efficiently assist in sulfuration.

Recently, Kaushik and co-workers [153] have reported benzyltriethylammonium tetracosathioheptamolybdate, $[(PhCH_2)N(C_2H_5)_3]_6[Mo_7S_{24}]$, (**131**) as a superior sulfur transfer reagent for the preparation of disulfides from the corresponding alkyl halides. The reactions were carried under mild conditions resulting in good yield but it is likely this process does not involve S_2.



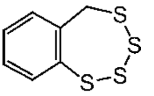
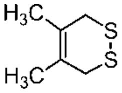
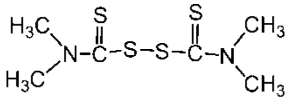
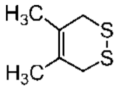
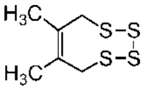
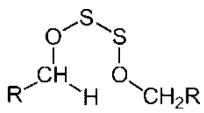
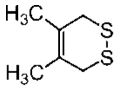
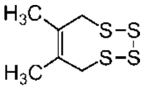
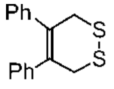
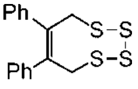
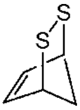
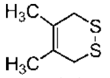
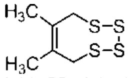
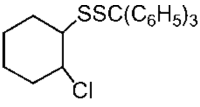
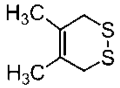
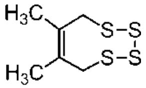
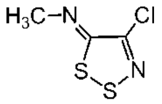
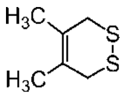
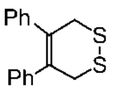
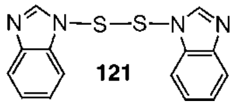
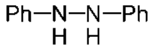
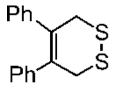
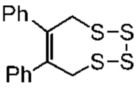
SCHEME 45

Table 1. Diatomic sulfur precursors; reactions with 1,3-butadienes **57** and/or **58**.

S_2 Precursor	Temp. (°C)	Products Yield[a]	Ref.
 **51** + Ph_3PBr_2 M = Si; R = C_6H_5, C_6H_{11}, p-$C_6H_4CH_3$	25	 **60**, 20% (42%)[b]	109
	25	 **59**, 35%	109
 **61**	80–110	 **60**, 85%	112
	80–110	 **59**, 60%	112
 **55**	130	 **60**, 54%	111
	130[c]	 **59**, 48%	111
 **76**	55[c]	 **59**, 25%	117
 + Ph_3PBr_2 **65**	55[c]	 **59**, 21%  **98**, 31%	113
 **80**	100[c]	 **60**, 25%  **82**, 28%	119

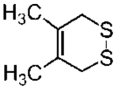
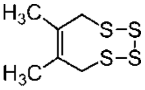
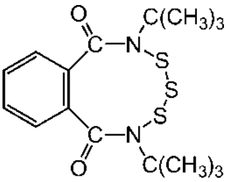
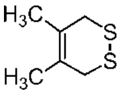
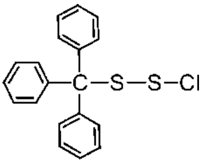
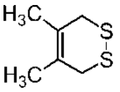
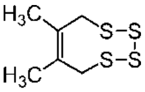
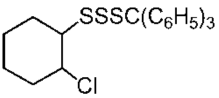
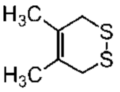
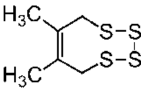
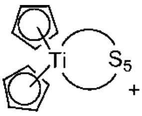
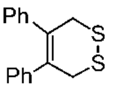
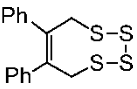
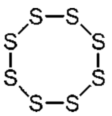
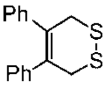
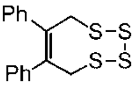
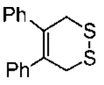
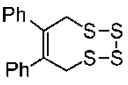
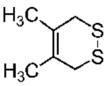
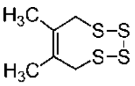
(*continued*)

Table 1. Continued.

S_2 Precursor	Temp. (°C)	Products Yield[a]	Ref.
 **93**	150[c]	 **59,** 21%	127
 **99**	60[c]	 **59**, 8%  **98**, 33%	133
 R = *p*-$C_6H_4NO_2$ **46**	100[c]	 **59**, 43%  **98**, 36%	131
	130	 **60**, 50%  **82,** 35%	132
 **95**	155[c]	 **59,** low yield  **98**, detected[b]	129
 **116**	77	 **59**, detected  **98**, 69%	141
 **104**	145[c]	 **59**, 19%  **60**, 29%	135
 **121** +  $\underset{H}{Ph-N}-\underset{H}{N}-Ph$ **122**	77	 **60**, 9%  **82**, 8%	145

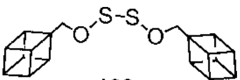
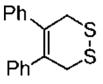
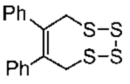
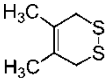
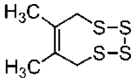
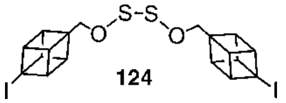
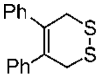
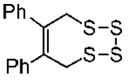
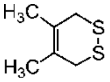
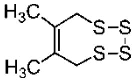
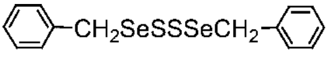
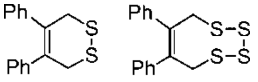
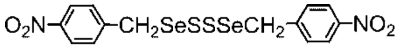
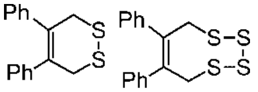
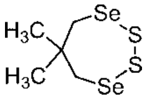
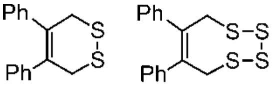
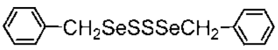
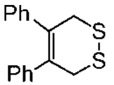
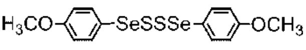
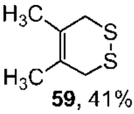
(*continued*)

Table 1. Continued.

S_2 Precursor	Temp. (°C)	Products Yield[a]	Ref.
	60^c	 **59**, 8%  **98**, 33%	145
 **100**	250	 **59**, detected	134
 **37**	35	 **59**, 35%  **98**, 30%	130
 **120**	77	 **59**, detected  **98**, 65%	141
 + DMSO **105**	125^b	 **60**, 38%  **82**, 4%	137
 + DMSO	125^b	 **60**, 70%  **82**, 15%	138
S_{10} + xylene/CS_2	120	 **60**, 38%  **82**, 4%	144
S_{10} + toluene/CS_2	90	 **59**, 36%  **98**, 6%	144

(*continued*)

Table 1. Continued.

S_2 Precursor	Temp. (°C)	Products Yield[a]	Ref.
 **123**	125[c]	 **60**, 48%  **82**, 23%	146
	125[c]	 **59**, 18%  **98**, 51%	146
 **124**	125[c]	 **60**, 31%  **82**, 42%	146
	110[c]	 **59**, 31%  **98**, 55%	146
 125[c] **126b**	125[c]	 (**60** + **82**), 56%	149
 **126d**	125[c]	 (**60** + **82**), 44%	149
 **55**	125	 (**60** + **82**), 51%	149
 + **126b** S_8	125	 **60**, 50%[d]	149
 + **126e** S_8	125	 **59**, 41%[d]	149

[a] Unless mentioned, yields are all isolated and based on one equivalent of S_2 precursors.
[b] By ^{1}H–NMR. [c] Olefin was used in excess. [d] Sulfur was in excess.

Most recently, the sulfur transfer reagent **131** was correctly formulated as benzyltriethylammonium tetrathiomolybdate, $[(PhCH_2)N(C_2H_5)_3]_2[MoS_4]$, (**132**) [154]. The correct formulation helps rationalize the unusual properties of **131** [153].

It is noteworthy to mention that, Chandrasekaran and co-workers [155] have pioneered the use of **132** in organic synthesis and shown this complex to be a versatile sulfur-transfer reagent for the convenient synthesis of a variety of organic sulfur compounds under mild reaction conditions. Various Mo-S compounds have been reported in the literature to convert alkyl halides to the corresponding disulfides [156–161].

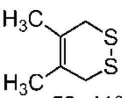
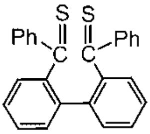
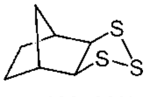
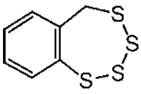
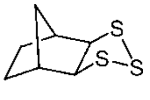
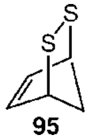
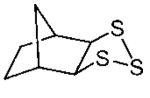
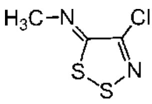
For a comparison between different methods of sulfuration, table 1 presents a chronological summary of the main diatomic sulfur precursors that have been designed over the years. Only the methods that are likely to have produced diatomic sulfur by trapping reaction are reported in table 1. The sulfuration efficiency of almost all these methods has been tested toward either 2,3-dimethyl-1,3-butadiene (**57**) or 2,3-diphenyl-1,3-butadiene (**58**). 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.

Other claims of diatomic sulfur involvement in the decomposition of some reagents have been made [102–106]. However, the decomposition pathway of these compounds remains, for the most part unclear; the proposed mechanisms for the production of diatomic sulfur were not conclusively supported by trapping reactions.

Of the known diatomic sulfur precursors reported in table 1, only some of them have been reacted with norbornene (**101**). These reactions are summarized in table 2.

In conclusion, from the many examples described above it appears that two sulfur atoms must be adjacent to each other in a molecule in order for it to be considered a viable diatomic sulfur precursor. In many synthetically useful generations, the proposed intermediate for the

Table 2. Diatomic sulfur precursors; reactions with norbornene (**101**).

S_2 Precursor	Temp. (°C)	Products Yield[a]	Ref.
 **59**, 41%[d]	80–110	 **61**	112
 **103**, 88%	150[b]	 **93**	127
 **103**, 89%	150–160[b]	 **95**	129
 **103**, 61%	140–150[b]	 **104**	135

[a] Yields are all isolated and based on one equivalent of S_2 precursors.

[b] Olefin was used in excess.

generation of S_2 was a four-membered ring species. These intermediates could provide direct S_2 formation or the transfer of two sulfur atoms to a 1,3-diene. The presence of two adjacent sulfur atoms make many molecules potential singlet diatomic sulfur precursors, these include di-and polysulfides.

Acknowledgements

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References

[1] R.C. Weast (Ed.). *Handbook of Chemistry and Physics*, p. 176, CRC Press, Ohio (1972).
[2] R.C. Weast (Ed.). *Handbook of Chemistry and Physics*, p. 31, CRC Press, Ohio (1972).
[3] E.V. Anderson. *Chem. & Eng. News*, May 5, 1975, 30 (1975).
[4] A. Senning (Ed.). *Sulfur in Organic and Inorganic Chemistry*, Marcel Dekker Inc., New York, Vol. 2, Chap. 15 and 16 (1972).
[5] P.G. Stecher (Ed.). *The Merck Index*, p. 545, Merck & Co. Ltd. Inc., New Jersey (1968).
[6] B.E. Douglas, D.H. Mcdaniel. *Concepts and Models of Inorganic Chemistry*, p. 43, Blaisdell Pub. Co., London (1965).
[7] D. Brewer, R. Rahman, S. Safe, A. Talyor. *J. Chem. Soc., Chem. Commun.*, 1571 (1968).
[8] N. Nagarjan, L.H. Huckstep, D.H. Lively, D.C. Delong, M.M. Marsh, N. Neuss. *J. Am. Chem. Soc.*, **90**, 2980 (1968).
[9] M.J. Janssen. *Organosulfur Chemistry*, p. 2, Interscience Pub., New York (1967).
[10] K.V. Jost, V. Debabov, H. Nesvabda, J. Rudinger. *Coll. Czech. Chem. Commun.*, **29**, 419 (1964).
[11] J. Rudinger, K. Jost. *Experimenta*, **20**, 570 (1964).
[12] N. Kharasch. *Organic Sulfur Compounds*, p. 453, Pergamon Press, New York (1961).
[13] M. Koike, L.J. Reed. *J. Am. Chem. Soc.*, **81**, 505 (1959).
[14] E.E. Reid. *Organic Chemistry of Bivalent Sulfur*, Vol. 1, p. 107, Chemical Pub. Co., New York (1958).
[15] M.R. Bell, J.R. Johnson, B.S. Wildi, R.B. Woodward. *J. Am. Chem. Soc.*, **80**, 1001 (1958).
[16] K.G. Stren, A.J. White. *Biol. Chem.*, **117**, 95 (1937).
[17] E.S. West, R.W. Todd, H.S. Mason, J.T. van Bruggen. Textbook of Biochemistry, 4th edn, Macmillan Co. Ltd., London (1970).
[18] B.M. Trost. *Acc. Chem. Res.*, **11**, 453 (1978).
[19] E. Block. *Aldrichimica Acta*, **11**, 51 (1978).
[20] E. Block, *Reactions of Organosulfur Compounds*, Academic Press Inc., New York (1978).
[21] R. Steudel. *Chem. Rev.*, **102**, 3905 (2002).
[22] J. Bougault, E. Cattelain, P. Chabrier. *Comp. Rend.*, **208**, 657 (1939).
[23] J. Bougault, E. Cattelain, P. Chabrier. *Bull. Soc. Chim. France*, **7**, 781 (1940).
[24] S. Yamada, H. Ohsawa, T. Suzuki, H. Takayama. *J. Org. Chem*, **51**, 4934 (1986).
[25] W.L. Mock. *J. Am. Chem. Soc.*, **97**, 3666 (1975).
[26] C.R. Williams, D.N. Harpp. *Sulfur Reports*, **10**, 103 (1990).
[27] B.P. Stark, A.J. Duke. *Extrusion Reactions*, p. 72, Pergamon Press, Oxford (1967).
[28] J.D. Loudon. In *Organic Sulfur Compounds*, N. Kharaseh (Ed.), Vol. 1, p. 299, Pergamon Press, Oxford (1961).
[29] S. Radl. *Janssen Chim. Acta.*, **5**, 3 (1987).
[30] F.S. Guziec, Jr., L.J. Sanfilippo. *Tetrahedron*, **44**, 6241 (1988).
[31] K.J. Miller, K.F. Moschner, K.T. Potts. *J. Am. Chem. Soc.*, **105**, 1705 (1983).
[32] JANAF Thermochemical Tables, Dow Chemical Co., Midland Mich (1966).
[33] D.N. Harpp. In *Prespectives in the Organic Chemistry of Sulfur*, B. Zwanenburg, A. J. H. Klunder (Eds.), pp. 1–22, Elsevier, Amsterdam (1987).
[34] H.R. Snyder, M. Stewart, J.B. Ziegler. *J. Am. Chem. Soc.*, **69**, 2637 (1947).
[35] D.B. Denny, M.S. Boskin. *J. Am. Chem. Soc.*, **82**, 4736 (1960).
[36] Y. Gao, B. Sharpless, *J. Org. Chem.*, **53**, 4114 (1988).
[37] W. Ando, A. Itami, T. Furuhata, N. Tokitoh. *Tetrahedron Lett.*, 1787 (1987).
[38] G.A. Tolstikov, B.M. Lerman, L.I. Umanskya. *Izv. Akad, Nauk SSSR, Ser. Khim.*, 1367 (1982); *Chem. Abstr.*, **97**, 162438d (1982).
[39] D. Seyferth, W. Tronich, K.S. Marmor, W.E. Smith. *J. Org. Chem.*, **37**, 1537 (1972).
[40] T. Sato, Y. Goto, T. Tohyama, S. Hayashi, K. Hata. *Bull. Chem. Soc. Jpn.*, **40**, 2975 (1967).
[41] E.P. Adams, K.N. Ayad, F.P. Doyle, D.O. Holland, W.H. Hunter, J.H.C. Nayler, A. Queen. *J. Chem. Soc.,Chem. Commun.*, 2665 (1960).
[42] C.G. Moore, M. Proter. *J. Chem. Soc., Chem. Commun.*, 2062 (1958).

[43] A. Schonberg, K. Fateen, M.A. Sammour. *J. Am. Chem. Soc.*, **79**, 6020 (1957).
[44] C.O. Guss, D.L. Chamberlain, Jr. *J. Am. Chem. Soc.*, **74**, 1342 (1952).
[45] G.P. Hagen, R.M. Burgison. *J. Am. Pharm. Assoc.*, **39**, 7 (1950).
[46] M. Mousseron, M. Bousquet, G. Marett. *Bull. Soc. Chim. France*, 84 (1948).
[47] A. Schonberg, L. von Vargha. *Chem. Ber.*, **64B**, 1390 (1931).
[48] A. Schonberg, L. von Vargha. *Justus Liebigs Ann. Chem.*, **483**, 176 (1930).
[49] M.A. Youtz, P.P. Perkins. *J. Am. Chem. Soc.*, **51**, 3508 (1929).
[50] A. Schonberg. *Chem. Ber.*, **58**, 1793 (1925).
[51] H. Staudinger, J. Siegwart. *Helv. Chim. Acta.*, **3**, 840 (1920).
[52] H. Staudinger, J. Siegwart. *Helv. Chim. Acta.*, **3**, 833 (1920).
[53] E. Lutz, J.-F. Biellmann. *Tetrahedron Lett.*, 2789 (1985).
[54] W. Chew, R.C. Hynes, D.N. Harpp. *J. Org. Chem.*, **58**, 4398 (1993).
[55] W. Chew, D.N. Harpp. *J. Org. Chem.*, **58**, 4405 (1993).
[56] W. Chew, D.N. Harpp. *Sulfur Lett.*, **15(6)**, 247 (1993).
[57] K.P.C. Vollhardt, R.G. Bergman. *J. Am. Chem. Soc.*, **95**, 7538 (1973).
[58] W.E. Parham, V.J. Traynelis. *J. Am. Chem. Soc.*, **77**, 68 (1955).
[59] R. Grigg, R. Hayes, J.L. Jackson. *J. Chem. Soc., Chem. Commun.*, 1167 (1969).
[60] W.H. Mueller. *J. Org. Chem.*, **34**, 2955 (1969).
[61] L. Field, N.E. Heimer, R.I. McNeil, R. Neal, A.J. Swinson, J.R. van Wazer. *Sulfur Lett.*, **1**, 135 (1983).
[62] R. Jahn, U. Schmidt. *Monatsh. Chem.*, **109**, 161 (1978).
[63] K. Gollnick, E. Leppin. *J. Am. Chem. Soc.*, **92**, 2217 (1970).
[64] E. Leppin, K. Gollnick. *J. Am. Chem. Soc.*, **92**, 2221 (1970).
[65] O. Foss. *Acta. Chem. Scand.*, 4 (1950).
[66] O. Foss. In *Organic Sulfur Compounds*, N. Kharasch (Ed.), pp. 75–77, Pergamon Press, New York (1961).
[67] W. Chew, D.N. Harpp. *Tetrahedron Lett.*, **33**, 45 (1992).
[68] W. Ando, H. Sonobe, T. Akasaka. *Tetrahedron Lett.*, **46**, 5093 (1990).
[69] G.W. Kutney, K. Turnbull. *Chem. Rev.*, **82**, 333 (1982).
[70] D.N. Harpp, K. Steliou, C.J. Cheer. *J. Chem. Soc., Chem. Commun.*, 825 (1980).
[71] R.E. Davis. *J. Am. Chem. Soc.*, **80**, 3565 (1958).
[72] M. Kamata, K. Murayama, T. Suzuki, T. Miyashi. *J. Chem. Soc., Chem. Commun.*, 827 (1990).
[73] R. Huisgen, J. Rapp. *J. Am. Chem. Soc.*, **109**, 902 (1987).
[74] R. Gleiter, G. Krennrich, D. Cremer, K. Yamamoto, I. Murata. *J. Am. Chem. Soc.*, **107**, 6874 (1985).
[75] R.K. Howe, B.R. Shelton. *J. Org. Chem.*, **46**, 771 (1981).
[76] J.T. Edward, R.H. Sheffler. *J. Org. Chem.*, **50**, 4855 (1985).
[77] C.R. Williams, D.N. Harpp. *Tetrahedron Lett.*, **32**, 7633 (1991).
[78] A. Senning, H.C. Hansen, M.F. Abdel-Majeed, W. Mazurkiewicz, B. Jensen. *Tetrahedron*, **42**, 739 (1986).
[79] A. Ishii, T. Akazawa, T. Maruta, J. Nakayama, M. Hoshino, M. Shiro. *Angew. Chem. Int. Engl.*, **33**, 777 (1994).
[80] C.R. Williams, J.G. McDonald, D.N. Harpp, R. Steudel, S. Förster. *Sulfur Lett.*, **13**(6), 247 (1992).
[81] C.R. Williams, D.N. Harpp. *Sulfur Lett.*, **16**(2), 63 (1993).
[82] I.A. Abu-Yousef, D.N. Harpp. *Tetrahedron Lett.*, **36**, 201 (1995).
[83] I.A. Abu-Yousef, D.N. Harpp. *J. Org. Chem.*, **62**, 8366 (1997).
[84] I.A. Abu-Yousef, D.N. Harpp. *Sulfur Reports*, **20**, 1 (1997).
[85] C. Schweitzer, R. Schmidt. *Chem. Rev.*, **103**, 1685 (2003).
[86] J. Wahlen, D.E. De Vos, P.A. Jacobs, P.L. Alsters. *Adv. Synth. Catal.*, **346**, 152 (2004).
[87] H.H. Wasserman, R.W. Murray. *Singlet Oxygen*, Academic Press, New York (1989).
[88] B. Meyer. *Chem. Rev.*, **76**, 367 (1976).
[89] A. Muller, W. Eltzner, N. Mohan. *Angew. Chem., Int. Ed. Engl.*, **18**, 168 (1979).
[90] S. Oae. *Phosphorus, Sulfur, and Silicon and Rel. El.*, **59**, 79 (1991).
[91] N.N. Greenwood, A. Earnshaw. *Chemistry of the Elements*, Pergamon Press, New York (1986).
[92] G. Herzberg. *Molecular Spectra and Molecular Structure*, Vol. 1, Nostrand, Princeton, NJ (1950).
[93] R.F. Barrow, R.P. Duparcq. In *Elemental Sulfur*, B. Meyer, (Ed.), Interscience, New York (1965).
[94] J.M. Ricks, D. Barrow. *Can. J. Phys.*, 2423 (1969).
[95] G.D. Brabson, A. Citra, L. Andres, R.D. Davy, M. Neurock. *J. Am. Chem. Soc.*, **118**, 5469 (1996).
[96] K. Steliou, Y. Gareau, G. Milot, P. Salama. In *Phosphorus, Sulfur and Silicon*, C. T. Pedersen, J. Becher (Eds.), pp. 209–241, Gordon and Breach, Science Publishers Inc., England, (1989).
[97] A. Taylor. In *Microbial Toxins VII*, S. Kadis, A. Ciegler, J. S. Ajl (Eds.), pp. 337–376, Academic, New York (1971).
[98] H. Staudinger, H. Freudenberger. *Chem. Ber.*, **61**, 1576 (1928).
[99] Q.E. Thompson, M.M. Crutchfield, M.W. Dietrich, E. Pierron. *J. Org. Chem.*, **30**, 2692 (1965).
[100] K. Steliou. *Acc. Chem. Res.*, 341 (1991).
[101] S.L. Tardif, A.Z. Rys, C. B. Abrams, I.A. Abu-Yousef, P.B.F. Leste-Lasserre, E.K.V. Schultz, D.N. Harpp. *Tetrahedron*, **53**, 12225 (1997).
[102] B.L. Chenard, R.L. Harlow, A.L. Johnson, S.A. Vladuchick. *J. Am. Chem. Soc.*, **107**, 3871 (1985).
[103] A. Orahovatz, M.J. Levinson, P.J. Carroll, M.V. Lakshmikanthan, M.P. Cava. *J. Org. Chem.*, **50**, 1550 (1985).
[104] W. Ando, Y. Kumamoto, N. Tokitoh. *Tetrahedron Lett.*, **28**, 4833 (1987).
[105] P.D. Barlett, T. Ghosh. *J. Org. Chem.*, **52**, 4937 (1987).

[106] R. Jahn, U. Schmidt. *Chem. Ber.*, **108**, 630 (1975).
[107] J.A. Elvidge, S.P. Jones, T.L. Peppard. *J. Chem. Soc., Perkin Trans. 1*, 1089 (1982).
[108] J. Steudel. *Top. Curr. Chem.*, **102**, 149 (1982).
[109] K. Steliou, Y. Gareau, D.N. Harpp. *J. Am. Chem. Soc.*, **106**, 799 (1984).
[110] P.D. Bartlett, M. Lonzetta. *J. Am. Chem. Soc.*, **105**, 1984 (1983).
[111] M. Schmidt, U. Görl. *Angew. Chem., Int. Ed. Engl.*, **26**, 887 (1987).
[112] K. Steliou, P. Salama, D. Brodeur, Y. Gareau. *J. Am. Chem. Soc.*, **109**, 926 (1987).
[113] D.N. Harpp, J.G. McDonald. *J. Org. Chem.*, **53**, 3812 (1988).
[114] Y. Kishi, T. Fukayama, S. Nakatsuka. *J. Am. Chem. Soc.*, **95**, 6490 (1973).
[115] Y. Kishi, T. Fukayama, S. Nakatsuka. *J. Am. Chem. Soc.*, **95**, 6492 (1973).
[116] Y.S. Tsantrizos, P.L. Folkins, J.F. Britten, D.N. Harpp, K.K. Ogilvie. *Can. J. Chem.*, **70**, 158 (1992).
[117] W. Ando, H. Sonobe, T. Akasaka. *Tetrahedron Lett.*, **28**, 6653 (1987).
[118] K.C. Nicolaou, C.-K. Hwang, M.E. Duggan, P.J. Carroll. *J. Am. Chem. Soc.*, **109**, 3801 (1987).
[119] K.C. Nicolaou, C.-K. Hwang, S. DeFrees, N.A. Stylianides. *J. Am. Chem. Soc.*, **110**, 4868 (1988).
[120] J.E. Bishop, S.A. Dagam, H. Rapoport. *J. Org. Chem.*, **54**, 1876 (1989).
[121] C. Wentrup, S. Fischer, A. Maquestiau, R. Flammang. *J. Org. Chem.*, **51**, 1908 (1986).
[122] H. Bender, F. Carnovale, J.B. Peel, C. Wentrup. *J. Am. Chem. Soc.*, **110**, 3458 (1988).
[123] C.R. Constabel, G.H.N. Towers. *Planta Medica*, **55**, 35 (1989).
[124] C.S. Foote. *Acc. Chem. Res.*, **1**, 104 (1968).
[125] T. Matsuura. *Tetrahedron*, **33**, 2869 (1977).
[126] A. Naqui, B. Chance, E. Cadenas. *Ann. Rev. Biochem.*, **55**, 137 (1986).
[127] R. Sato, S. Satoh, M. Satio. *Chem. Lett.*, 139 (1990).
[128] T.L. Gilchrist, J.E. Wood. *J. Chem. Soc., Chem. Commun.*, 1460 (1992).
[129] T.L. Gilchrist, J.E. Wood. *J. Chem. Soc. Perkin Trans.*, **1**, 9 (1992).
[130] C.R. Williams, D.N. Harpp. *Tetrahedron Lett.*, **32**, 7651 (1991).
[131] S. Tardif, C.R. Williams, D.N. Harpp. *J. Am. Chem. Soc.*, **117**, 9067 (1995).
[132] S. Tardif, D.N. Harpp. *J. Org. Chem.*, **65**, 4791 (1995).
[133] W. Chew, D.N. Harpp. *Tetrahedron Lett*. **32**, 7633 (1991).
[134] A.S. Micallef, S.E. Bottle. *Tetrahedron Lett*. **38**, 2303 (1997).
[135] R.F. English, O.A. Rakitin, C.W. Rees, O.G. Vlasova. *J. Chem. Soc., Perkin Trans. 1*. **39**, 201 (1997).
[136] O.A. Rakitin, C.W. Rees, O.G. Vlasova. *Tetrahedron Lett*. **37**, 4589 (1996).
[137] A.Z. Rys, D.N. Harpp. *Tetrahedron Lett*. **39**, 9139 (1998).
[138] A.Z. Rys, D.N. Harpp. *Tetrahedron Lett*. **38**, 4931 (1997).
[139] K. Okuma, S. Kuge, Y. Koga, K. Shioji, H. Wakita, T. Machiguchi. *Heterocycles*, **48**, 1519 (1998).
[140] I.A. Abu-Yousef, D.N. Harpp. *J. Org. Chem.*, **63**, 8654 (1998).
[141] I.A. Abu-Yousef, R.C. Hynes, D.N. Harpp. *Tetrahedron Lett.*, **34**, 4289 (1993).
[142] I.A. Abu-Yousef, D.N. Harpp. *Tetrahedron Lett.*, **35**, 7167 (1994).
[143] I.A. Abu-Yousef, D.N. Harpp. *Sulfur Reports*, **24**, 255 (2003).
[144] P. Leste-Lasserre, D.N. Harpp. *Tetrahedron Lett.*, **40**, 7961 (1999).
[145] A.M. Sawayama, P. Leste-Lasserre, D.N. Harpp. *Sulfur Lett*. **23(4)**, 7961 (2000).
[146] R. Priefer, P.G. Farrell, D.N. Harpp. *Tetrahedron Lett*. **43**, 8781 (2002).
[147] Y. Hou, A.Z. Rys, I.A. Abu-Yousef, D.N. Harpp. *Tetrahedron Lett.*, **44**, 4279 (2003).
[148] A.Z. Rys, D.N. Harpp. *Tetrahedron Lett*. **41**, 7169 (2000).
[149] A.Z. Rys, Y. Hou, I.A. Abu-Yousef, D.N. Harpp. *Tetrahedron Lett.*, **45**, 9181 (2004).
[150] A. Ogawa, H. Tanaka, H. Yokoyama, R. Obayashi, K. Yokoyama, N. Sonoda. *J. Org. Chem.*, **57**, 111 (1992).
[151] A. Ogawa, R. Obayashi, N. Sonoda, T. Hirao. *Tetrahedron Lett.*, **39**, 1577 (1998).
[152] J.Y.C. Chu, J.W. Lewicki. *J. Org. Chem.*, **42**, 2491 (1977).
[153] V. Polshettiwar, M. Nivsarkar, J. Acharya, M.P. Kaushik. *Tetrahedron Lett.*, **44**, 887 (2003).
[154] B.R. Srinivasan, S.N. Dhuri, A.R. Naik. *Tetrahedron Lett.*, **45**, 2247 (2004).
[155] K.R. Prabhu, N. Devan, S. Chandrasekaran. *Synlett*, 1762 (2002) and references therein.
[156] N. Devan, D. Sureshkumar, I. Beadham, K.R. Prabhu, S. Chandrasekaran. *Indian J. Chem.*, **41B**, 2112 (2002).
[157] J.G. McDonald, D.N. Harpp. *Tetrahedron Lett.*, **25**, 703 (1984).
[158] P. Dhar, S. Chandrasekaran. *J. Org. Chem.*, **54**, 2998 (1989).
[159] A.R. Ramesha, S. Chandrasekaran. *Synth. Commun.*, **22**, 3277 (1992).
[160] S. Sinha, P. Ilankumaran, S. Chandrasekaran. *Tetrahedron Lett.*, **65**, 14769 (1999).
[161] P. Ilankumaran, K.R. Prabhu, S. Chandrasekaran. *Synth. Commun.*, **27**, 4031 (1997).