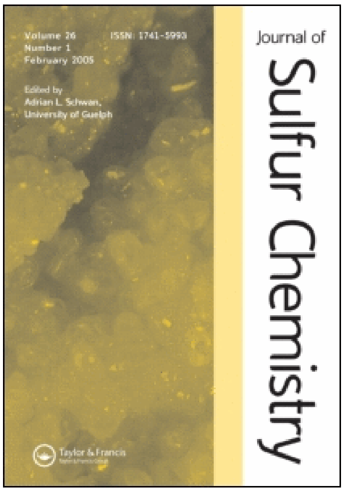

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New Sulfenyl Chloride Chemistry: Synthesis, Reactions and Mechanisms Toward Carbon-Carbon Double Bonds

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NEW SULFENYL CHLORIDE CHEMISTRY: SYNTHESIS, REACTIONS AND MECHANISMS TOWARD CARBON–CARBON DOUBLE BONDS

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This review summarizes recent publications about sulfenyl chlorides including aspects of their methods of preparation, chemistry and mechanisms with carbon–carbon double bonds and disulfides **85** **2**. Special attention has been paid to triphenylmethanesulfenyl chloride **2** and the thio **3** and dithio homolog **4**.

Keywords: Sulfenyl chloride; Thiosulfenyl chloride; Dithiosulfenyl chloride; Thiirane; Disulfides; Thiols; Diselenides; Polychacolgenides; Diaminodisulfides; Diaminotrisulfides

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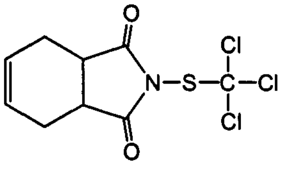
1. BACKGROUND

Sulfenyl chlorides (RSCl) were first discovered by Rathke [1] in 1870 through chlorination of carbon disulfide (CS_2). They can be formally considered as the acid chloride derivatives of the unstable sulfenic acid (RSOH). Their usefulness in industry was discovered when Kittleson [2] in 1952 derived 'Captan' (a potent fungicide) **1**, which utilizes a sulfenyl halide in the preparation.



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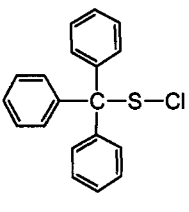
A wide variety of sulfenyl halides (RSX) can be obtained by varying the R and X, each with different physical and chemical properties. They can also undergo a host of reactions including addition, displacements, oxidations and reductions. Because of their versatile chemistry, sulfenyl halides have found wide applications. Among some of their uses are the following. 2,4-Dinitrobenzenesulfenyl chloride is used as an analytical reagent for characterizing many compounds by solid derivative formation [3], in the synthesis of peptides, nucleosides and nucleotides [4]. Sulfenyl halides are used as blocking groups and as selective chlorinating agents in hydrocarbon chemistry preferentially replacing tertiary hydrocarbon atoms [5]. In addition, the nature of sulfenyl intermediates plays an important role in the chemistry of wool, sulfur-containing fibers and in the preparation of various heterocyclic compounds [5].

Sulfenyl halides have proven their value as alkyl or aryl sulfur transfer reagents as is revealed in a large number of publications and reviews in the literature [3,6].

Triphenylmethanesulfenyl chloride (**2**) was first prepared in 1913 [7] and eventually led to its use in protective group chemistry as well as newer varieties such as triphenylmethanethiosulfenyl chloride (**3**) [8] and dithiosulfenyl chloride (**4**) [9].



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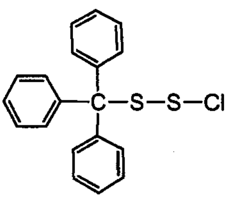

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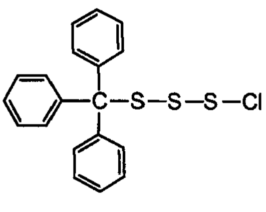

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For example, protected penicillins and cephalosporins have been prepared with Compound **2** [10]. In addition, *N*-sulfenated β-lactams (thiamazins) have been prepared as potential antibiotics with **2** as one of the starting materials [11]. *o*-Sulfenylated carbohydrate derivatives can be prepared with **2** [12]. Further, **2** has been used to decrease the flammability of polypropylene [13], and uracil derivatives have been *N*-protected with **2** [14], in which deprotection is possible with aqueous iodine [15].

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

2. STRUCTURES

The structures of a few chloromonosulfides have been investigated but these studies have been limited mainly to small molecules that allowed for easy spectroscopic analysis. The geometry of sulfur dichloride (SCl_2) has been determined using microwave spectroscopy [16,17] and electron diffraction [18]. The structure of methanesulfenyl chloride [19–21] (**5**) was also investigated by microwave spectroscopy, while the trichloro- (**6**) [22] and trifluoro- (**7**) [23] derivatives were examined with electron diffraction. Electron diffraction has also been used to measure the geometry of benzenesulfenyl chloride (**8**) [24].

$H_3C{-}S{-}Cl$

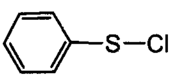
5

$Cl_3C{-}S{-}Cl$

6

$F_3C{-}S{-}Cl$

7



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The sulfur–chlorine bond length is found to range between 2.006(4) Å for sulfur dichloride [18] and 2.051(6) Å for benzenesulfenyl chloride. The carbon–sulfur bond length ranges from a low of 1.764(12) Å in benzenesulfenyl chloride to a high of 1.824(6) Å found in trifluoromethylsulfenyl chloride [23]. The C–S–Cl bond angle varies from a low of 98.3(15)° for trichloromethylsulfenyl chloride [22] to a high of 103.0(4)° for sulfur dichloride [18].

The structure of disulfur dichloride (S_2Cl_2) was determined in 1969 by electron diffraction [25] and more recently by microwave spectroscopy [26,27]. The sulfur–chlorine bond is longer than reported for any chloromonosulfide at 2.057(2) Å and the S–S–Cl angle larger at 108.2(3)°. The structure of chloro(trifluoromethyl) disulfide (**3**) has been studied using vibrational analysis [28,29]. Overall, the chlorodisulfides exhibit bond angles larger than those of the corresponding chloromonosulfides and longer sulfur–chlorine bonds.

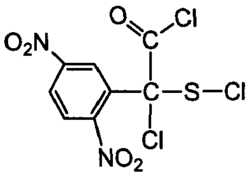
Harpp and co-workers [9] reported the X-ray structures of Compounds **2**, **3** and **4** for the first time. Selected bond lengths and angles are given in Table I.

The sulfur–chlorine and carbon–sulfur bond distances for **2** were in the range of those obtained for other monosulfides as was the observed angle about the sulfur atom. The crystal structure of a chloromonosulfide, α-chloro-α-chlorosulfenyl-4-nitro-2,5-dimethoxyphenylacetyl chloride (**9**), was reported [30], which showed a sulfur–chlorine bond length of 1.98 Å, a carbon–sulfur bond length of 1.84 Å and a C–S–Cl angle 99.42°. These measurements are in agreement with those measured for **2**, only slightly smaller. The smaller bond lengths and bond angles in **9** probably resulted from electronic effects from the strong withdrawing groups near the S–Cl bond.

TABLE I Selected bond lengths and angles from the X-ray structures of the chloro(triphenylmethyl)sulfides

	Monosulfide[a] *(2)*	*Disulfide*[b] *(3)*	*Trisulfide*[c] *(4)*
Bond lengths (Å)			
S–Cl	2.018(3)	2.073(2)	2.026(4)
S–S		1.975(2)	2.035(6) 2.011(4)
C–S	1.854(6)	1.912(4)	1.88(1)
Bond angles[c] (deg)			
S–S–Cl		108.44(8)	104.7(2)
S–S–S			107.3(2)
C–S–S		111.5(1)	107.9(3)
C–S–Cl	105.2(2)		
S–S dihedral		99.3(2)	−80.2(3) −102.4(3)

[a]Gave a satisfactory sulfur analysis using an Antek Sulfur Analyzer; [b]correct elemental analysis; [c]the angle is that of the central atoms listed.



9

Surprising structural features were found in the X-ray crystal analysis of the intermediate disulfur chloride **3**. The length of the sulfur–chlorine bond, 2.073(2) Å, is to our knowledge the longest bond of this type ever reported. The length of the sulfur–sulfur bond is quite short (1.975(2) Å), with only disulfur dichloride and compounds with known sulfur–sulfur double bonds being shorter. A comparison of bond lengths for compounds with known sulfur–sulfur double bonds with **3** is given in Table II. Disulfur dichloride is included because it is known to exhibit some double bond character. The disulfide bond length of **3** falls between that of disulfur dichloride and normal open chain disulfides (*ca.* 2.05 Å).

The observed angles about the sulfur atoms in **3** are two of the largest ever reported for a bivalent sulfur atom. The angle in C–S–S is 111.5(1)°, which is larger than the bond angles of S_8 (108°) but smaller than the O–S–S bond angle of S_2O_2 (112.7°) [38]. The large angle in the structure of S_2O_2 led [38] to a proposal of double bond character for the sulfur–sulfur bond. The short bond length coupled with the large sulfur dihedral angle suggested a similar double bond character for **3**. The dihedral or torsional angle (99.3°) is also larger than those of open chain disulfides which are normally in the range 85–95° [38]. The large dihedral angel is probably a result of steric hindrance. Snyder reported the dihedral angle of di-*tert*-adamantyl disulfide (**10**) to be 110.5(9)° [39]. The large dihedral angle is believed to be due to steric factors.

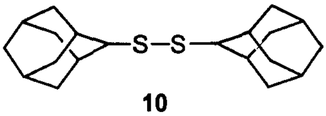


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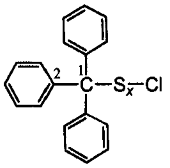
TABLE II Molecules with sulfur–sulfur double bonds

Compound	*Bond length* (Å)
$F_2S=S$	1.860 [31]
S=S=O	1.884 [32]
F–S–S–F	1.888 [31]
S=S	1.892 [33]
$(RO)_2S=S$	1.901 [34]
R–N=S=S	1.898 [35]
$Ph_3NSN=S=S$	1.908 [36]
Cl–S–S–Cl	1.931 [25]
Disulfide **3**	1.975 [9]
Open chain CS–SC	2.02–2.06 [37]

TABLE III Summary of the ^{13}C-NMR chemical shifts ($CDCl_3$, ppm) for the chloro(triphenylmethyl)sulfides



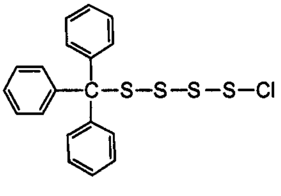
Sulfide	*C1*	*C2*
2	72.21	141.76
3	77.60	142.17
4	74.36	142.60
11	73.92	142.45
12	81.32	145.19

The S–Cl, S–S and C–S bond lengths for **4** are in the range measured for normal chloromonosulfides and dialkyldisulfides [38]. The angles about the sulfur atoms, although large, are in the range for S_8. The dihedral angles for the two S–S bonds differ greatly; the S–S adjacent to the triphenylmethyl group has a much larger dihedral angle than the S–S bond distant from the triphenylmethyl group. The reason for this difference is not known, but may be a result of the hindered rotation of the triphenylmethyl group. A similar structural arrangement of dihedral angles was observed in the X-ray crystal structures of organometallic trisulfides [40].

All of the sulfides **2**, **3** and **4** exhibit a distortion in the tetrahedral arrangement about the central carbon that is attached to the sulfur atom. This distortion may be attributed to an interaction between the electron pairs on the α-sulfur and the π-clouds of the aromatic rings, which would be intensified by rotational constraints of the triphenylmethyl group.

Like the results of the X-ray structure analysis, the ^{13}C nuclear magnetic resonance (NMR) spectrum of **3** differed significantly from that of **2** and **4**. The ^{13}C-NMR chemical shifts relative to tetramethylsilane are presented in Table III. The carbon atoms were identified by the numbering system shown in the table.

The NMR signals for **11** were identified from a mixture with the decomposition product triphenylchloromethane (**12**). The chemical shifts for **12** are included here for comparison [9].



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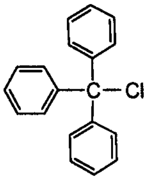

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3. METHODS OF PREPARATION

3.1. From Disulfides

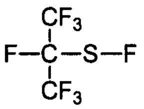
Sulfenyl halides are generally produced by treatment of alkyl or aryl disulfides **13** with halogen (Scheme 1) [41] or with sulfuryl chloride [42]. The reversibility of this reaction makes it practical only for chlorine or bromine [41].

$$\underset{\mathbf{13}}{R{-}S{-}S{-}R} + X_2 \rightleftharpoons 2R{-}S{-}X$$

R = alkyl, aryl; X = Cl, Br

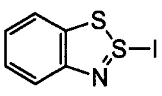
SCHEME 1

Isolation of sulfenyl fluorides such as **14** [43], or sulfenyl iodides such as **15** [44] or **16** [45], is known for only a limited number of these types of compounds [45].



$F{-}C(CF_3)_2{-}S{-}F$

14



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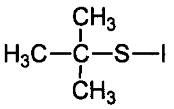


$H_3C{-}C(CH_3)_2{-}S{-}I$

16

One of the disadvantages associated with this approach is that chlorination of the disulfide may lead to carbon–sulfur scission, forming an alkyl chloride and sulfur monochloride instead of the desired sulfenyl chloride [46]. Alternatively, the mercaptan may be treated in a similar fashion to generate first the disulfide which then reacts to form the sulfenyl chloride; however, the yields are much lower with this process (Scheme 2) [47].

$$R{-}SH + Cl_2 \rightleftharpoons R{-}SCl + HCl$$

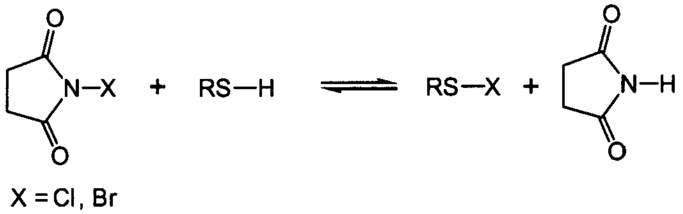
$$R{-}SH + R{-}SCl \rightleftharpoons RS{-}SR + HCl$$

$$RS{-}SR + Cl_2 \rightleftharpoons 2R{-}SCl$$

SCHEME 2

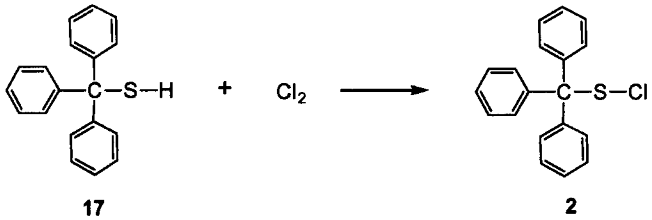
3.2. From Mercaptans

A better approach involves treating the thiol with *N*-chloro- or *N*-bromosuccinimide (Scheme 3) [48].



SCHEME 3

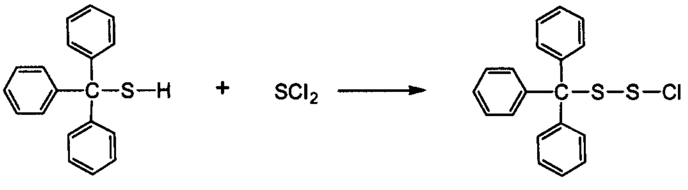
Triphenylmethanesulfenyl chloride (**2**) [7] has been known since 1913 and has been widely employed as a protecting group in amine chemistry [49]. Triphenylmethanethiosulfenyl (**3**) [8] and dithiosulfenyl chloride (**4**) have been recently researched [9]. Compound **2** was obtained by the direct chlorination of triphenylmethanethiol (**17**) following the procedure of Volander and Mittag (Scheme 4) [7]. In addition, Bowman and Richardson [50] reported that Compound **2** could be prepared from the treatment of 2-chloro-2-nitropropane with triphenylmethanethiolate anion.



17 **2**

SCHEME 4

Thiosulfenyl chlorides (also known as chlorodisulfanes or chlorodisulfides) are less well known owing to their lower stability. Moltzen and Senning [51] reported the preparation of a number of these compounds but there is little structural information available. Harpp and Ash [8] in 1971 reported the first synthesis for triphenylmethanethiosulfenyl chloride (**3**) from the reaction of thiol **17** with sulfur dichloride (Scheme 5).



17 **3**

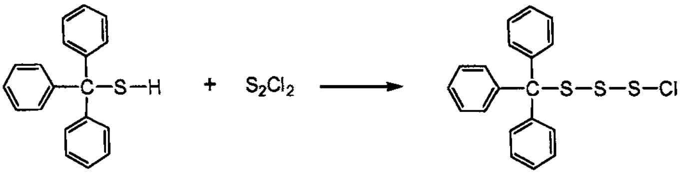
SCHEME 5

Compound **3** has received very little attention. It was first used to prepare unsymmetrical trisulfides [8] and later used to prepare di- and trisulfides in the synthesis of fungal metabolites [52]. The higher sulfides are prepared *in situ* only and used to synthesize hydrotetrasulfides (RSSSSH). To date they have not been isolated [53].

TABLE IV Summary of physical properties for the chloro(triphenylmethyl)sulfides

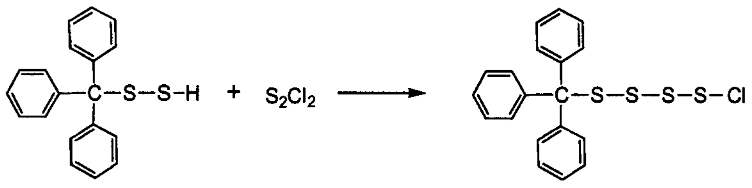
Sulfide	*Color*	*Melting Point (°C)*
2	Light yellow	135–137
3	Dark orange	91–93.5
4	Light orange	76–78
11	Light orange	Decomposes

Harpp and coworkers [9] reported the first synthesis of triphenylmethanedithiosulfenyl (**4**) and trithiosulfenyl chloride (**11**) from the condensation of disulfur dichloride with thiol **17** and dithiol **18** [54] respectively (Schemes 6 and 7). The physical properties of the sulfides are summarized in Table IV.



17 **4**

SCHEME 6



18 **11**

SCHEME 7

4. REACTIONS

The reactivities of compounds containing sulfur–chlorine bonds have been extensively studied [55]. It was therefore not considered necessary to do an exhaustive study of the chemistry of **2**, **3** and **4** but a few representative reactions were investigated. Many of the reactions were carried out only to show the typical reactivities of these chlorosulfides and they are discussed below.

4.1. With Nucleophiles

Yabuta and co-workers [56] reported that chlorosulfides **2**, **3** and **4** underwent normal displacement reactions with butylmagnesium chloride and gave the corresponding butyl(triphenylmethyl)sulfide **19** (Scheme 8) [165]. The yield was low (17%) in the case of sulfide **2** compared with **3** and **4**.

$$(C_6H_5)_3C{-}S_x{-}Cl \;+\; BuMgCl \longrightarrow (C_6H_5)_3C{-}S_x{-}Bu \;+\; MgCl_2$$

19

SCHEME 8

Displacement of the chlorine atom of the chlorosulfides **2**, **3** and **4** with butyllithium also yielded sulfide **19** (Scheme 9).

$$(C_6H_5)_3C{-}S_x{-}Cl \;+\; BuLi \longrightarrow (C_6H_5)_3C{-}S_x{-}Bu \;+\; LiCl$$

19

SCHEME 9

Unsymmetrical sulfides **19** were previously prepared (50–80%) by Harpp and Ash [8] in 1971 by the condensation of butylthiol with chlorosulfides **2**, **3** and **4** (Scheme 10).

$$(C_6H_5)_3C{-}S_x{-}Cl \;+\; Bu{-}SH \longrightarrow (C_6H_5)_3C{-}S_{x+1}{-}Bu \;+\; HCl$$

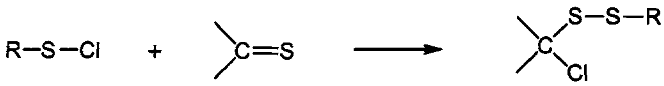
19

SCHEME 10

The reaction of **2**, **3** and **4** gave sulfides **19** identical to those obtained in the reaction of chlorosulfides **2**, **3** and **4** with either butyllithium or butylmagnesium chloride, as expected.

4.2. With Thioketones

Senning and co-workers [57] have studied the reaction of sulfenyl chlorides with various thioketones. They found that chloromonosulfide reacts smoothly with thioketones to give the addition adducts, α-chlorodisulfides **20** (Scheme 11).



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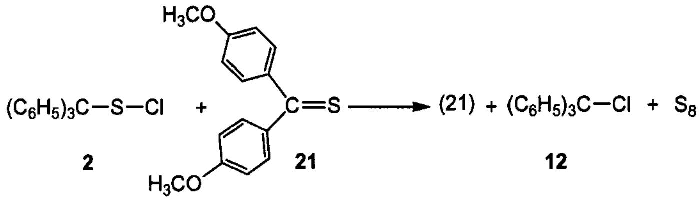
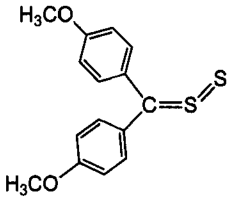
SCHEME 11

Williams and Harpp [58] investigated an interesting reaction of triphenylmethanesulfenyl chloride (**2**) where its sulfur atom was extruded quantitatively and *catalytically* by a reaction with thioketones; adducts such as **20** were isolated. They discovered that when **2** and 4,4′-dimethoxybenzophenone (**21**) were mixed in chloroform at room temperature a yellow precipitate was observed almost immediately. The precipitate was identified as sulfur and was isolated in near quantitative yield as expected for the conversion of **2** to triphenylmethyl chloride (**12**). Analysis of the reaction mixture using ^{13}C-NMR spectroscopy showed the presence of only two components, the starting thioketone **21** and **12**. The proposed reaction sequence is shown in Scheme 12. It was proposed that intermediates **22** and **23** were formed. These intermediates were suggested by Senning *et al.* in 1986 [59].



SCHEME 12



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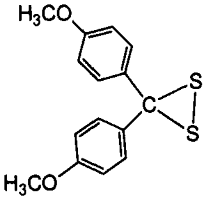
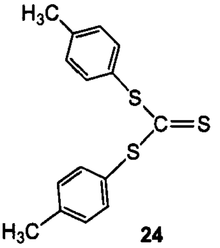


23

In another investigation, the same authors found that the reaction of chlorosulfide **2** and bis(4-tolyl)trithiocarbonate (**24**) resulted in the precipitation of elemental sulfur from the reaction mixture. Sulfur was also isolated almost quantitatively in the conversion of **2** to **12**.



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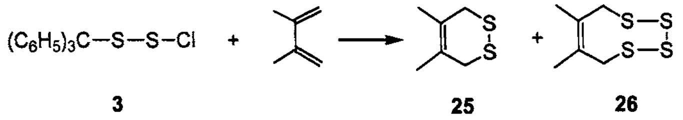
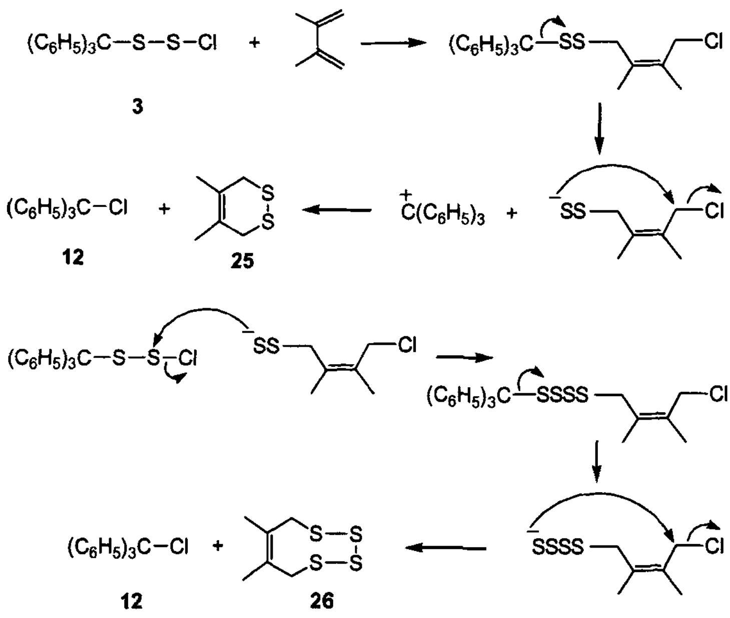
4.3. With 1,3-Butadienes

In 1991, Williams and Harpp [60] showed that the reaction of triphenylmethanethiosulfenyl chloride (**3**) with 1,3-dienes affords a 1,4-addition product which subsequently produces cyclic disulfide **25** (1,2-dithia-4,5-dimethyl-4-cyclohexene) and cyclic tetrasulfide **26** (1,2,3,4-tetrathia-6,7-dimethyl-6-cyclooctene) in good overall yield. The net effect of the latter transformation is to deliver a two- and four-sulfur fragment to the diene. The overall reaction for the decomposition of disulfide **3** to form the two trapped adducts is shown in Scheme 13.



SCHEME 13

They demonstrated [60] that the mechanism involves a transfer of two sulfur units to the 1,3-butadiene along with concomitant formation of chlorotriphenylmethane **12** as shown in Scheme 14.

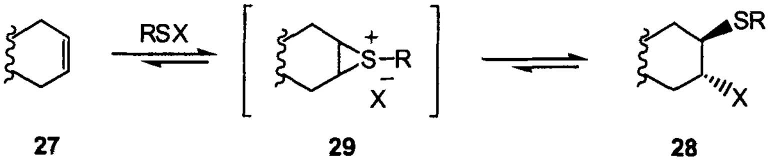


SCHEME 14

4.4. With Alkenes

4.4.1. Electrophilic Addition To Carbon–Carbon Double Bonds

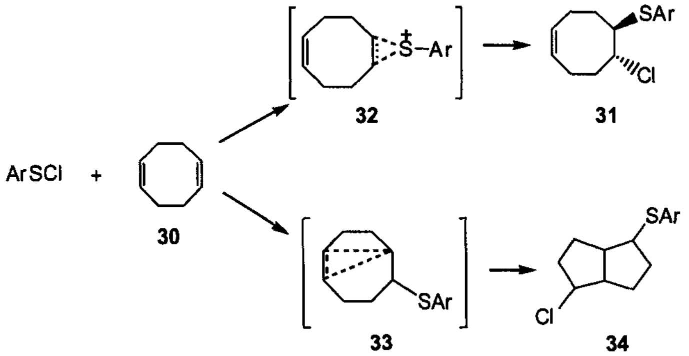
Electrophilic addition to the carbon–carbon double bond is a fundamental reaction in organic chemistry and has been extensively reviewed [61]. Among these reactions is the electrophilic addition of aryl- and alkylsulfenyl halides (RSX) to olefins **27** that produces *trans*-β-haloaryl(alkyl)sulfides **28** (also known as β-halo thioethers); it is a very well-established process (Scheme 15) [6c,62].



SCHEME 15

The reaction proceeds through an episulfonium salt intermediate **29** [63] that yields products usually resulting from predominant or exclusive attack of the halide ion at the more positively polarized carbon atom as shown in Scheme 15 [61,64].

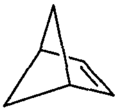
The carbon residue R is usually an alkyl or aryl group and X is mostly chlorine and sometimes bromine. The ability of sulfenyl halides to undergo addition reactions with unsaturated compounds is a well-known and a widely used method for the functionalization of alkenes [65]. The most commonly used are arenesulfenyl chlorides and methanesulfenyl chlorides [65,66]. The addition of arenesulfenyl chlorides to alkenes has been extensively studied by a number of workers [67]. For example, Schmid [68] reported the reaction of 2,4-dinitrobenzenesulfenyl chloride with *cis,cis*-1,5-cyclooctadiene (**30**) in chloroform solution to give the monosulfide adduct **31** in good yield (Scheme 16).



SCHEME 16

The structural determination of **31** was based on analytical and NMR data. The formation of **31** indicates that the transition state leading to it was similar to an episulfonium ion intermediate **32** rather than a carbonium ion intermediate **33** which would lead to a bicyclic product **34** as shown in Scheme 16 [69].

Bond [70] reported that the addition of 2,4-dinitrobenzenesulfenyl chloride to bicyclo[2.2.1]hex-2-ene (**35**) gave the monosulfide adduct **36**. The structure of the reaction product was established by ^{1}H-NMR.



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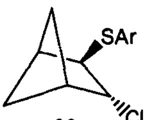

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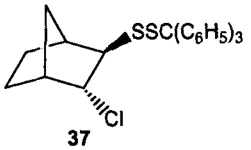
The reaction of trichloromethanesulfenyl chloride with norbornene to give the *trans*-adduct **37** in good yield was studied by Madsen and Lawessen [71]. It is believed to be formed by a polar electrophilic addition involving an episulfonium ion intermediate. Martin and Koster [72] studied the reaction of *p*-toluenesulfenyl chloride with benzonorbornadiene (**38**); *endo*-2-chloro-*exo*-1-thiocresylbenzonorbornene (**39**) was formed in low yield and identified by NMR spectroscopy.



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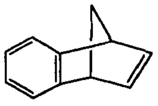

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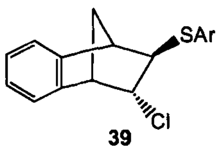
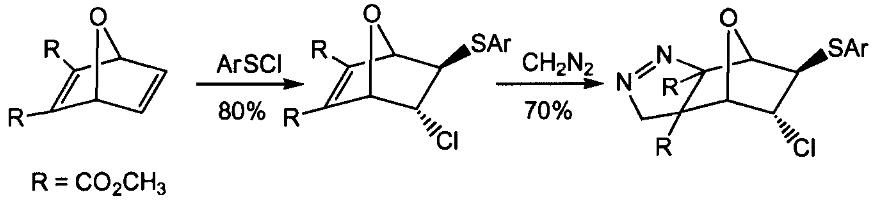


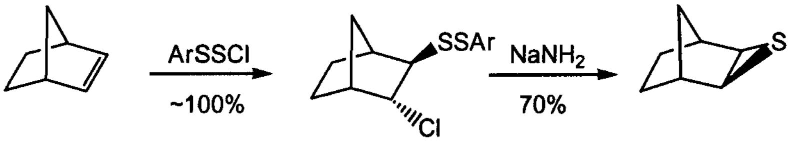
39

2,4-Dinitrobenzenesulfenyl chloride was reported to react with 7-oxabicyclo[2.2.1]-heptadiene derivatives in methylene chloride solution. Only normal addition products were formed (Scheme 17) [73]. The absence of rearranged products in Scheme 17 was shown by reaction with diazomethane to give pyrazoline derivatives. Similar results were obtained with 7-oxabicyclo[2.2.1]heptene derivatives.



SCHEME 17

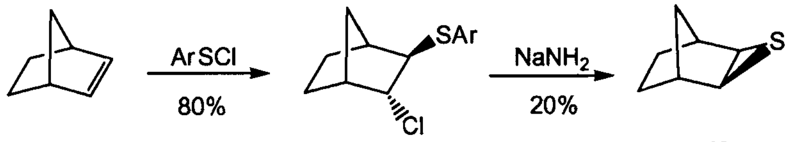
Fujisawa and Kobori [74] studied the reaction of arenethiosulfenyl chloride with norbornene (**40**) to give disulfide adduct **41** in nearly quantitative yield. They found that, when the crude adduct **41** was slowly added to sodium amide or sulfide at a temperature of 90–95°C under reduced pressure, an oily product was collected in good yield in a cold trap and identified as *exo*-2,3-epithionorbornane (**42**) (Scheme 18).



40 **41** **42**

SCHEME 18

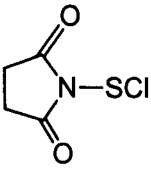
In another investigation, the same authors also obtained **42** in 20% yield by the treatment of monosulfide adduct **43**, prepared from norbornene (**40**) and *o*-nitrobenzenesulfenyl chloride, with sodium amide (Scheme 19).



40 **43** **42**

SCHEME 19

The same authors [75] reported a new series of sulfur transfer reagents to olefins, arenethiosulfenyl chlorides, which lead to the disulfide adducts and could be easily treated with sodium amide or sulfide to get the corresponding episulfide in better yields. The imidosulfenyl chlorides **44** or **45** have been found to react rapidly with norbornene (**40**) (and other alkenes) to give the corresponding adduct **46** or **47** respectively [76].



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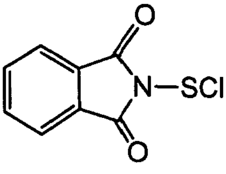

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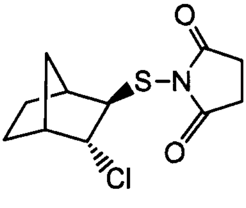

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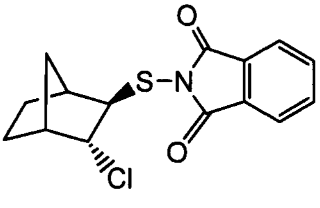
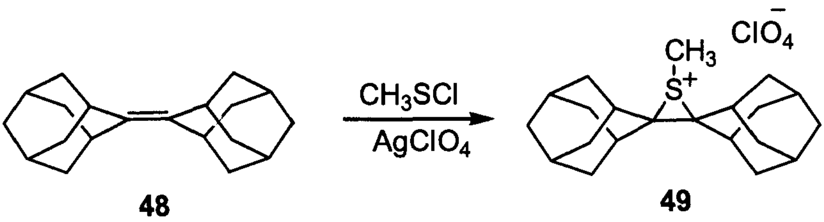


47

On the other hand, Bolster and Kellogg [77] studied the reaction of adamantylideneadamantane (**48**) with methanesulfenyl chloride in the presence of silver perchlorate ($AgClO_4$). They found that the thiiranium salt **49** was formed and no evidence for 1,2-addition products of the sulfenyl chlorides to **48** was obtained (Scheme 20).



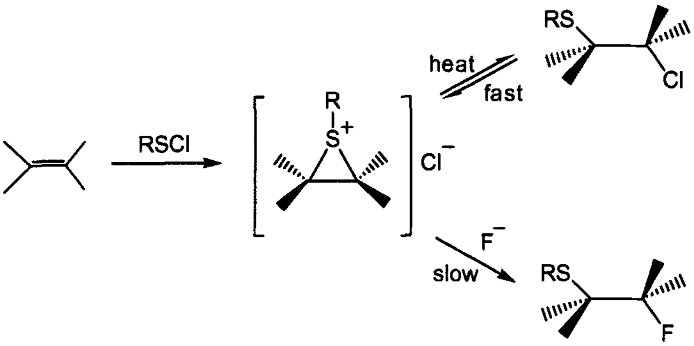
SCHEME 20

The reaction of triphenylmethanesulfenyl chloride (**2**) with norbornene (**40**) had been investigated [78] previously. In this reaction a number of products were reported but details were lacking and neither their stereochemistry nor the mechanism of the reaction was demonstrated. Indeed, other similar types of sulfenyl halides have been shown to add to carbon–carbon double bonds; this has resulted in preparation methods for episulfides [74–76].

Haufe *et al.* [79] reported that the reaction of dimethyl(methylthio)-sulfonium tetrafluoroborate (DMTSF) and triethylaminetrishydrofluoride with olefins leads to β-fluoroalkylmethyl thioethers in high yield. The main disadvantage of this method is the relatively difficult preparation of DMTSF, which requires the use of trimethyloxonium tetrafluoroborate, which is rather unstable and expensive.

Purrington and Correa [80] proposed another way to obtain β-fluoroalkylphenyl thioethers by the action of phenylsulfenyl chloride on an olefin in the presence of silver fluoride in acetonitrile solution.

In 1991, Haufe and co-workers [81] reported a new method leading to β-fluoroalkylphenyl (or methyl) thioethers, using halogen exchange between β-chloroalkylphenyl (or methyl) thioethers and a fluoride ion (Scheme 21).



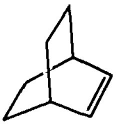
SCHEME 21

As a result, the **Ad$_E$2** (**Ad**dition, **E**lectrophilic, **bi**molecular) reaction of sulfenyl halides appears to be one of the most efficient ways to transfer alkenes into synthetically useful products and it has been extensively studied and reviewed by a number of workers [6c,61a,62c,65,82].

The chemistry of triphenylmethanesulfenyl chloride (**2**) and its thio (**3**) and dithio (**4**) homologs are much less examined.

4.4.2. Reaction of Olefins with Triphenylmethanesulfenyl Chloride (2)

Recently, we reported [83,84] that the addition of an equimolar amount of triphenylmethanesulfenyl chloride (**2**) to various bicyclic alkenes (norbornene (**40**) and bicyclo[2.2.2]octane (**50**)) leads, contrary to expectation, to *β*-chlorodisulfides **51** (*endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.1]heptane) and **52** (*endo*-2-chloro-*exo*-1-(triphenylmethyldithio)bicyclo[2.2.2]octane) respectively, in good isolated yields (*ca.* 47%), rather than to *β*-chlorosulfides. The identity of these adducts **51** and **52** was confirmed by ^{1}H- and ^{13}C-NMR, combustion and X-ray analysis. The X-ray crystallographic structures of **51** and **52** were reported [83] for the first time.



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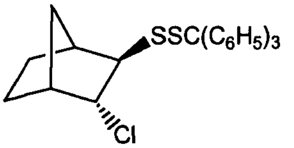

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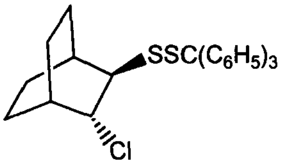
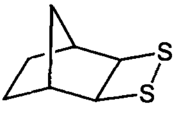


52

We have initiated a study of some of the chemistry of this type of addition for the preparation of a new series of di- and trisulfides hoping that these reagents can be used to develop a useful pathway to dithietanes **53** as potentially stable intermediates and/or diatomic sulfur precursors [83,84].



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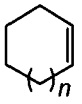
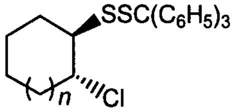
4.4.3. Reaction of Olefins with Triphenylmethanethiosulfenyl Chloride (3)

Triphenylmethanethiosulfenyl chloride (**3**) reacts nicely with bicyclic alkenes **40** and **50** to furnish excellent yields of *β*-chlorodisulfides **51** and **52** [83].

In more recent work, we reported [84,85] a new reaction of sulfenyl chlorides with various cyclic alkenes. Triphenylmethanethiosulfenyl chloride (**3**) has been found to react with cyclopentene (**53**) and cyclohexene (**54**) to give stable addition products **55** and **56** respectively, in high isolated yields (*ca.* 95%).



53; *n* = 0
54; *n* = 1

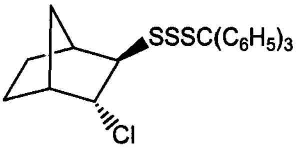


55; *n* = 0
56; *n* = 1

The structural determination of Compounds **55** and **56** was based on ^{1}H- and ^{13}C-NMR as well as elemental analysis. The assignments of relevant ^{13}C-NMR chemical shifts relative to tetramethylsilane of dithio adducts are reported in Table V. The carbon atoms were identified using the numbering system shown in the table.

4.4.4. Reaction of Olefins with Triphenylmethanedithiosulfenyl Chloride (4)

In the same manner, triphenylmethanedithiosulfenyl chloride (**4**) reacts with norbornene (**40**), cyclopentene (**53**) and cyclohexene (**54**) to give stable addition products **57**, **58** and **59** respectively, in high isolated yields (*ca.* 93%) [84,85]. The identity of adducts **57**, **58** and **59** was based on ^{1}H- and ^{13}C-NMR spectra as well as on elemental analysis. In addition, the X-ray structures of **58** and **59** were reported for the first time [85].



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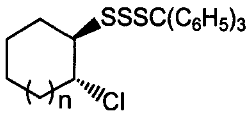
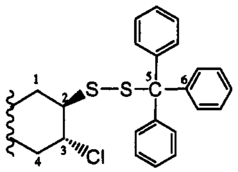


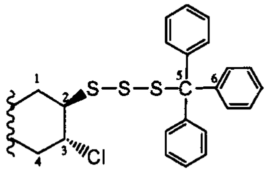
58; *n* = 0
59; *n* = 1

TABLE V Assignments of relevant ^{13}C-chemical shifts ($CDCl_3$, ppm) for dithio compounds



Disulfide	*C1*	*C2*	*C3*	*C4*	*C5*	*C6*
51	42.57	58.76	66.41	44.82	71.26	143.74
52	28.71	55.86	65.00	33.99	71.16	143.76
55	28.89	55.25	65.79	33.66	71.38	143.57
56	28.62	52.78	62.66	32.76	71.44	143.77

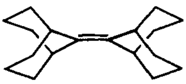
TABLE VI Assignments of relevant ^{13}C-chemical shifts (CDCl$_3$, ppm) for trithio compounds



Trisulfide	*C1*	*C2*	*C3*	*C4*	*C5*	*C6*
57	43.15	62.58	66.38	44.52	73.52	143.26
58	29.69	59.39	65.08	34.33	73.29	143.23
59	30.33	56.49	61.51	34.30	73.42	143.33

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

In addition, we investigated [84,86–88] the reaction of triphenylmethanesulfenyl chloride (**2**) and its thio **3** and dithio **4** homologs with more hindered olefins such as adamantylideneadamantane (**48**) and bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**60**). 1,2-Addition products such as **51** and **52** were not isolated; instead, cyclization takes place forming the corresponding episulfides adamantylideneadamantane thiirane (**61**) and bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane thiirane (**62**) respectively.



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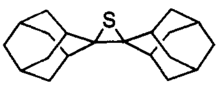

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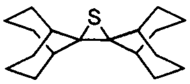
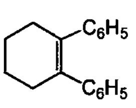


62

In another study [84], we examined the reaction of triphenylmethanesulfenyl chloride (**2**) and its thio **3** and dithio **4** homologs with another series of olefins. Cyclic olefins such as 1,2-diphenylcyclohexene (**63**), 1,2-diphenylcyclobutene (**64**), 1,4-dimethylcyclohexene (**65**), (1*R*)-(+)-α-pinene (**66**), (1*S*)-(−)-β-pinene (**67**), 3-carene (**68**), camphene (**69**), 3,4-dihydro-2*H*-pyran (**70**), 2,5-dihydrofuran (**71**) and 2,5-dimethoxy-2,5-dihydrofuran (**72**) did not react with the series of sulfenyl chlorides.



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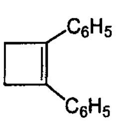

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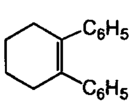

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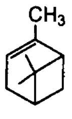

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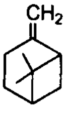

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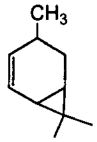

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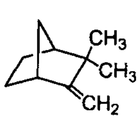

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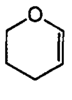

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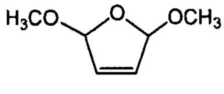
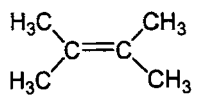


72

Acyclic olefins such as 1,1,2,2-tetramethylethylene (**73**), 1,1,2,2-tetraphenylethylene (**74**), 1,1,2,2-tetracyanoethylene (**75**), *trans*-stilbene (**76**), *cis*-stilbene (**77**), 1-bromo-2-methylpropene (**78**), styrene (**79**), bromostyrene (**80**) and vinylcyclohexane (**81**) were also tried [84].



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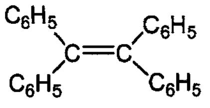

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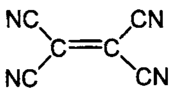

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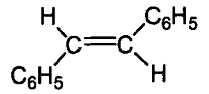

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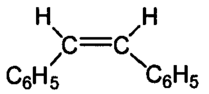

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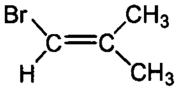

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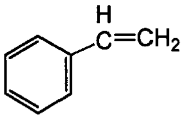

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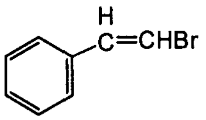

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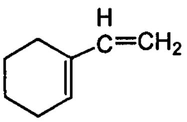


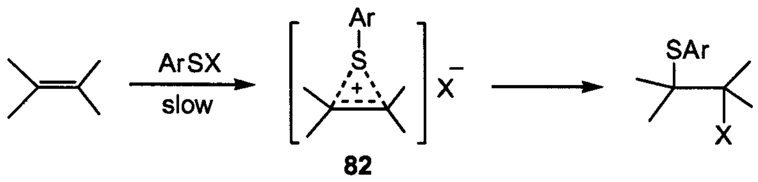
81

We discovered [84] that these olefins **63**–**81** remained unaffected even if the reactions were carried out over a few weeks. This behavior can be explained by the fact that the reaction must take place at room temperature because sulfenyl chlorides **2** or **3** and **4** decomposed on heating and most of the olefins are stable to addition chemistry, either as a result of conjugation or because they are vinyl halides.

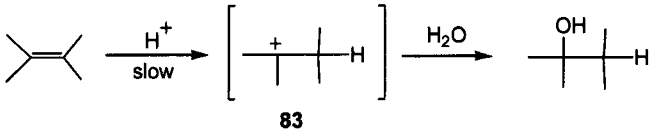
We found that, when each of the 1,2-addition products **51**, **52** or **55**–**59** was decomposed in the presence of 2,3-dimethyl-1,3-butadiene, evidence was obtained of the delivery of diatomic sulfur to conjugated dienes [84].

4.4.5. Mechanism of Electrophilic Addition to Carbon–Carbon Double Bonds

In investigating the mechanism of addition to a carbon–carbon double bond, the intermediate and the transition states leading to them may be divided into two distinct types. On the one hand, there are those reactions that proceed through bridged transition states and intermediates **82** (Scheme 22). Alternatively, there are those that involve the rate-determining attack at carbon to form open carbonium ions **83** (Scheme 23) [65,89].



SCHEME 22



SCHEME 23

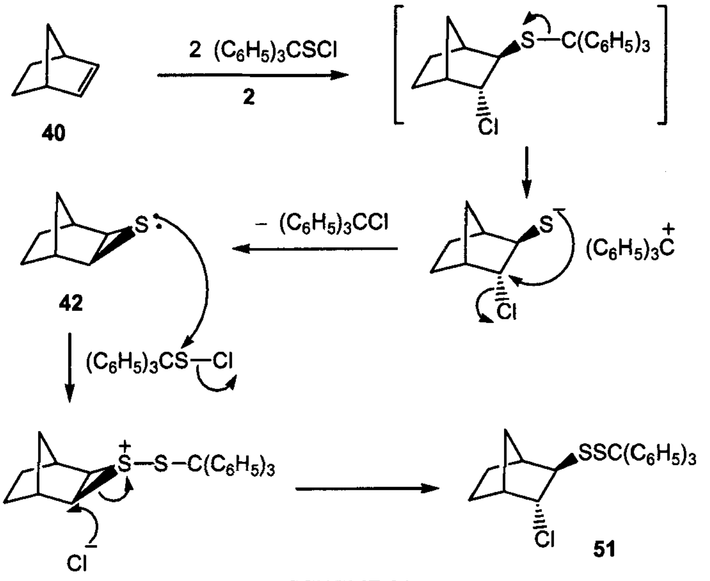
The best example of the first class of reactions is addition of sulfenyl halide [82f,90] to olefins as shown in Scheme 22. Protonation of alkenes in an acid-catalyzed hydration is a reaction which clearly fits in the second category [91] as shown in Scheme 23.

The mechanism of sulfenyl halide addition is securely based on rate–structure correlations, product stereochemistry and direct observation of the bridged intermediates [90]. In terms of the mechanism of the hydration reaction, it is supported by the correlation of rates with structure, solvent isotope effects, acidity dependence and other kinetic criteria [91].

An open carbonium ion such as **83** [92] can give a mixture of *cis*- and *trans*-addition products in cyclic alkenes or with certain steric or conformational effects that cause attack at one or the other side of the carbonium ion giving nonstereospecific addition products.

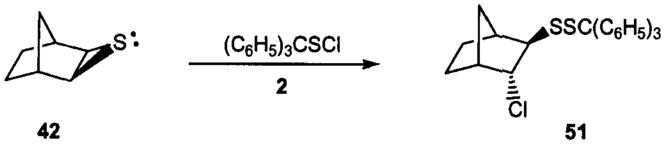
On the other hand, a bridged species such as **82** [93] can open stereospecifically to *trans*-addition products. In addition, for such an ion if formed from an unsymmetrical olefin, isomeric products would be expected resulting from attack at both carbon atoms of the intermediate. Thus, while the products are stereospecific they are not regiospecific. Both of these mechanisms are designated **Ad$_E$2**.

The stereochemistry of the product involving addition to olefins **40** and **50** has been determined by an X-ray analysis. It revealed that the regiochemistry of **51** and the symmetry of **52** permits only one isomer. Elemental and X-ray analysis demonstrated that the addition products **51** and **52** contained two sulfur atoms rather than one. A plausible mechanism showing the explanation for the presence of the second sulfur atom is indicated by the pathway in Scheme 24 [83,84].



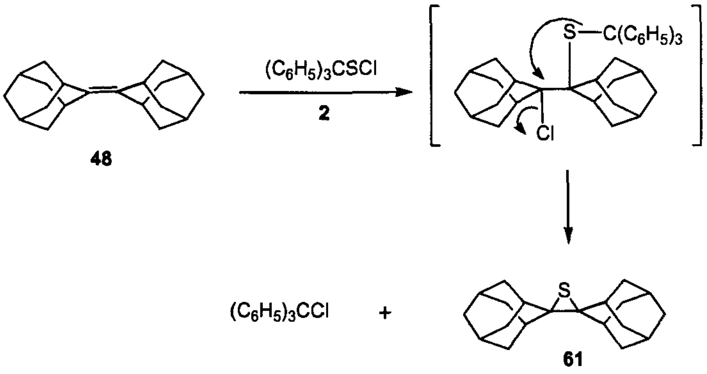
SCHEME 24

It is important to mention that the formation of thiirane **42** was demonstrated as the first step in this reaction and the stereochemistry of addition has been determined by X-ray analysis. To demonstrate the likelihood of this mechanism, we independently prepared *exo*-episulfide **42** and treated it with triphenylmethanesulfenyl chloride (**2**). Dithio **51** was isolated in 90% yield (Scheme 25).



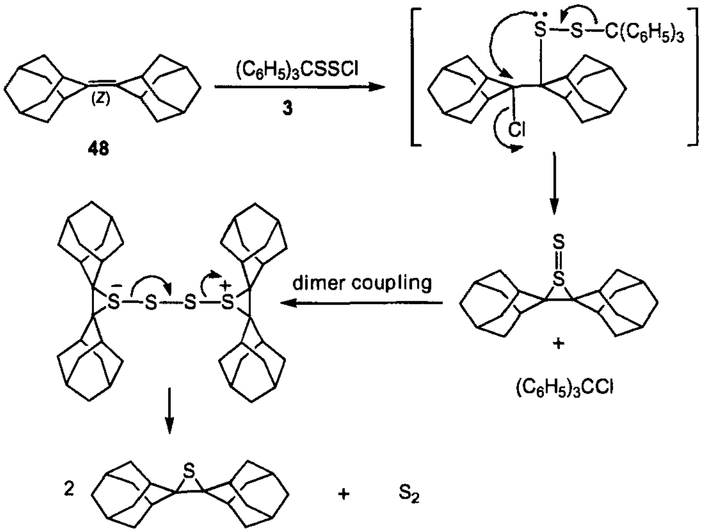
SCHEME 25

The most probable mechanism for the formation of adamantylideneadamantane thiirane (**61**) from the reaction of sulfenyl chloride **2** and adamantylideneadamantane (**48**) is shown in Scheme 26.



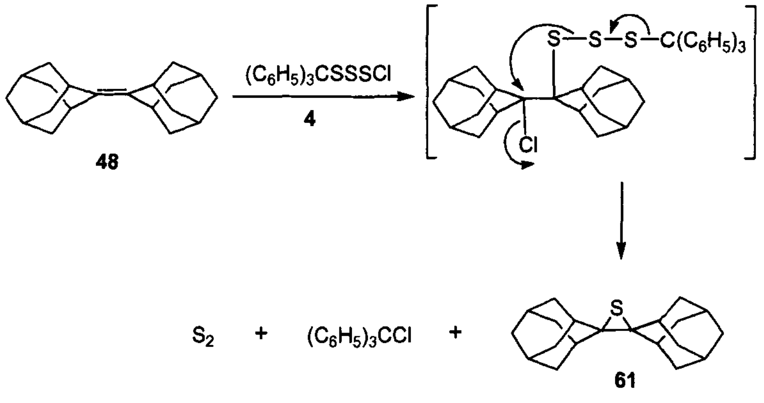
SCHEME 26

The mechanism for the formation of thiiran **61** *via* the reaction of thiosulfenyl chloride **3** and olefin **48** is probably as portrayed in Scheme 27.



SCHEME 27

In addition, the mechanism for the formation of thiirane **61** from the reaction of dithiosulfenyl chloride **4** and adamantylideneadamantane (**48**) is probably as portrayed displayed in Scheme 28.



SCHEME 28

4.5. With Disulfides

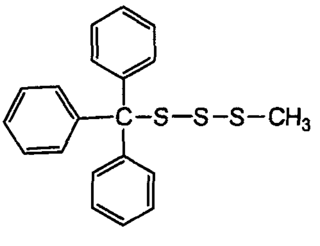
4.5.1. Reaction of Triphenylmethanethiosulfenyl Chloride (3)

Recently, we found [94] that treatment of thiosulfenyl chloride **3** with disulfides **84** smoothly produces tetrasulfides **85** in high isolated yields (Scheme 29) [8].

$$\underset{\mathbf{84}}{RSSR} + \underset{\mathbf{3}}{(C_6H_5)_3CSSCl} \xrightarrow[72\text{–}95\%]{} \underset{\mathbf{85}}{RSSSSR} + \underset{\mathbf{12}}{(C_6H_5)_3CCl}$$

SCHEME 29

The production of tetrasulfides **85** probably involves the formation of unsymmetrical trisulfide intermediate **86** (in the case of $R = CH_3$). As a result, this reaction allows an easy one-pot conversion of di- to tetrasulfide adducts.



86

4.5.2. Reaction of Triphenylmethanedithiosulfenyl Chloride (4)

As a continuation of our work [94] on the reaction of thiosulfenyl chlorides **3** with disulfides, we have discovered [95] that the reaction of dithiosulfenyl chloride **4** and disulfides **84** (Scheme 30) selectively affords pentasulfides **87** as the major product in good yield. This reaction can serve as an effective method to synthesize this difficult class from the more widely available disulfides.

$$\underset{\mathbf{84}}{RSSR} + \underset{\mathbf{4}}{(C_6H_5)_3CSSSCl} \xrightarrow[61\text{–}74\%]{} \underset{\mathbf{87}}{RSSSSSR} + \underset{\mathbf{12}}{(C_6H_5)_3CCl}$$

SCHEME 30

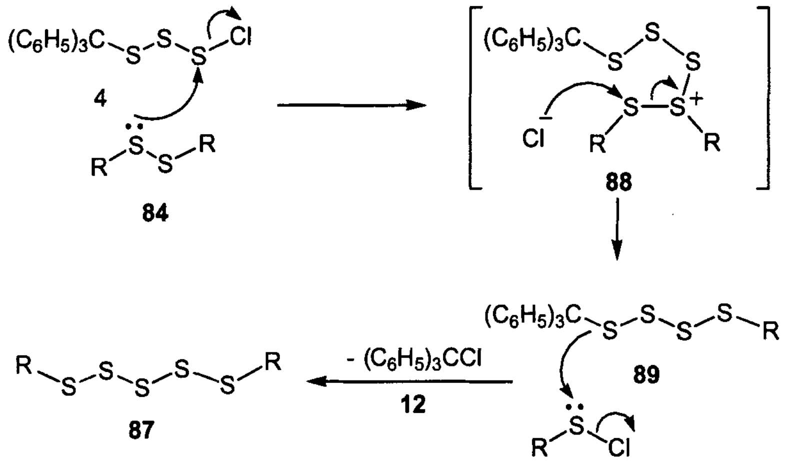
The reaction of chloro(triphenylmethyl)trisulfide (**4**) and a solution of dimethyl disulfide (**84a**) in either CH_2Cl_2, $CHCl_3$ or benzene results in the formation of dimethylpentasulfide (**87a**) as the main product (Table VII). Dimethyltri-, tetra- and hexasulfide were obtained as minor products [96]. In order to inhibit the further reaction of other reaction products with reagent **4**, only one equivalent of **4** is used.

The first step of the reaction is believed to be a nucleophilic cleavage of the S–Cl bond by the disulfide [94]. This is similar to the reaction of arenesulfenyl chlorides with organic disulfides studied by Moore and Porter [97] and Pietra and Vitali [98]. When this attack takes place with the relatively electron-rich sulfur atom in disulfide **84** engaging the electron-deficient sulfur in chloro(triphenylmethyl)trisulfide (**4**), a sulfonium salt **88** is formed as an intermediate and eventually triphenylmethylalkyl/phenyltetrasulfide (**89**) and sulfenyl chloride **5** are generated. The subsequent attack of the sulfur atom adjacent to the triphenylmethyl group in intermediate **89** on the sulfenyl chloride leads to the formation of final product, pentasulfide **87** (Scheme 31). This mechanism is consistent with the electronic effect displayed by the reaction and the difficulty of inducing the same reaction with secondary and tertiary disulfides.

TABLE VII Three sulfur unit insertion into symmetric disulfides

Entry	*R*	*Sulfide*	*Time* (h)	*Product*	*Selectivity* (%)[a]	*Yield* (%)[b]
1	CH_3	**84a**	2	**87a**	86	67
2	CH_3CH_2	**84b**	2	**87b**	83	73
3	$PhCH_2$	**84c**	9	**87c**	90	74
4	$HOCH_2CH_2$	**84d**	2	**87d**	87	67
5	$CH_2{=}CHCH_2$[c]	**84e**				
6	4-NH_2Ph[d]	**84f**				
7	4-CH_3OPh	**84g**	2	**87g**	71	68
8	4-CH_3Ph	**84h**	48	**87h**	60	44
9	4-NO_2Ph[e]	**84i**				
10	*i*-Propyl	**84j**	12	**87j**[f]	86	74
11	*t*-Butyl	**84k**	12	**87k**[g]		

[a] The percentage of pentasulfides in all polysulfides formed as calculated from the integration of appropriate peaks in the ^{1}H-NMR spectra. [b] Calculated according to peak intergration of the crude reaction mixture that includes some starting material and intermediate **89**. [c] Reacted with the double bond. [d] Dramatic reaction with the NH_2 group. [e] 90% of starting disulfide remained after one week. [f] Underwent disproportionation on the column. [g] Negligible yield.



SCHEME 31

4.5.3. Reaction of Triphenylmethanesulfenyl Chloride (2)

Most recently, we have been able to show [99] that the reaction of triphenylmethanesulfenyl chloride (**2**) with acyclic symmetric disulfides **84** gives the corresponding trisulfides **90** (Scheme 32) in moderate to good yield and selectivity (Table VIII). This reaction serves as an alternative method of preparation of trisulfides using easily accessible disulfides.

$$\begin{array}{ccccccc} \text{RSSR} & + & (C_6H_5)_3\text{CSCl} & \longrightarrow & \text{RSSSR} & + & (C_6H_5)_3\text{CCl} \\ \mathbf{84} & & \mathbf{2} & & \mathbf{90} & & \mathbf{12} \end{array}$$

SCHEME 32

The insertion reaction is effective with diamino disulfides **91** as substrates. The preparation of diaminotrisulfide **92** (Scheme 33) is simpler and proceeds under milder conditions compared with the reported method [106]. Diaminotrisulfides **92** were isolated in good yield and selectivity (Table IX).

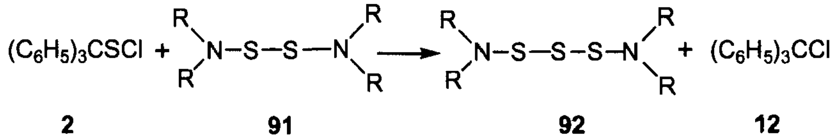
TABLE VIII One sulfur unit insertion into symmetric disulfides

Entry	*R*	*Sulfide*	*Time* (h)	*Product*	*Yield* (%)[a]	*Selectivity* (%)[b]
1	CH_3	**84a**	2	**90a** [100]	88	95
2	CH_3CH_2	**84b**	18	**90b** [101]	80	95
3	$C_6H_5CH_2$	**84c**	24	**90c** [102]	56	87
4	$HOCH_2CH_2$	**84d**	48	**90d** [103]	42	80
5	$CbzNHCH_2CH_2$	**84e** [104]	72	**90e**	55	75
6	$4\text{-}CH_3OC_6H_5$	**84g**	48	**90g** [105]	52	77

[a]Isolated yield. [b]Selectivity refers to the molar percentage of trisulfides **90** in the mixture of trisulfides and tetrasulfides obtained from the reaction. The value was calculated from peak area ratios in the ^{1}H-NMR spectra of the crude reaction mixtures.

TABLE IX One sulfur unit insertion into symmetric diamino disulfides

Entry	*Sulfide*	*Time* (h)	*Product*	*Yield* (%)
1	Dimorpholinodisulfide (**91a**) [107]	24	Dimorpholinotrisulfide (**92a**)	75
2	Bis(*N*-benzyl-*N*-methyl)disulfide (**91b**) [108]	16	Bis(*N*-benzyl-*N*-methyl)trisulfide (**92b**)	85
3	Bis(*N*,*N*-diethyl)disulfide (**91c**) [109]	24	Bis(*N*,*N*-diethyl)disulfide (**92c**)	80



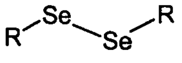
SCHEME 33

We propose that this reaction shares a parallel mechanism as the reactions between chlorodisulfide **3** [94] or chlorotrisulfide **4** [95] with acyclic disulfides. Reagent **2** shows much less reactivity than the two other reagents; however, unlike the reaction with **4**, intermediates **86** *via* **3** and **89** *via* **4** were never directly observed.

In conclusion, the current method provides a novel and convenient preparation of acyclic symmetric tri-, tetra- and pentasulfides from easily accessible staring materials, disulfides, under very mild conditions *via* sulfenyl chlorides **2**, **3** and **4** respectively.

4.6. With Diselenides

Recently, we discovered [110] that sulfenyl chloride **2** (or its thio **3** or dithio **4** homolog) reacts smoothly under mild conditions with symmetric diselenides **93** affording polychacolgenides **94**–**96** as the main products, respectively. The reactions are generally very rapid and the procedure was optimized according to temperature, solvent and molar ratio of the substrate in order to maximize the yield of polychacolgenides **94**–**96** (Table X).



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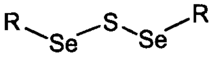
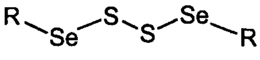
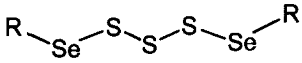


94a; R = CH_3
94b; R = $C_6H_5CH_2$



95a; R = CH_3
95b; R = $C_6H_5CH_2$
95c; R = C_6H_5



96a; R = CH_3
96b; R = $C_6H_5CH_2$
96c; R = C_6H_5

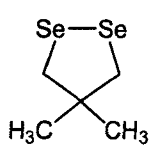
The identity of polychacolgenide adducts was confirmed by ^{1}H- and ^{13}C-NMR spectroscopy as well as by elemental analysis. The X-ray crystallographic structures of **95b** and **96b** were successfully determined [110].

We find [111] that, when dithiosulfenyl chloride **3** is treated with cyclic diselenide **97**, two sulfur units are smoothly delivered to furnish cyclic polychacolgenides **98** in high

TABLE X Sulfur insertion into symmetric diselenides

Compound	*R*	*Reaction time* (min)	*Yield* (%)
94a	CH_3	10	93
94b	$PhCH_2$	10	93
95a	CH_3	5	98
96a	CH_3	5	96
95b	Ph	30	92
96b	Ph	30	90
95c	$PhCH_2$	10	96
96c	$PhCH_2$	5	94

isolated yield. When polychacolgenides **94**–**96** and **98** are decomposed in the presence of 1,3-butadiene, evidence was obtained of the trapping of diatomic sulfur [110]. Work is continuing in this area.



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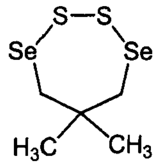

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