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RECENT ASPECTS OF THIIRANE CHEMISTRY

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This review is not meant to be exhaustive. Several reviews on the synthesis, physical properties, and reactivity of thiiranes have appeared in the past 17 years. This effort is to update previous work on thiiranes with an emphasis on research reported from 1985 to September, 1992.

Key words: Thiirane, episulfide, desulfurization, sulfur extrusion.

CONTENTS

1. GENERAL

1.1. *Introduction*

It is almost inevitable that a comparison be made of thiiranes **1** with their oxygen counterpart oxiranes in view of their similarities in structure and proximity of their heteroatoms to each other in the periodic table. In contrast to the chemistry of oxiranes which has been studied enormously, thiiranes or episulfides have received much less attention. The limited literature on thiirane chemistry may be attributed to their lack of easy availability, limited stability and characteristic unpleasant smell of the lower molecular weight members. Thiiranes are more prone to spontaneous polymerization than oxiranes and are less convenient to store. Desulfurization is a common pathway in the reaction of thiiranes but deoxygenation of oxiranes is seldom observed. The ring-opening reactions of thiiranes have received less consideration in contrast to the ring-opening reactions of oxiranes.

It is only in the last decade that researchers discovered the importance of thiirane and its chemistry. A number of novel methods of synthesis have been developed and the behaviour of thiiranes in many reactions have been examined in these reviews.[1] Several new technical applications of thiiranes have also been demonstrated in recent years. A variety of biologically active substances have been synthesized containing the thiirane functionality and in some cases have been found to be more potent than its oxirane analogue. Thiiranes have also been employed in synthetic carbohydrate chemistry.[2]

1.2. *Nomenclature*

Three-membered rings containing one sulfur atom are named thiiranes **1** with the ring numbering starting at the sulfur atom. Several systems of nomenclature have been used:[3]

a) A substitution method whereby the position of the sulfur atom which replaces the carbon atom in the parent molecule is indicated by a number and the "thia" prefix;

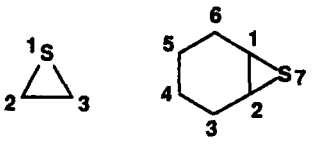
b) Name of alkene + episulfide;

c) Name of alkene + sulfide;

d) Epithioalkane with position of functional group given by numbers;

e) Episulfide + "name of alkene."

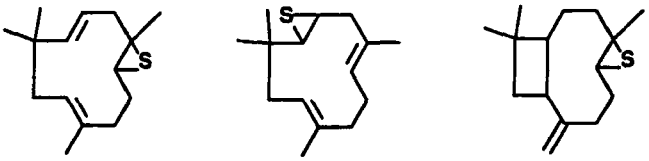
Thus compound **2** may be called 7-thiabicyclo[4.1.0]heptane, cyclohexene episulfide, cyclohexane sulfide, 1,2-epithiocyclohexane, or episulfide of cyclohexene according to the nomenclature systems a) through e), respectively. For larger molecules, the episulfide or epithio designation is commonly used. In most cases, however, thiirane is the more general term used to define compounds containing this functional group.



1 2

1.3. *Naturally Occurring Thiiranes and Biological Activity*

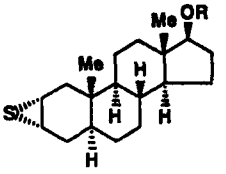
Only a small number of naturally occurring substances containing the unique 3-membered heterocycle are known. In 1980, Peppard and co-workers[4] discovered, by gas chromatographic analysis, that about 10–350 ppm of the components of hop oils were three sesquiterpenes, two humulenes (**3a** and **3b**) and an epithiocaryophyllene **3c**.



3a **3b** **3c**

An epithio specifier protein was found to be present in both turnip tissue and crambe seed.[5] The parent thiirane molecule, ethylene sulfide and 2-methylthiirane are two compounds of over 90 other organic substances identified in the aroma of canned beef and of cooked mutton.[6] Cabbage and rutabagas are found to contain 2-(cyanomethyl)thiirane and thiiranecarboxylic acid is found in white asparagus. Some thiiranes are found during degradation of the sulfur-containing amino acids cysteine, cystine, and methionine. Acanthifolicin, a polyether carboxylic acid from the extracts of a marine sponge contains an episulfide ring.[7]

Many thiiranes are known to be very useful as potent drugs. Epithiostanol **4** and its derivatives are antitumor drugs which are effective against breast cancer but studies also show these compounds are toxic in rats.[8] Other epithiosteroidal derivatives such as the carbenolides are useful as respiratory stimulants and blood pressure increasing agents.[9] Two thiiranyl steroids which have been synthesized were demonstrated to be useful inhibitors of human placental aromatase[10] and lanosterol 14α demethylase ($P450_{14dm}$) which is a cytochrome enzyme responsible for the first stage in the biosynthesis of cholesterol from lanosterol.[11] Thioglycidates **5**, which have been shown to control hypertension, are useful as hypoglycemic agents.[12] They act by irreversible inhibition of mitochondrial carnitine palmitoyl transferase-A enzyme which is responsible for converting long-chain fatty acids into their ester derivatives. This inhibitory action effectively prevents further oxidation of these acids as they cannot enter the mitochondrion where oxidation takes place. Thus, the blood glucose levels are lowered.[13]



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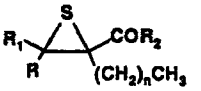
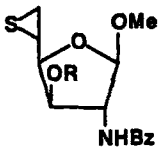


R = R_1 = H or Alkyl
R_2 = OH, alkoxy, amino
n = 10-15

5

Cyclohexene sulfide is known to inhibit both L-glutathione transferase and aryl hydrocarbon hydroxylase enzymes which are responsible for inducing skin tumors.[14] Substituted propylene sulfides have been reported to be active against tuberculosis.[15] Thiirane is found to be more potent than oxirane as an antibacterial agent. Adducts of amines with thiiranes act as immunosuppressants. The furanoid epithio sugar **6** has been reported as a potential immunostimulant.[16] The sulfur analogue of epoxyeicosatrienoic acid **7** has been synthesized as an arachidonate epoxygenase inhibitor albeit it is less potent than the nitrogen or oxygen analogues.[17] They are prepared by the treatment of the epoxyeicosatrienoic acids with KSCN. Alpha-adrenergic blocking agents were prepared with ethylene sulfide as the precursor.[18]



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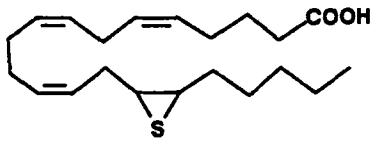

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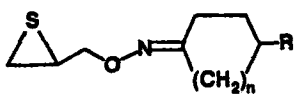
1.4. *Technical Applications of Thiiranes*

A number of useful applications of thiiranes have been reported. 2-Methylthiirane has been used as a fuel gas odorant, 2,3-dimethyl- and 2,3-diphenylthiirane in liquid crystals,[19] thiirane in the enhancement of respiration of tobacco leaves and 2-(methoxymethyl)thiirane as a tobacco additive which reduces the nicotine and phenol levels in smoke. Fluorinated thiiranes are useful as refrigerants and fire extinguishing agents.[20] Thiiranes have also appeared in components of pain and varnish coatings, insulating materials, semi-conductors and antioxidants.

Polymeric materials containing the epithio functionality possess excellent mechanical properties. Epoxy resin compound **8** is resistant to heat[21] and aryloxypropene sulfides have been proposed as light and heat stabilizers for poly(vinyl chloride) and co-polymers of vinyl chloride.



R = H, CH_3
n = 1, 2

8

The oxirane analogues of the sulfides are found to be less effective.[22] Other resin compounds are useful as photoresistors. The poly(ethylene glycol) ether of 2-(hydroxymethyl)thiirane caused improvement of the antistatic properties of fiber and films. Poly(ethylene sulfides) have the properties of high tensile strength.[23] 2-(Fluoromethyl)thiirane has recently been used in various rubbers.[24]

A study has shown that thiiranes proved to be the most active against insects.[25] Thiophosphates of 2-(mercaptomethyl)thiirane are strong insecticides[26] and several thiirane 1-oxides have been reported to kill weeds, insects and snails.[27] Chloropropene sulfide has been claimed to be an effective nematocide.[28]

2. STRUCTURE AND SPECTRAL CHARACTERISTICS

The physical properties of the parent thiirane have been reviewed by Dittmer[3] and Sander.[29] Typical C—C bond lengths in thiiranes fall between 1.37 Å and about 1.60 Å and the C—S bond lengths range from 1.73 Å to 1.92 Å. The C—C bond length in thiirane suggests partial double bond character as the length of a typical sp^3—sp^3 C—C bond is about 1.55 Å and that of a C=C bond 1.34 Å. The CSC angle is about 48° for the parent thiirane but this varies somewhat depending on the substituents present in the molecule. Table 1 lists bond lengths and angles for the parent thiirane and their oxides as well as data for its analogues aziridine, oxirane, and phosphorane. The sharp difference between the strain energy of cyclopropane and its heteroatom analogues is indicative of the higher degree of stabilization of the heterocyclic compounds by π-electrons of the heteroatom. The contribution of the π-electrons enhances the unsaturated character of the thiirane ring which is responsible for its greater stability compared with the oxirane ring. The increase in stability of thiirane is also reflected in a lower strain enthalpy and entropy compared with oxirane (59.2 eu and 38.4 kcal/mol for oxirane and 21.5 eu and 17.6 kcal/mole for thiirane).[30]

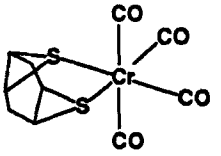
TABLE 1 Bond lengths and bond angles for 3-membered heterocycles.

	X					
	O[31]	NH[32]	P[33]	S[31]	SO[34]	SO_2[35]
C—C	1.472	1.480	1.502	1.492	1.504	1.590
C—X	1.436	1.488	1.807	1.819	1.822	1.731
C—X—C	61°24′	—	47°24′	48°26′	48°46′	54°40′
C—C—X	59°18′	—	66°18′	65°48′	65°37′	62°40′

The principal ions observed in the mass spectra of thiiranes are due to loss of a hydrogen atom or an alkyl group. Loss of neutral SH is often observed as well as loss of sulfur. A rearrangement to a thioaldehyde or thioketone, followed by loss of hydrogen or an alkyl group, is also a preferred route in electron impact mass spectroscopy. Absorptions in the UV spectra of thiiranes are usually found

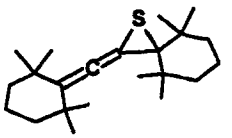
between 205 nm and 260 nm. The IR spectrum of thiirane has been extensively analyzed[36] but aside from the parent compound, little IR and Raman work has been done on this class of compounds. The reported C—S stretching vibration frequencies for thiirane are 651 cm^{-1} and 611 cm^{-1}.[37] Vibrational circular dichroism spectra for 2,3-dimethylthiirane have also been measured.[38]

A number of X-ray crystallographic structures of thiiranes have been documented. The first such structure of a thiirane ring system was reported in 1972 by Bates.[39] They found that the shortness of the C—C bond joining the episulfide ring supported the view that the carbons in such a ring are between sp^2 and sp^3 hybridized. The first metal carbonyl derivative containing two coordinated episulfide rings was recently reported.[40] The *cis*-1,4-cyclohexadiene bisepisulfide complex of chromium tetracarbonyl **9** showed C—S bond lengths of 1.915 Å which appear to be the longest observed to date in episulfide ring systems. The C—S—C bond angle of 47.3° is within the expected range for the episulfide ring.

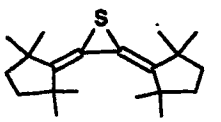


9

An unusual ruthenium metal complex containing the thiirane moiety was recently synthesized with the structural parameters of the thiirane fragment closely resembling those of the free heterocycle.[41] Another metal substituted thiirane, (triphenylsilyl)thiirane, was shown to have a propeller-type molecular structure with the C—C and C—S bonds significantly shortened.[42] The X-ray crystal structures of two highly hindered thiiranes, 2,2-di-*t*-butyl-3,3-diphenylthiirane[43] and adamantylideneadamantane thiirane,[44] revealed long C—S bonds. Longer C—C bonds from the thiirane ring to the *t*-butyl and phenyl groups were also observed. Crystallographic data of thiiranes containing exocyclic double bonds have also been reported.[45] Thiirane **10a**, containing one exocyclic double bond, showed inherent ring strain as well as an unsymmetrical ring structure whereas thiirane **10b** proved to be nearly symmetrical with a characteristic shortening of the C—C bond of the thiirane ring.



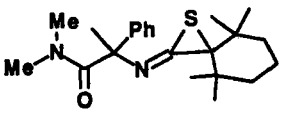
10a



10b

The crystal data of a related molecule, thiiranimine **11**, also show the unsymmetrical nature of the thiirane ring due to the exocyclic C=N double bond.[46]

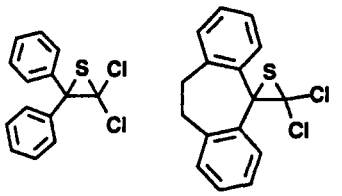
Another thiiranimine has also been reported[47] as well as a similar α-thiolactone with an exocyclic C=O.[48]



11

Several other crystal structures of thiiranes have been examined including steroidal thiiranes,[49] spiro thiiranes,[50] a Dewar-type thiophene derivative,[51] and a polyether antibiotic, acanthifolicin, which contains the rare thiirane functionality in a natural product.[7] The reported bond lengths and bond angles are all within the expected range in episulfide rings. Only a few X-ray structures of episulfoxides[52] have been reported and to our knowledge only one X-ray structure of an episulfone has been cited.[53]

Our studies on the reactivity of episulfides led us to examine the different substrates. X-ray crystal structures of two episulfides were determined, 2,2-dichloro-3,3-diphenylthiirane **12** and 3′,3′-dichlorospiro[5*H*-dibenzo[*a*,*d*]cycloheptene-5,2′-thiirane] **13**.[54]



12 13

As predicted, the phenyl groups of **12** are arranged in such a fashion as to minimize their interaction. The thiirane ring structure is unsymmetrical and the C—C bond of the ring was found to be somewhat shorter (1.43 Å) than usually found in the literature[43,44] but comparable to others.[45b,55] As with **12**, the thiirane ring in **13** is slightly unsymmetrical and the C—C bond of the ring is of a length in general agreement with those in other thiirane ring systems (1.507 Å). The dihedral angle between the planes of the benzo groups was found to be ~60° indicating the non-planarity of the rings.

3. SYNTHESIS OF THIIRANES

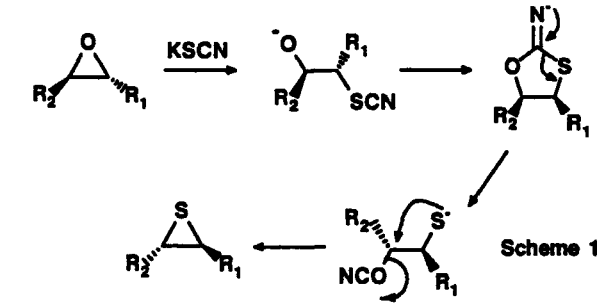
3.1. *Introduction*

The majority of synthetic studies on thiiranes is devoted not only to develop novel methods of synthesis but also to modify the classical methods in order to improve the range of reagents used and to improve the yields. There have been

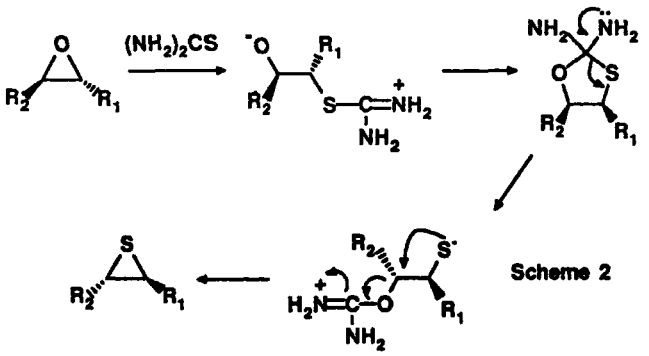
numerous studies on the effect of reaction conditions in the formation and yields of thiiranes. With the discovery of new sulfurating agents, it has been possible to design new non-traditional methods of synthesis.

3.2. *Preparation from Oxiranes*

One of the most important and frequently used methods to prepare thiiranes is the reaction of oxiranes with thiourea or alkali metal thiocyanates (Scheme 1).[56] The yields are high and the products easily isolable. The accepted mechanism of the reaction with thiocyanate involves a nucleophilic attack by the thiocyanate resulting in a C—O bond cleavage intermediate, followed by an intramolecular S to O cyano migration and ring closure (Scheme 1).[57]



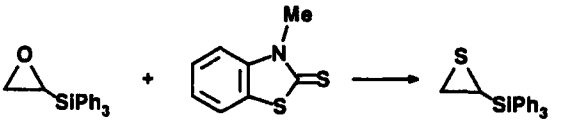
Scheme 1



Scheme 2

A similar mechanism can be envisaged with thiourea (Scheme 2). The stereochemistry is preserved and an optically active (R,R)-oxirane gives an optically active (S,S)-thiirane. A number of new thiiranes with a variety of substituents have thus been obtained which were previously unavailable.[24,58,59] This reaction is slow if the oxirane ring is tri- or tetra-substituted or if the substituents are electron withdrawing. Most thiirane products are unstable due to the ease of sulfur elimination if the substituents are electron withdrawing.[60] The reaction of glycidic esters with thiourea, however, gave the thioglycidic esters although in low yield.[61] Thiiranes containing electron attracting substituents have been synthesized.[62]

Other sulfur reagents have been successfully employed in the preparation of thiiranes. Triphenylphosphine sulfide in the presence of acid has been used with success to convert the corresponding oxiranes to thiiranes with retention of configuration.[63] A silylthiirane was formed by interaction of the corresponding oxirane with 3-methylbenzothiazole-2-thione **14** (Scheme 3).[64]

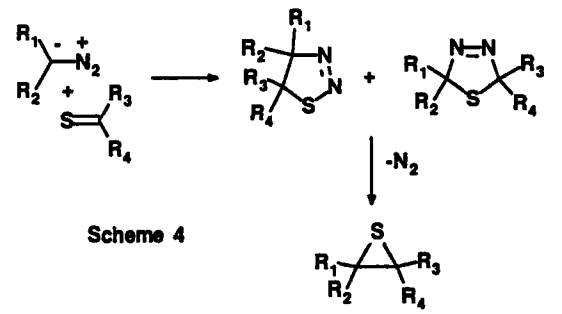


14 **Scheme 3**

The corresponding perhydrobenzothiazole-2-thione derivative has also been used.[65] One of the most effective new thiono compounds is *N,N*-dimethylthioformamide which has also been used to prepare thiiranes.[66] Also effective are 2-mercaptobenzothiazole[67] and 5-mercapto-1-phenyltetrazole.[68]

3.3. *Condensation of Diazo Compounds*

The coupling of diazo compounds with thiocarbonyls is one of the oldest methods to prepare thiiranes. Between 1916 and 1920, Staudinger reported the formation of thiiranes from diazo compounds and thiocarbonyls.[69] An unstable 1,2,3- or 1,3,4-thiadiazoline was postulated as an intermediate which is converted to the thiirane with concomitant evolution of nitrogen (Scheme 4).

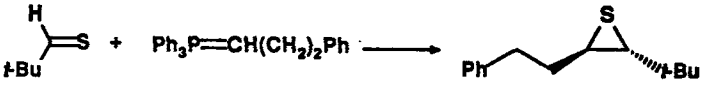


Scheme 4

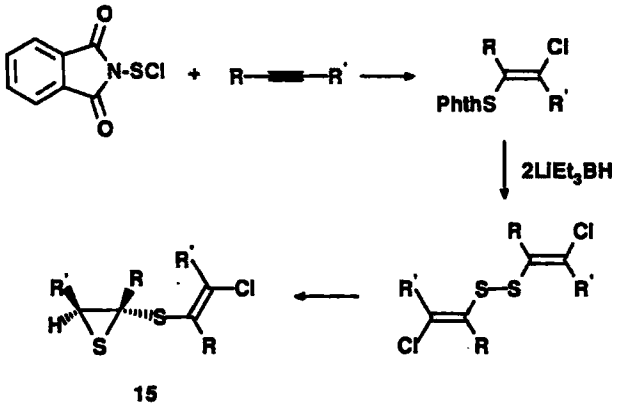
The reactions in these systems can easily be accounted for by initial formation of a carbene.[70] This method has been employed with a wide range of both diazo reagents and thioketones resulting in many different thiiranes.[71,72] Grignard reagents[73] and phenyl(trihalomethyl)mercury compounds[74] have also been used as sources of carbenes to prepare thiiranes. A more recent carbene precursor, phenyliodonium bis(phenylsulphonyl)methylide, has also been used in reactions with thioketones to prepare thiiranes.[75]

3.4. *Other Methods*

Thiiranes have been prepared by other methods which include the addition of sulfur to alkenes[76] although the yields are low, and pyro- and photolytic methods,[77] as well as reactions involving cyclization *via* a thiolate anion.[78] A convenient synthesis of thiiranes is by addition of sulfenyl chlorides to alkenes, followed by ring closure.[79] A perfluorinated thiirane was recently synthesized *via* addition of disulfur dichloride to an alkene, followed by chlorination.[80] The use of sodium sulfide with alkenes also yields thiiranes.[81] A new method was discovered by Zipplies[82] in which the reaction of *N*,*N*-dimethylaniline *N*-oxide with CS_2 in the presence of alkenes produced thiiranes. The reaction of a hindered thioaldehyde with a Wittig reagent also gives a thiirane (Scheme 5).[83] 2-Hydroxyalkanesulfenyl chlorides are converted stereospecifically to thiiranes with triphenylphosphine;[84] diethoxytriphenylphosphorane was used to transform a 2-hydroxy thiol to a thiirane.[85] An unusual class, vinylthio substituted thiiranes **15**, have recently been synthesized with sulfenyl chlorides in the presence of alkynes and a boron superhydride.[86] More recently, thiiranes were prepared by a reaction of a dithioiminocarbonate and a thiazoline with an aldehyde promoted by fluoride ion.[87]

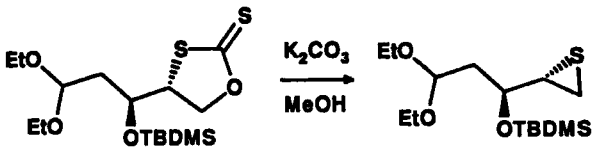


Scheme 5



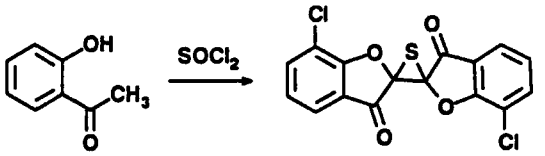
Tetraalkyl orthocarbonates under acidic conditions have been demonstrated as potent cyclodehydrating agents for 2-mercaptoalkanols to give thiiranes.[88] The photolysis of tetraalkyl-1-pyrazolin-4-thiones cleanly give rise to isopropylidenethiirane.[89] The cyclic xanthate **16**, when treated with potassium carbonate in methanol, gave thiirane **17** which was subsequently used in the preparation of 4′-thionucleosides.[78c] Similarly, sodium carbonate was used to prepare L-methi-

onine analogues bearing an episulfide function which could be good inhibitors of *S*-adenosyl transferase.[90]



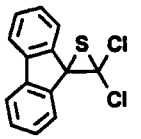
16 17

Thiiranes have also been prepared by treatment of 2-chloro disulfides with lithium aluminum hydride.[91] Thiiranecarboxylic acids are prepared by reaction of methyl cysteinate with sodium nitrite in aqueous HCl.[92] A preparation of enamines involved the synthesis of intermediate thiiranes[93] which were prepared according to the Eschenmoser sulfide contraction method.[94] Bis(trimethylsilyl)-thiirane has also been synthesized by reduction of bis(thiocyanato)-1,2-bis(trimethysilyl)ethene.[95] In an unusual reaction, treatment of 2-hydroxyacetophenone with thionyl chloride in pyridine afforded thiirane **18**.[96]



18

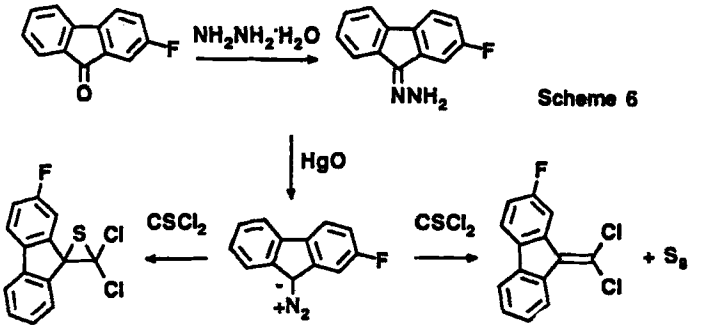
Our interest in the mechanism of sulfur extrusion of thiiranes (*cf.* Section 4.2) prompted us to synthesize novel derivatives of 2,2-dichloro-3-(9-fluorenyl)ethene sulfide **19**, based on the method of Staudinger[69] and to study their reactivities. The ready availability of monosubstituted fluorenones induced us to attempt a preparation of the thiiranes in three steps. We initiated work on 2-fluoro-9-fluorenone. However, treatment of diazo compound **20** with thiophosgene only gave a ~3:1 ratio of olefin **22** to 3′,3′-dichloro-2-fluorospiro[fluorene-9,2′-thiirane] **21** (Scheme 6).



19

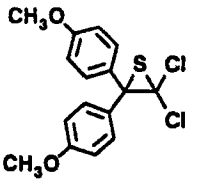
Several attempts to prepare **21** were unsuccessful most likely due to the instability of the 3-membered heterocyclic ring with the additional fluorine atom. The appearance of both **21** and **22** indicates that the fluorine assists in the stabilization

of the reactive intermediate as **21** desulfurizes to **22**. On the other hand, thiirane **23** was successfully prepared from readily available 4,4′-dimethoxybenzophenone.



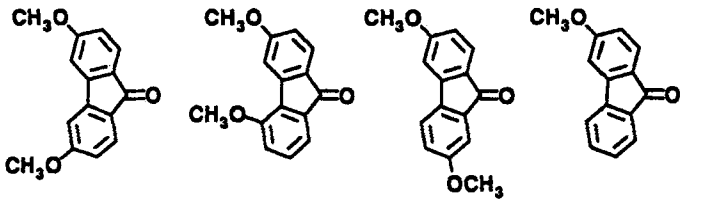
Scheme 6

21 **20** **22**

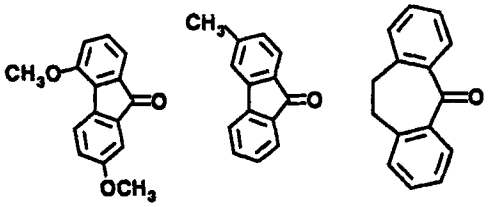


23

Several other novel fluorenones were synthesized[97] and attempts were made to prepare their corresponding thiiranes by the method of Staudinger.[69] Thus, from fluorenones **24–30**, only the corresponding thiiranes from **28** and **30** were prepared for the first time while only desulfurized products resulted from the other fluorenones.



24 **25** **26** **27**



28 **29** **30**

The instability of the derivatives is attributed to the presence of activating groups which enhance decomposition by stabilizing the developing cationic intermediate in the unimolecular pathway (*vide infra*). The stability of the thiirane of 2,5-dimethoxyfluorenone **28**, on the other hand, is ascribed to the destabilizing effect of the methoxy substituents on the ionic intermediate.

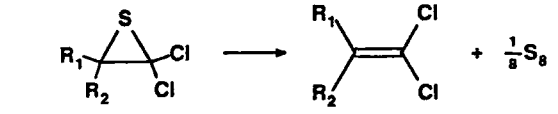
4. THERMAL AND PHOTOCHEMICAL REACTIONS: MECHANISTIC CONSIDERATIONS

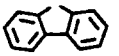
4.1. *Introduction*

The lower ring strain of thiiranes compared to other 3-membered rings (oxirane, aziridine and cyclopropane) suggests that thiiranes would be less reactive than oxirane (*cf.* Section 2). However, it is the lower bond energy of C—S (66 kcal/mol) compared with the C—O bond (91 kcal/mol) that overrules the lower strain energy and accounts for much of the reactivity of this class of compounds. The thermal or photochemical reactions involve either the cleavage of the carbon-sulfur bond, which often leads to rearrangement products, isomeric or polymeric materials, or extrusion of sulfur which results in the formation of alkenes. Thiiranes which are highly aryl substituted or substituted with electron attracting groups, are more likely to promote the abstraction of sulfur. The gas phase thermal and photochemical reactions of thiirane and its nitrogen and oxygen relatives have been reviewed by Braslavsky.[98]

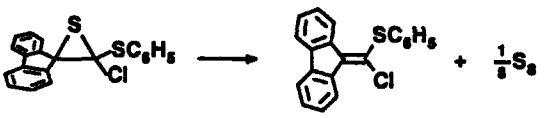
4.2. *Sulfur Extrusion and Stereochemistry*

There are many non-thermal reactions that involve the extrusion of sulfur from thiiranes but little work has been done on the thermally induced desulfurization reaction. A recent review on thermal decomposition of sulfur compounds including thiiranes, is given by Williams and Harpp.[99] Articles on the elimination of sulfur from thiiranes have also appeared in the last few years.[100] It seems that the first case involving spontaneous loss of sulfur from thiiranes substituted by aryl or halogen was reported by Staudinger and Siegwart[69] (Scheme 7) and Schönberg (Scheme 8).[101] The thermolysis reaction of *cis*- or *trans*-2,3-divinylthiirane **31a** involves sulfur loss at 90 °C affording a mixture of *cis*- and *trans*-1,3,5-hexatrienes plus rearrangement to dihydrothiepins.[58a,102]



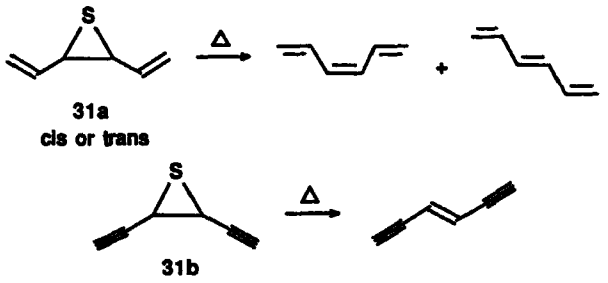
$R_1 = R_2$ = phenyl, 

Scheme 7



Scheme 8

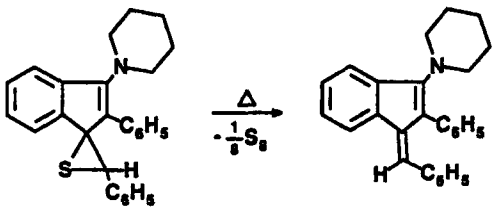
However, Bergman[103] showed that *trans*-2,3-diethynylthiirane **31b** when heated at 100 °C in toluene gave predominantly *trans*-alkene, but at 395 °C in the gas phase, the stereospecificity is lowered.



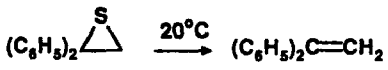
31a
cis or trans

31b

A cheletropic extrusion of a sulfur atom could explain the retention of stereochemistry but it was considered unlikely and the authors concluded that the reaction was more complicated.[104] In 1985, Lutz and Biellmann[105] studied the mechanism of sulfur extrusion of 2,2-dichloro-3-(9-fluorenyl)thiirane **19**. Their conclusion was that the sulfur loss was not a cheletropic extrusion but that a more complex process was involved. Bouda and co-workers[106] described the decomposition of furanic and aromatic thiiranes at moderate temperatures (90 °C), but at low temperatures (0 °C) desulfurization does not take place. When thiirane **32** was heated gently, elemental sulfur was obtained and the thiirane converted to the ethylene derivative **33**.[107] In the reaction of thiobenzophenone with diazomethane or diazoethane, thiirane **34** was produced but sulfur was lost at room temperature (with a half-life of 16 h) to give the olefin **35**.[108]

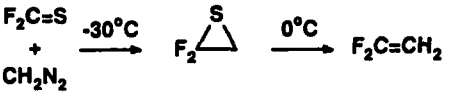


32 **33**



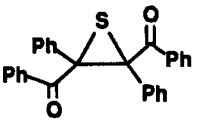
34 **35**

In the reaction of thiocarbonyl fluoride with diazomethane, 2,2-difluorothiirane was formed but spontaneously lost sulfur at 0 °C (Scheme 9).[109] Aliphatically substituted thiiranes such as fenchane spirothiirane **36** extrude sulfur when heated.[110] Three recent articles have appeared which show that episulfides lose sulfur spontaneously to give the olefin,[111a] biaryl compounds,[111b] and a diazepine.[111c]



Scheme 9

36

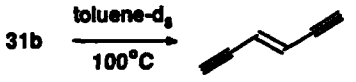


37

Several examples have been reported in the literature where photochemical reactions involve sulfur loss.[112] The photolysis of dibenzoylstilbene thiirane **37** affords dibenzoylstilbene. The loss of sulfur was explained by a cleavage of the C—S bond of the three-membered ring forming a biradical intermediate which is then followed by loss of atomic sulfur.[113] A similar conclusion was proposed when Becker[114] investigated the photochemistry of tetraphenylthiirane. Another photochemical study was conducted by Trozzolo on tetraphenyloxirane but the authors favoured an ionic mechanism rather than homolytic cleavage.[115]

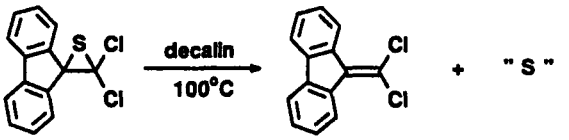
Detailed kinetic studies on the decomposition of thiiranes have rarely been reported in the literature. In many of these reactions, elemental sulfur is lost but no detailed mention of the mechanism involved in the extrusion is reported. There appear to be three examples in the literature which deal with kinetic studies in the thermal decomposition of thiiranes.

Bergman's[103] work suggests that thermal sulfur extrusion from 1,2-diethynylthiirane **31b** takes place in a bimolecular fashion at high concentrations of thiirane. As the concentration of thiirane decreases during the reaction, the bimolecular step changes to a unimolecular process. A simple cheletropic extrusion of a sulfur atom was ruled out as a likely pathway; the authors concluded that the reaction involves a more complicated mechanism.



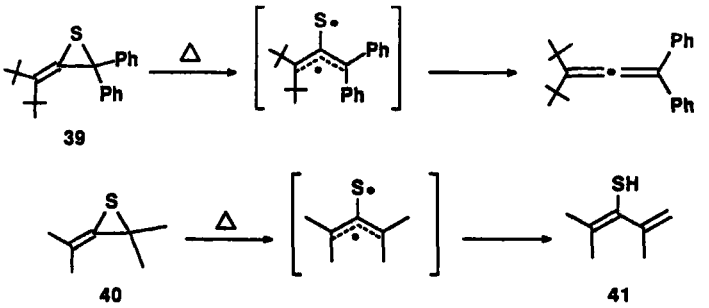
Lutz and Biellmann[105] studied the thermally induced extrusion reaction of 2,2-dichloro-3-(9-fluorenyl)ethene sulfide **19** in decalin at 100 °C querying whether the loss of sulfur was a unimolecular process (Scheme 10). They concluded that the decomposition of **19** is not a first order reaction. Clean kinetic behaviour

was not observed and it was suggested that the sulfur loss is not a cheletropic extrusion of a sulfur atom but that a more complex process was involved. It was proposed that an "unknown species" acquires a sulfur atom which reacts further with another molecule of thiirane.



19 38 Scheme 10

Finally, the mechanism of extrusion of a related molecule, an allene episulfide, was examined by Ando and coworkers.[104] The thermally catalyzed desulfurization of **39** in *o*-dichlorobenzene at 150 °C led the authors to postulate a thioallyl radical intermediate. The observed rate acceleration in diglyme was rationalized by the dipole moment of the C—S bond biradical intermediate with a small contribution of a zwitterionic structure. A similar kinetic study was undertaken by the same authors on **40** but only 2,4-dimethyl-1,3-pentadiene-3-thiol **41** was obtained *via* an intramolecular 1,4 hydrogen shift and no allene was recovered.[116]



One vital aspect of thiirane chemistry to address is the stereochemical outcome of these desulfurization reactions. It is known that the higher oxidized analogues of thiiranes, episulfoxides and episulfones, extrude sulfur monoxide and sulfur dioxide, respectively, under thermolytic and pyrolytic conditions. The stereochemistry of the substituents is preserved but in some cases the stereochemical integrity is lost.

There are several reported cases in the literature which discuss stereochemical aspects of the degradation of thiiranes. In reactions of thiiranes with certain reagents, desulfurization occurs non-stereospecifically as evidenced by the formation of mixtures of *cis*- and *trans*-olefins.[58b,117] In contrast, reactions with a number of reagents give olefins stereospecifically.[118] In these reactions, the reagents are believed to attack the sulfur atom, followed by ring opening to give the olefin.

Thermally induced desulfurizations in general, can be classified as non-stereospecific. Pommelet[102] suggested that a competition between C—C and C—S bond cleavage occurs upon thermolysis of **31a** to rationalize the formation of the different isomers. A similar conclusion was also adopted by Schneider.[58a] Thus, *cis*- or *trans*-2,3-divinylthiirane **31a** gave the same proportion of 20% *cis*- and 80% *trans*-isomer. Both ionic and biradical intermediates were postulated to account for other products. Bergman[103] emphasized a strong dependence of the stereochemistry on the temperature and classified these reactions as non-stereospecific. Nevertheless, Strausz argued that low temperature thermolysis of *cis*- or *trans*-2-butene episulfides is stereospecific with greater than 90% retention of configuration.[119] In cases where thiiranes undergo photolysis, formation of the diradical by C—S bond cleavage would most likely give non-stereospecific products.[112] Padwa[113] however, claimed that the photodesulfurization of **37** is stereoselective and that the loss of sulfur is best explained by cleavage of the C—S bond forming a diradical which is then followed by loss of atomic sulfur. It was also suggested that the non-stereospecificity in the thermolysis could be attributed to photoisomerization of the thiirane.

One can clearly see that the stereochemical consequences of these thermal desulfurizations are unpredictable. Several mechanisms have been postulated to account for the observed products.

We have carefully re-examined the kinetics of the thermal decomposition of 2,2-dichloro-3-(9-fluorenyl)ethene episulfide **19** (Scheme 10).[120] There is strong evidence regarding the nature of the desulfurization process; a typical rate profile in toluene at 80 °C is shown in Figure 1.

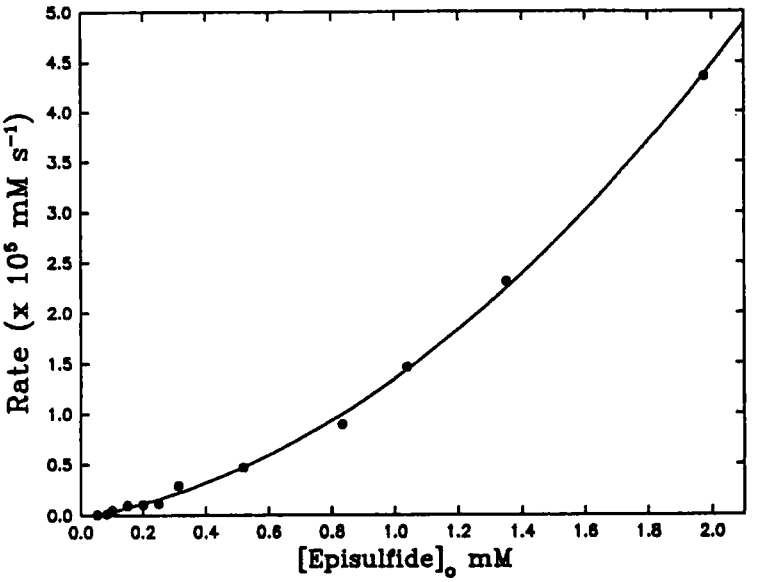


FIGURE 1. Rate behaviour in the decomposition of **19** in toluene at 80 °C.

It is clear that the reaction is *not* first order and thus not a simple unimolecular decomposition. From this detailed kinetic study and studies in many other solvents of varying polarity we were able to conclude that the mechanism of sulfur loss is consistent with a two-term rate expression, as shown in Eq. (1).[121]

$$\text{Rate} = k_1[E] + k_2[E]^2 \qquad (1)$$

k_1 in s^{-1}

k_2 in $mM^{-1}\,s^{-1}$

[E] = conc. of episulfide

Typical rate constants for five solvents are shown in Table 2.

TABLE 2 k_1 and k_2 rate constants derived from Eq. (1).

Solvent	$k_1 \times 10^5$ (s^{-1})	$k_2 \times 10^5$ ($mM^{-1}\,s^{-1}$)	Relative rate $k_{rel}(k_1)$	$k_{rel}(k_2)$
DMF	109 ± 32	173 ± 112	218	192
2-Chloroethanol	8.3 ± 5.0	12 ± 4	17	13
1,1,2,2-Tetrachloroethane	1.9 ± 0.3	2.2 ± 0.5	4	2
Chlorobenzene	0.8 ± 0.3	1.3 ± 0.3	2	1
Toluene	0.5 ± 0.2	0.9 ± 0.4	1	1

In general, the unimolecular rate constants in the solvents do show the expected trends with respect to the polarities. DMF which is the most polar, has higher rates and 2-chloroethanol, which is moderately polar, has lower rates. The less polar aromatic solvents all have similar, slow rates. Chlorobenzene which is more polar than toluene, gives slightly higher rates for both the uni- and the bimolecular reaction.

In each solvent, at low concentration of episulfide, the reaction follows a unimolecular, first order process, but at higher concentrations a bimolecular pathway becomes more important. The unimolecular term in Eq. (1) predominates at low concentration levels and as the concentration increases, the second order or bimolecular term becomes more important. In toluene, a more than 400-fold increase in the rate of desulfurization is observed when the concentration is increased 38-fold, thus reflecting the contribution of the bimolecular term. At low concentration levels (*ca.* 0.10–0.15 mM) it was found that the nearly exclusive pathway is a unimolecular decomposition while at higher concentrations (*ca.* 20 mM), the bimolecular path is actually followed by *ca.* 4:1. In the case of DMF at low concentrations, the exclusive pathway is unimolecular and at higher concentrations the unimolecular pathway is favored by *ca.* 2:1.

The thermal decomposition of **19** was conducted at various temperatures which permitted the determination of activation parameters. These are shown in Tables 3a and 3b with increasing $\Delta G^{\neq}$.

TABLE 3a Activation parameters derived from k_1 rate constants.

Solvent	E_{act}[a,b]	$\Delta H^{\neq}$[c]	$\Delta S^{\neq}$[d]	$\Delta G^{\neq}$[e]
DMF	12.4 ± 0.5	11.8 ± 0.5	−47.3 ± 1.4	25.9 ± 1.5
1,1,2,2-Tetrachloroethane	14.0 ± 0.7	13.4 ± 0.7	−45.4 ± 2.0	26.9 ± 2.1
Toluene	16.4 ± 0.7	15.8 ± 0.7	−37.6 ± 2.0	27.0 ± 2.1
Chlorobenzene	30.4 ± 0.7	29.8 ± 0.7	6.6 ± 2.0	27.8 ± 2.1
2-Chloroethanol	32.6 ± 0.5	32.0 ± 0.5	13.0 ± 1.5	28.1 ± 1.6

[a]Activation parameters derived from k_1 rate constants; [b]in kcal mol^{-1}; [c]kcal mol^{-1}; [d]cal mol^{-1} K^{-1}; [e]kcal mol^{-1}.

TABLE 3b Activation parameters derived from k_2 rate constants.

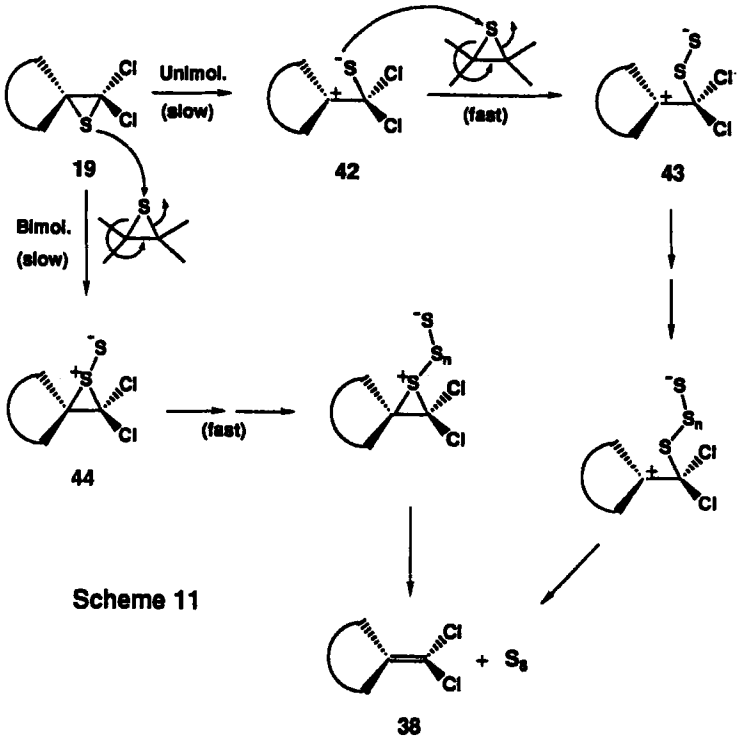
Solvent	E_{act}[a,b]	$\Delta H^{\neq}$[c]	$\Delta S^{\neq}$[d]	$\Delta G^{\neq}$[e]
DMF	12.7 ± 1.2	12.1 ± 1.2	−39.1 ± 3.8	23.7 ± 4.0
1,1,2,2-Tetrachloroethane	8.8 ± 0.7	8.2 ± 0.7	−57.0 ± 1.9	25.2 ± 2.0
Chlorobenzene	9.4 ± 0.7	8.8 ± 0.7	−56.6 ± 2.0	25.7 ± 2.2
Toluene	17.8 ± 0.8	17.2 ± 0.8	−33.4 ± 2.3	27.2 ± 2.4
2-Chloroethanol	23.0 ± 0.6	22.5 ± 0.6	−19.6 ± 1.8	28.3 ± 1.9

[a]Activation parameters derived from k_2 rate constants; [b]in kcal mol^{-1}; [c]kcal mol^{-1}; [d]cal mol^{-1} K^{-1}; [e]kcal mol^{-1}.

A high $\Delta H^{\neq}$ value for chlorobenzene in the k_1 determinations indicates some desolvation in the transition state which is consistent with a dipolar process. Solvent interaction in the ground state by chlorobenzene might be attributed to the greater polarizability of the aromatic π-electrons.[122] DMF, a strong solvating agent, would experience little desolvation in the transition state and consequently have a lower $\Delta H^{\neq}$ value. The differences in $\Delta H^{\neq}$ are most likely a result of differences in interaction of solvent with the ground state rather than differences in the interaction of solvent in the transition state.

The somewhat large negative values of the entropy of activation suggest a highly ordered transition state in which the solvent plays a strong stabilizing role. The ground state would have less ordering of solvent molecules. This further implicates ionized intermediates. Ionization reactions are usually accompanied by a large negative $\Delta S^{\neq}$ because of the loss of entropy of the solvent when going to the transition state. We observe that in the solvents the molecules are somewhat unordered in the ground state but on solvation in the transition state they lose their freedom of motion and suffer a greater loss of entropy. Solvents which are already ordered in the ground state will suffer a smaller loss of entropy upon solvation in the transition state. Numerical values for $\Delta S^{\neq}$ of the bimolecular term are generally more negative than the $\Delta S^{\neq}$ in the unimolecular term. This is consistent with the fact that a bimolecular reaction usually involves more ordering of solute and solvent molecules as two reacting species must come together for reaction to occur. The observed linear free energy relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ also provides an indication that the desulfurization of **19** proceeds by the same mechanism.[120]

From the desulfurization kinetics of episulfide **19**, the following mechanism is proposed to account for the observations. At low concentrations, thermal ionization of the C—S bond in **19** (Scheme 11) likely occurs at the first and rate determining step. Such an intermediate has been suggested, such as in the reaction between 9-diazoxanthene and coumarin-2-thione.[123] Cleavage of the C—S bond of **19** at the carbon bearing the two chlorines would be unfavorable due to their electron-withdrawing effect. The positive charge on the carbon bearing the fluorenyl substituent would be stabilized by resonance. The fast step would involve subsequent attack by the sulfur anion species **42** on another molecule of episulfide **19**, giving intermediate **43**. This species would acquire sulfur atoms sequentially until stable sulfur rings are formed along with **38**. Both S_6 and S_8 are formed with S_8 predominating.[124]



Scheme 11

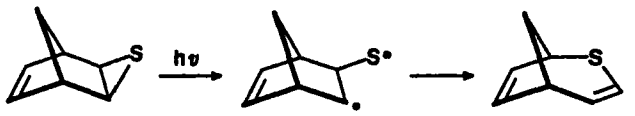
As the concentration of episulfide **19** increases, the second term in the rate equation becomes more important and a competing bimolecular mechanism is followed (Scheme 11). The sulfur atom from one episulfide molecule abstracts the sulfur atom from another in the rate determining step, giving intermediate **44**. The fast step is the subsequent concatenation of more sulfur atoms until S_8 is formed. At even higher concentration levels, the bimolecular route actually becomes the rate-determining step.

An extensive solvent study showed the reaction rates to be proportional to the

dielectric constant as well as the π^* scale of Kamlet and Taft.[125] A solvent isotope effect showed an overall decrease in rate. These studies are consistent with a dipolar ionic mechanism.[120] A radical mechanism is ruled out by a rate study in the presence of radical inhibitors.[120]

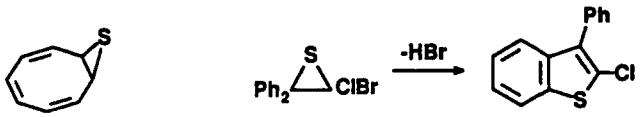
4.3. *Rearrangement Reactions*

The other pathways in thermal reactions of thiiranes involve C—S or C—C bond fission. Many unusual rearrangement or isomeric products are isolated, especially in substituted thiiranes. The C—S bond is either cleaved homolytically or heterolytically leading to various products. When *exo*-2,3-epithionorborn-5-ene **45** is photolyzed, 2-thiabicyclo[3.2.1]octa-3,6-diene **46** is obtained *via* a stepwise mechanism involving a homolytic cleavage of the C—S bond.[126]



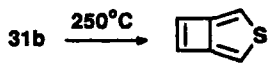
45 **46**

Triene **47** undergoes a similar rearrangement to afford thiabicycles.[127] Formation of benzothiophene **49** was observed when thiirane **48** was heated in refluxing benzene.[74] Recently, it was shown that thiirane rearranges to thioacetaldehyde under photolytic conditions.[128]



47 **48** **49**

Only a few examples in the literature have shown the C—C bond to be cleaved thermally. The formation of dihydrothiepins from the thermal rearrangement of 2,3-divinyl thiirane[58a,102] and Bergman's *cis*-2,3-diethynylthiirane isomerization to the thienocyclobutadiene **50** are believed to take place *via* C—C bond cleavage.[103] Ando[129] reported that in the reaction of palladium(0) with allene episulfide, a bicyclothiahexane derivative was isolated and that this compound can be rationalized by C—C bond breaking in an intermediate step. Kamata described the [3+2] cycloaddition of thiiranes to tetracyanoethylene *via* a C—C bond cleavage.[130]



50

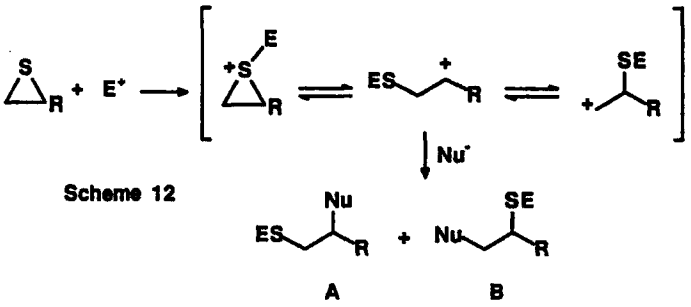
4.4. *Polymerization*

Another common reaction pathway for thiiranes involves polymerization under the influence of heat or light. Polymerization reactions of alkene sulfides appeared in a review by Sander.[29] At room temperature, both the parent molecule and 2-phenylthiirane polymerize; 2-methylthiirane polymerizes on exposure to light.[29] Most thermal and photochemical polymerizations probably proceed by diradical intermediates which may be trapped by various acceptors. In the thermolysis of cyclohexene sulfide, desulfurization occurs with the formation of cyclohexene. Six other products were also observed which may be derived either from the diradical intermediate (homolytic cleavage of a C—S bond) or reactions with elemental sulfur.[131] The polymerization of thiirane initiated by a Zn-*N*-substituted porphyrin has recently been shown.[132]

5. NON-THERMAL REACTIONS OF THIIRANES

5.1. *Electrophilic Reactions of Thiiranes: Attack on Sulfur*

Electrophilic reactions involving thiiranes usually yield sulfonium salts or ring-opened cations (Scheme 12). Depending on which isomer exists, two products can result. In the open form, product A would be formed if substituent R can stabilize the cation. If the sulfonium salt predominates, then an S_N2 mechanism predicts product B to be formed due to nucleophilic attack at the least hindered site. Thiiranes are less reactive toward electrophilic reagents than oxiranes, owing to the lower dipole moment of the C—S bond. Almost all reactions of thiiranes involve ring openings similar to that of oxiranes and are more reactive than oxiranes due to the lower C—S bond energy.

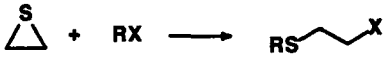


Scheme 12

In the presence of acids, thiiranes usually are protonated and polymerization takes place. Upon acid-catalyzed addition of nucleophiles, ring opening products are observed and polymerization occurs when another molecule of thiirane acts as the nucleophile. Polymerization is often observed in the presence of Lewis acids whereas thiiranes form complexes with many metals. In some cases, Lewis

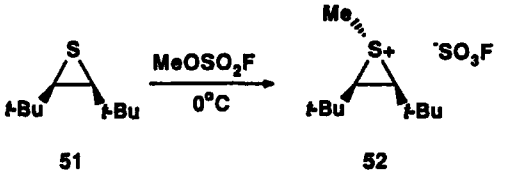
acids promote isomerization of thiiranes.[133] However, desulfurization is observed with molybdenum,[134] rhodium,[118a] ruthenium,[135] osmium,[136] and iron[137] metal complexes. Palladium(0) in the reaction with allene episulfide gave rearrangement products[129] whereas palladium(II) gave 5-membered cyclic aminothio carbene compounds.[138]

Ring opening products are usually observed in the presence of alkyl or acyl halides. The sulfonium salt is formed in the intermediate, but halide attack results in ring opening. Treatment of thiiranes with alkyl chlorides or bromides gives 2-chloro- or 2-bromoethyl sulfides (Scheme 13). For weak or non-nucleophilic anions, the *S*-alkylthiiranium salts can be isolated, but are frequently unstable and result in polymeric materials.

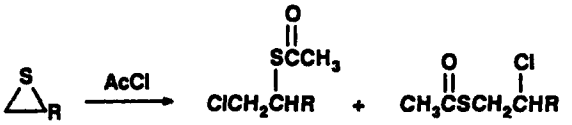


Scheme 13

The *S*-methylthiirane salt **52** is isolated when *cis*-1,2-di-*t*-butylthiirane **51** is treated with $MeOSO_2F$ at 0 °C. *S*-Acetyl derivatives result when thiiranes are treated with acetyl chloride (Scheme 14).

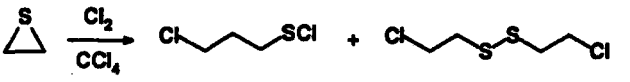


51 **52**

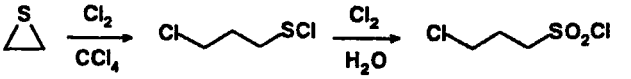


Scheme 14

In many cases, halogenation reactions of thiiranes give sulfenyl halides or disulfides such as in the case of the chlorination of ethylene sulfide (Scheme 15). The iodination reaction gives only disulfide but it can also be used to desulfurize thiiranes. Chlorination reactions carried out in hydroxylic solvents result in sulfonyl chlorides as the sulfenyl chlorides are further oxidized (Scheme 16). The reaction of chlorine atoms with thiiranes however, results in desulfurization and has been used as a source of SCl radicals.[139]

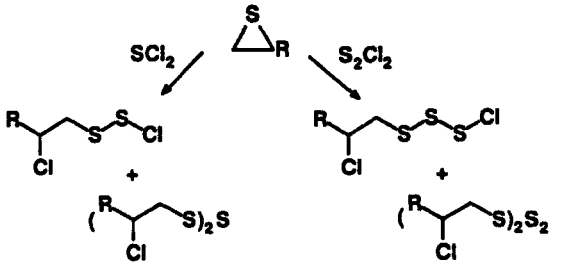


Scheme 15



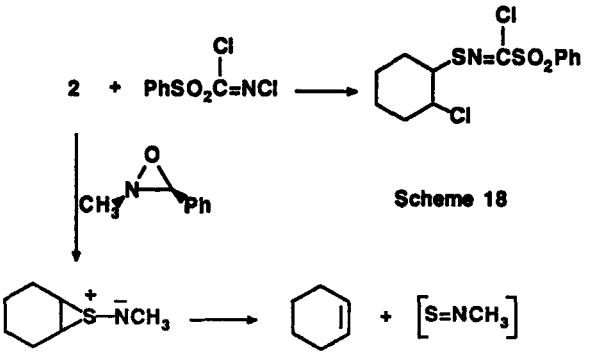
Scheme 16

Scheme 17 shows the general behaviour of thiiranes when treated with disulfur dichloride or sulfur dichloride. With sulfur dichloride, a chloro disulfide is obtained and a chloro trisulfide results upon treatment with disulfur dichloride. A 2:1 ratio of sulfur halide to thiirane gives tri- or tetrasulfides.



Scheme 17

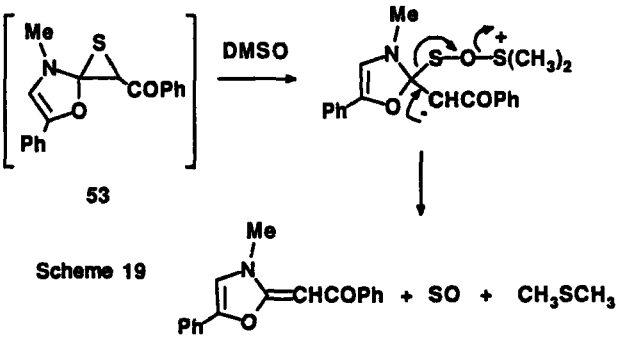
Attack by an electrophilic nitrogen on the sulfur atom may also occur as in the reaction of **2** with *N*-chlorobenzenesulfonylformimidoyl chloride (Scheme 18).[140] The formation of thionitrosomethane was evidenced by trapping experiments. Desulfurization may also occur with 2-methyl-3-phenyloxaziridine.[118f] Some phosphorus compounds are also known to react electrophilically with the thiirane sulfur.[141] Oxidation of thiiranes with peracid, singlet oxygen, or sodium periodate gives episulfoxides.[142]



Scheme 18

5.2. *Nucleophilic Reactions of Thiiranes: Attack on Sulfur*

The most widely used nucleophilic reaction of thiiranes is the desulfurization by trivalent phosphorus compounds to give the alkene and a phosphine sulfide. Triphenylphosphine[71e,118e,143] is most commonly used although triethylphosphine,[144] triethyl phosphite,[118a,145] tributylphosphine,[77c,118b] and tris(alkylamino)phosphines[146] have also been employed. Sulfur[147] and nitrogen[148] nucleophiles also attack the sulfur atoms of thiiranes. Oxygen nucleophiles usually attack at the carbon atom of the ring but it has been reported that desulfurization of thiirane **53** occurs by nucleophilic attack of the oxygen of the dimethyl sulfoxide solvent (Scheme 19).[149] Reaction of cyclohexene sulfide **2** with singlet oxygen was found to proceed by a persulfoxide intermediate.[150] Wittig reagents are also known to desulfurize thiiranes.[151] Other desulfurization methods have also been reported.[117a,152]

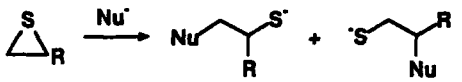


53

Scheme 19

5.3. *Nucleophilic Reactions of Thiiranes: Attack on Carbon*

A variety of nucleophiles attack the carbon atom of thiiranes to give ring opened products (Scheme 12 and 20). The reactivity is higher than in the analogous reaction with oxiranes; hence, thiiranes tend to polymerize more readily than oxiranes. Many different products are obtained from the thiolate anion generated. With oxygen nucleophiles such as hydroxide and alkoxide/aryloxide ions, the thiol derivative is usually obtained although polymerization occasionally occurs. A recent report showed that the alcoholysis of thiiranes in the presence of a catalytic amount of DDQ or Ce(IV) salts gave the corresponding alkoxy disulfides.[153] Under these conditions, a thiolate anion is formed which is much more reactive than the oxygen anion.[154] In many of these cases there is no preference for attack at either carbon. The polymeric materials obtained from these reactions have been used as light and water resistant agents.[155]



Scheme 20

Nitrogen nucleophiles also react to give 2-mercaptoethylamine derivatives. The general feature in reactions of thiiranes with amines is that the attack usually occurs regioselectively at the least hindered position. A thiirane ring is opened more easily than the corresponding oxirane ring.[156] The utility of these reactions was demonstrated in the preparation of drug polyamine conjugates[157] and for reactive diluants for epoxy resins.[158] Primary and secondary amines react readily whereas weakly basic and hindered amines are less reactive and require harsher conditions. Polymeric products result when tertiary amines or amide ions are used. The optimal conditions to effect the reaction would be to use polar media with weakly basic amines. This would accelerate nucleophilic opening of the thiirane ring. Unreactive thiiranes can also be made to react with highly basic amines under similar conditions.

Sulfur nucleophiles are more reactive towards thiiranes than oxygen or nitrogen nucleophiles and attack on the least substituted carbon is commonly observed. The thiolate anion reacts rapidly with many functional groups which, in most cases, leads to polymeric products. However, with effective acceptors of thiolates, which inhibit further polymerization, monomeric products can be obtained. Thiols cleave the C—S bond giving 2-alkylthioethanethiols as well as oligomerization products. In the reaction of thiirane with carbon disulfide in the presence of triethylamine, the ring is opened and a 1,3-dithiolane-2-thione is formed *via* a thiolate anion.[159]

Halogen nucleophiles are also known to react with thiiranes leading to ring opened products. They react preferentially on the most substituted carbon but attack on the less substituted carbon has also been reported.[118c,160]

Carbanions attack at the least hindered carbon atom of the thiirane.[161] These anions include Grignard[162] and alkyl lithium[163] reagents and metal complexes,[164] all which lead to ring-cleaved products. In some cases, desulfurization occurs with formation of the olefin and metal thiolate.[58b,71e,117b,156b,165]

Although the most common reaction of phosphorus compounds with thiiranes is the elimination of sulfur, there have been some reports where phosphorus compounds react on one of the carbon atoms leading to monomeric and polymeric products.[166]

ACKNOWLEDGEMENTS

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