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New advances in the chemistry of thiirans

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ABSTRACT. **Data concerning the methods of synthesis of thiirans, their reactions with nucleophiles and electrophiles, as well as their desulphurisation and homolytic reactions and their behaviour in cycloaddition reactions are surveyed.**

The bibliography includes 285 references.

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I. Introduction

Data on thiirans and their derivatives published after 1976 inclusive have been examined in a monograph.[1] Certain new ways of synthesising thiirans have been discussed in a review.[2] L'Abbé's communication[3] is devoted to a new type of thiirans—thiiran imines. Some of the studies published after 1976 have been included in annual publications on three-membered heterocycles[4–8] and in review articles.[9–12] These data reflect fairly completely the state of the chemistry of thiirans by the end of the 1970's but they do not enable one to obtain an idea about the pathways and trends followed in its development during the current decade.

The present review deals with the principal advances in the synthesis and in the study of the properties of thiirans and their derivatives published in the last ten years. The restricted size of the review precluded the inclusion in it of information about the theoretical and physicochemical studies of these substances and about their applications.

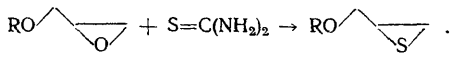
A characteristic feature of the latest studies in the field of thiirans is their increasing applied bias with expansion of the range of their applications. Thus the possibility of synthesising from these compounds of a wide variety of biologically active substances, for example adrenoblocking agents,[13] immunomodulators,[14] antiseptics,[15] antihypertension agents,[16] hypoglycaemic agents,[17] etc., has been demonstrated in recent years. New technical applications of thiirans have been developed: for the preparation of liquid crystals,[18] photoresistors,[19] components of paint and varnish coatings,[20,21] antioxidants,[22,23] thermostable insulating materials,[24] heat-resistant polymers,[25] semiconductors,[26] elastomers,[27] etc.

II. Methods of synthesis

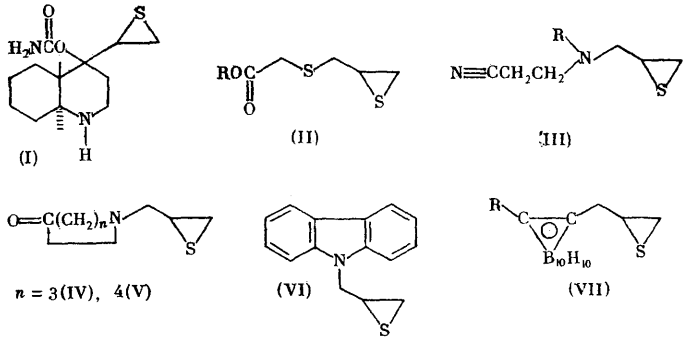
The classical methods of synthesis of thiirans[1] have been the basis of the majority of new synthetic studies in the field. During the past period, there has been an expansion of ideas concerning the effect of conditions on the formation and yield of thiirans in classical reactions, on the limits of their applications, and on the range of precursors of epithio-compounds. Ideas about the mechanisms of the formation of thiiran rings developed earlier have exerted a major influence on the new syntheses of thiirans.[1] By testing them with new models, it has been possible to discover new effective thiolating agents and to develop in a number of instances new non-traditional approaches to the synthesis of thiirans.

1. Conversions of oxirans into thiirans

The reactions of oxirans with thiourea have been used to obtain a large number of new epithio-compounds, including some which had been previously unavailable. With the aid of thiourea, substituted epithioglycidyl ethers containing polychloroalkyl,[28,29] 2-alkoxyethyl,[30] furfuryl,[31] organosilylalkyl, alkenyl, and alkynyl,[32,33] and t-butyl[34] end groups have been obtained.[28–34]

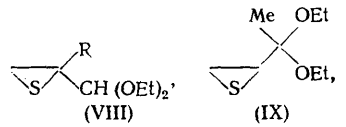


Acid catalysis has been used successfully in a number of instances.[31,34] The selection of the solvent, catalyst, and reaction conditions made it possible to devise simple methods of synthesis of a wide variety of epithioglycidyl ethers.[21,28–34] Many compounds containing the thiiran ring have been obtained by the reaction of thiourea with oxirans: the amide (I),[35] thioglycolic esters (II),[36] cyanoethylated amines (III),[37] the pyrrolidinone (IV) and the piperidinone (V),[38] the carbazole (VI),[39] and the *o*-carbaboranes (VII).[40]

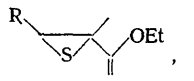


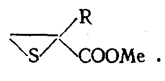
The presence of electron-accepting substituents in the ring of oxirans hinders their reactions with thiourea. The diethylacetals (VIII) have been obtained from the corresponding oxirans only on heating in methanol.[41,42] Acetylthiiran diethylketal (IX) was obtained similarly.[43] The ketals of 2-R-2-acetylthiirans polymerise under these conditions, while 2-R-2-(1-ethoxyvinyl)thiirans (X) are formed in preparative yields.[43] The reactions of sterically hindered

glycidates with thiourea in methanol are catalysed by H_2SO_4, which made it possible to obtain in high yields the thioglycidates (XI), which were previously difficult to synthesise.

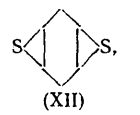

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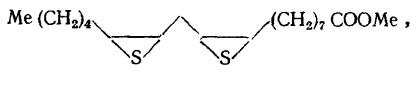
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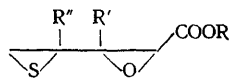

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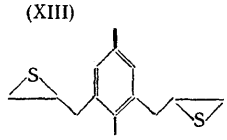

(XI)

Diepithio-compounds have been obtained by the reaction of thiourea with diepoxides. In the presence of H_2SO_4, *cis*- and *trans*-1,4-diepoxycyclohexanes were converted into the corresponding diepithio-compounds (XII).[44] The stereoisomers of the methyl esters of 9,10,12,13-diepithiooctadecanoic acid (XIII) have been synthesised in dioxan (XIII).[45] The sterically hindered esters of 3-substitutes and 3,4-disubstituted 2,3,4,5-diepoxyvaleric acids have been selectively converted in methanol (40 °C, 5–6 h) into the 3,4-epithio-derivative (XIV).[46] 2,5-Di(2,3-epithiopropyl)-1,4-dimethylbenzene (XV) has been obtained under mild conditions.[47]

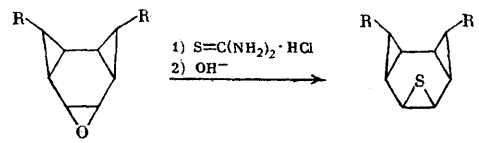

(XII)


(XIII)


(XIV)


(XV)

Thiourea salts are sometimes used for the thiolation of oxirans. Thus 3,4-epithiothiolan 1,1-dioxide has been obtained by the reaction of 3,4-epoxythiolan 1,1-dioxide with a thiourea salt.[48] *cis*-Thiatris-σ-homobenzenes have been obtained similarly.[49]

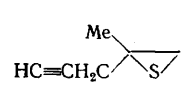


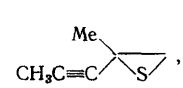
New aspects of the thiolation of oxirans by metal thiocyanates have been less thoroughly investigated. The use of potassium thiocyanate in toluene in the presence of silica gel made it possible to obtain substituted thiirans in 70–90% yield.[50]

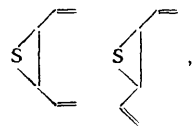


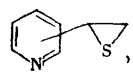
When an attempt was made to increase the rate of thiolation of oxirans by thiocyanates with the aid of a phase transfer catalyst, the yield of thiirans fell appreciably.[51]

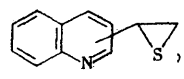
Under the conditions usual for the reactions of oxirans with KSCN, certain new epithio-compounds have been obtained. The thiirans with alkynyl substituents (XVI) and (XVII),[52] and *cis*- and *trans*-divinylthiirans (XVIII)[53] are formed in aqueous alcohol in yields up to 70%, while pyridyl-, quinolinyl-, and isoquinolinyl-thiirans (XIX)–(XXIII) are formed in a yield up to 50%.[54] The epithio-derivatives of limonene (XXIV) and terpinolene (XXV) have been obtained in anhydrous alcohol,[55] while a mixture of *cis*- and *trans*-dideuterio-thiirans have been synthesised in water.[56] Furyl- and thienyl-thiirans (XXVI) have been synthesised in the presence of small amounts of water.[57]

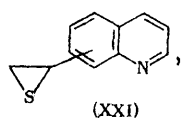

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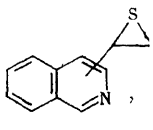

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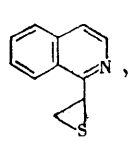

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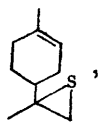

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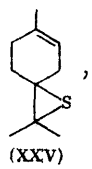

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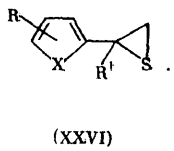

(XXI)


(XXII)

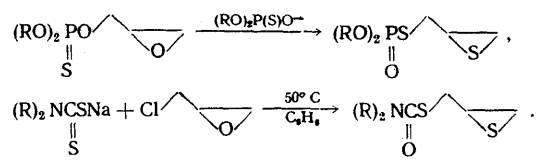

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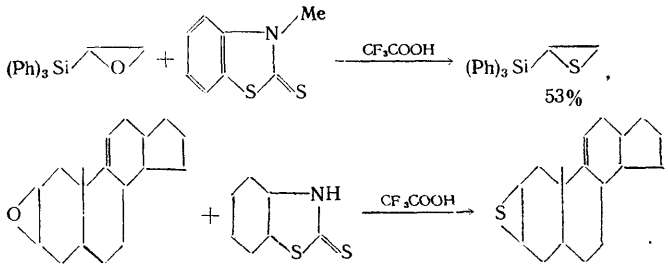

(XXVI)

Thiono-compounds have been used as thiolating agents for the conversion of oxirans into thiirans. Triphenylphosphine sulphide with an equimolar amount of CF_3COOH has been used to synthesise 3,4-epithiothiolan 1,1-dioxide.[58] 10β-Epithiosteroids have been obtained from epoxysteroids and triphenylphosphine sulphide in the presence of picric acid.[59] Ethylene and propylene sulphides are formed on reaction of the corresponding oxirans with the monoesters of alkylphosphonothioic acids.[60] A similar reaction occurs on heating glycidyl phosphorothioates with salts of dialkyl phosphorothioic acids.[61] The salts of dithiocarbamic acid also have similar properties.[62]



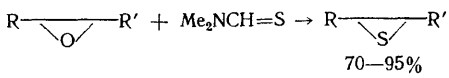
The interaction of triphenylsilyloxiran with an equimolar amount of 3-methylbenzothiazole-2-thione and CF_3COOH afforded the first representative of silylthiirans.[63] Epoxy-compounds are converted

into thiirans under the same conditions on treatment with perhydrobenzothiazole-2-thione.[64]



The thiono-derivatives of triazoline, imidazoline, benzimidazoline, and oxadiazoline thiolate oxirans also in the absence of CF_3COOH, which is indicated by the formation of 1-heteroaryl-2,3-epithiopropanes on interaction of azolethiones with epichlorohydrin.[65,66] Many side processes are ruled out in the presence of CF_3COOH.

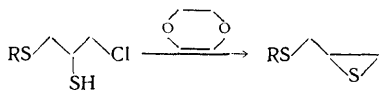
Among thiono-compounds investigated, dimethylthioformamide in the presence of catalytic amounts of CF_3COOH proved to be the most effective.[67]



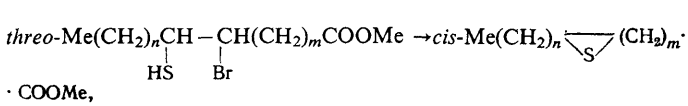
2-Mercaptobenzothiazole[68] and 5-mercapto-1-phenyltetrazole[69] were also found to be highly effective thiolating agents.

2. Cyclisation of 2-substituted thioles and their derivatives

2-Chloroalkanethiol fragments in a polymer matrix are converted into epithioalkyl groups even on solvation with 1,4-dioxan.[70]

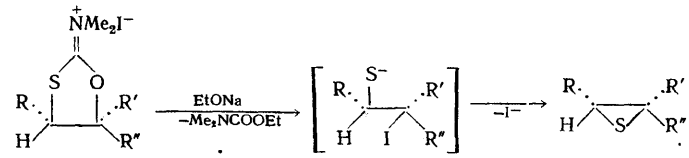


Analogous reactions are characteristic also of monomeric 2-halogenoalkanethiols. Thus the carbaboranylthiirans (VII) are formed rapidly from 3-chloro-2-mercaptopropyl-*o*-carbaboranes on heating in methanol.[71,72] 3-Halogeno-4-mercaptothiolan 1,1-dioxides are spontaneously converted into 3,4-epithiothiolan 1,1-dioxides.[73] In both cases, the formation of a ring is energetically so favourable that its opening by anhydrous HCl either does not occur or takes place to only a slight extent. 2-Chloro-1-trifluoromethylethanethiol is somewhat more stable, but on treatment with *N*-methylpyrrolidinone it is converted into trifluoromethylthiiran already at 20 °C.[74,75] The stereospecificity of the reactions considered, taking place with inversion of configuration has been demonstrated on new examples.[76]



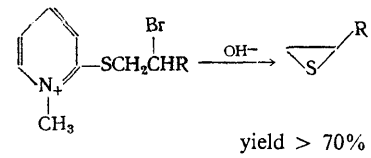
$n = m = 7$; $n = 10$, $m = 4$.

2-Halogenoalkanethiolate ions are precursors of thiirans in many reactions. The interaction of 3,4-dibromo-3-methylbutan-2-one oxime with Na_2S in acetone leads to the oxime of 2-acetyl-2-methylthiiran.[77] The methiodides of 2-methylimino-1,3-oxathiolans are converted into epithio-compounds,[78] apparently in accordance with the mechanism



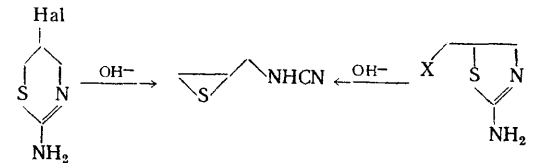
The vicinal alicyclic substituted iodine thiocyanates, including steroids are converted quantitatively into thiirans on treatment with $EtBH_3Li$.[79]

Ethylene sulphide or its polymer are formed from 2-bromoethylisothiuronium bromide[80] and 2R-thiirans are produced from 2-(2-bromoalkylthio)pyridinium salts.[81]

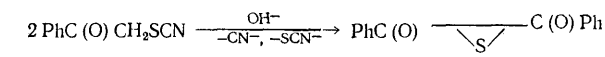


yield > 70%

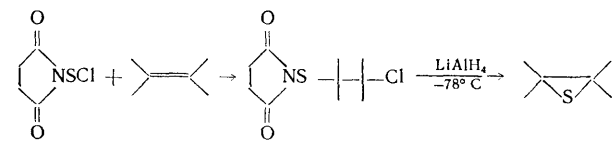
The skeletal rearrangement of cyclic 2-halogenoalkylisothioureas into 2,3-epithiopropylcyanamide can apparently be explained by the formation of 2-halogenoalkanethiolate anions.[82]



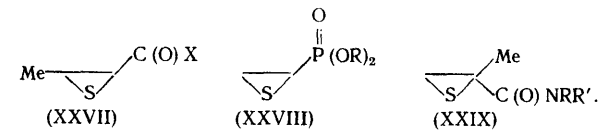
Dibenzoylthiiran is formed from α-thiocyanatoacetophenone on treatment with bases under phase transfer conditions.[83]



The adducts of *N*-chlorosulphenylated succinimides and phthalimides with alkenes also proved to be precursors of thiirans.[84,85] Their reduction with $LiAlH_4$ makes it possible to obtain thiirans in yields up to 90% and more.

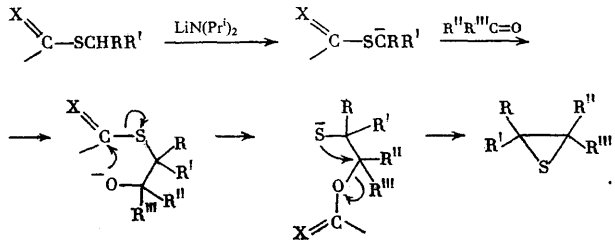


The thiirans (XXVII)–(XXIX), which readily lose the sulphur atom, have been obtained under mild conditions from β-acylthio-α-chloro-derivatives of carboxylic[86] or phosphonic[87] acids and from derivatives of 3-chlorothietan-2-one.[88]



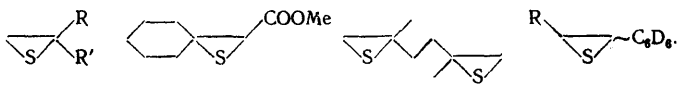
(XXVII) (XXVIII) (XXIX)

A new aspect of the synthesis of thiirans is based on the reactions of carbonyl compounds with sulphur-containing carbanions in which the sulphur atom is linked to a coordinatively unsaturated carbon atom.[89–94] The intermediate oxy-anions of these compounds rearrange to precursors of thiirans—2-substituted thiolate anions.



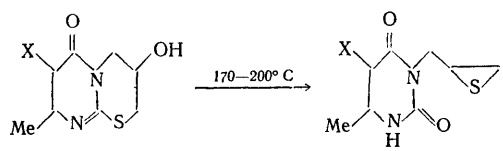
Thio- and dithio-carbonates and 2-alkylthio-1,3-oxazolines have been widely investigated in reactions with carbonyl compounds (aliphatic and aromatic aldehydes and acyclic and alicyclic ketones). The method makes it possible to obtain different thiirans, including optically active thiirans (XXX), substituted thioglycidates (XXXI), bisthiirans (XXXII), etc.

Instead of aldehydes and ketones, it is possible to use alkyl thiolocarboxylates; they acylate sulphur-containing carbanions to α-thiolated ketones, which after reduction afford thiirans, for example, compound (XXXIII), in high yields.[95]



(XXX) (XXXI) (XXXII) (XXXIII)

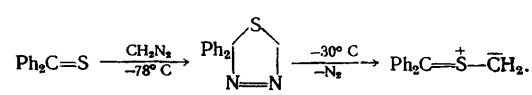
The thermal reactions of 2-hydroxyalkanethiol derivatives, in which the sulphur atom is linked to a coordinatively unsaturated atom, belong to this type. Thus, 2-R-thiirans and (especially readily) 2-R-2-R′-thiirans are formed on thermolysis of 2-hydroxyalkanethiol esters of phosphorus acids.[96] Epithiopropylpyrimidines are formed similarly from 3-hydroxypyrimidothiazines:[97]



trans-2-Bromocyclohexanol is converted into epithiocyclohexane in a similar way on interaction with an excess of KSCN in aqueous alcohol.[98]

3. Homolytic Methods of Synthesis

The biradical mechanism of the formation of thiirans by the reaction of diazoalkanes with thiones has been questioned. It is believed[99] that the interaction of thiobenzophenone with diazomethane leads initially to 1,3,4-thiadiazoline, which is converted into the thiocarbonylide (XXXIV) at –30 °C.

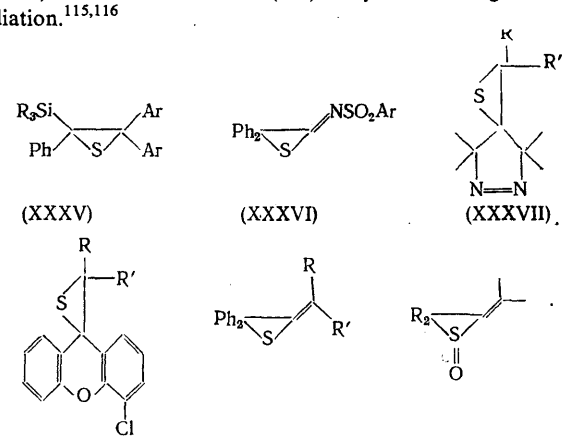


(XXXIV)

The following selective reactions of compound (XXXIV) are believed to constitute confirmation of its formation: isomerisation to 1,1-diphenylthiiran, dimerisation to 2,2,3,3-tetraphenyl-1,4-dithiane, and 1,3-dipolar addition to active dipolarophiles.

The data obtained in the above study[99] apparently reflect the anomalous behaviour of diazomethane in these reactions. Thus the same workers obtained only 3,3-diphenylthioglycidate in the reaction of thiobenzophenone with diazoacetic ester,[100] while the reactions with diazoethane and phenyldiazomethane afforded 3-methyl-2,2-diphenyl- and 2,2,3-triphenyl-thiirans.[101] The formation of thiocarbonylides was not demonstrated in such cases.

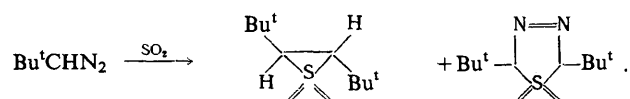
Two examples of this reaction have been investigated.[102–117] Thiirans are formed on interaction of Ph_2CN_2 with tetraphenyl-4-thiopyrone,[102] mono- and di-thio-*N*-arylphthalimides,[103] and *N*-substituted 3-aminoindene-1-thiones.[104] Silylated thiirans (XXXV) have been obtained by the reaction of diaryldiazomethanes with thioacylsilanes,[105,106] while the reactions with sulphonyl isothiocyanates afforded the thiiran imines (XXXVI).[107,108] Diazomethane, diazoethane, diazoacetic ester, and phenyl- and diphenyldiazomethanes interact under mild conditions with tetramethylpyrazoline-4-thione to form the spirothiirans (XXXVII).[109] Diphenyldiazomethane, 4-chloro-9-diazoxanthene, and 9-diazofluorene react with 4-chloroxanthene-9-thione, affording the spirothiirans (XXXVIII).[110] Thiirans have also been obtained in the reactions of 4,4-dimethoxythiobenzophenone with 1-diazo-2,3-dihydroindene,[111] of monothioanthraquinone with 10-diazoanthrone,[112] and of norbornanethiones and thiobenzophenone with diazopropellanes.[113] Diazoketones having the structure $ArCOCHN_2$ react with thiones in a complex manner:[114] aroylthiirans have been obtained only by reaction with fluorene-5-thione. Thioketens and thioketen *S*-oxides react with diazoalkanes to form the corresponding thiadiazolines, which are converted into the thiirans (XXXIX) and thiiran oxides (XL) only on heating or on UV irradiation.[115,116]



(XXXV) (XXXVI) (XXXVII)

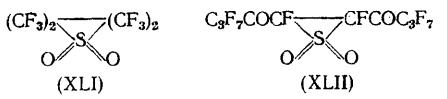
(XXXVIII) (XXXIX) (XL)

The effect of conditions on the mode of reaction of diazoalkanes with sulphur dioxide has been investigated.[117] In the case of t-butyldiazomethane, *trans*-2,3-di(t-butyl)thiiran 1,1-dioxide is formed together with a mixture of *cis*- and *trans*-thiadiazoline 1,1-dioxides whose decomposition affords a mixture of *cis*- and *trans*-thiiran dioxides:



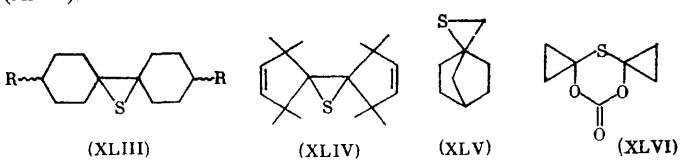
Mixtures of *cis*- and *trans*-thiiran dioxides have been obtained under similar conditions by the reactions of phenyl- and phenylmethyldiazomethanes.

Tetrakis(trifluoromethyl)thiiran 1,1-dioxide (XLI) is one of the products of the reaction of the highly electrophilic hexafluorodimethylsulphonene.[118] The dehydrofluorination of α-fluoro-α-fluoro-sulphonylmethyl perfluoropropyl ketone by the complex $NEt_3.BF_3$ led to 2,3-bis(perfluorobutyryl)-2,3-difluorothiiran 1,1-dioxide (XLII) as a mixture of the *cis*- and *trans*-isomers.[119] Thiiran 1,1-dioxide is believed[120] to be formed as an intermediate in the catalytic high-temperature oxidation of ethylene by sulphur dioxide.

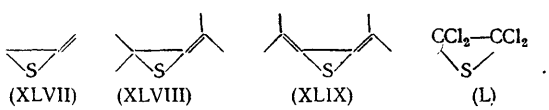


(XLI) (XLII)

Much attention has been devoted to the pyrolytic and photolytic methods of synthesis of thiirans. The thiirans (XLIII)[121,122] and (XLIV)[123] have been obtained by the thermolysis of spirocyclic 1,3,4-thiadiazolines. The relatively unstable methylenethiiran (XLVII) has been synthesised by the vacuum flash pyrolysis of the cyclopropanethione trimer, the episulphide (XLV), or the carbonate (XLVI).[124,125]



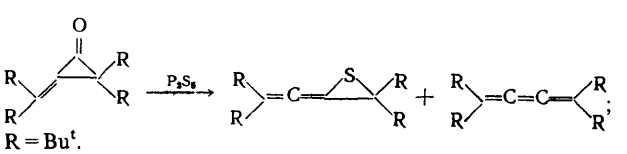
(XLIII) (XLIV) (XLV) (XLVI)



(XLVII) (XLVIII) (XLIX) (L)

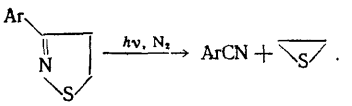
The episulphide derivative of the tetramethylallene (XLVIII) is formed on pyrolysis of the sodium salt of the tosylhydrazone of 2,2,4,4-tetramethylthietanone[126] and on photolysis of tetramethylcyclopropanethione.[127] The vacuum pyrolysis of 2,4-diisopropylidenethietanthione[128] or of the lithium salt of the tosylhydrazone of 4-isopropylidene-2,2-dimethylthietanone[129] has been used to synthesise diisopropylidenethiiran (XLIX). 2,4-Diisopropylidene-1,3-dithietan 1,1-dioxide[130] and tetrachloro-1,3-dithietan 1,1-dioxide[131] are converted on flash pyrolysis into the thiiran (XLIX) and tetrachlorothiiran (L) respectively. The vacuum flash pyrolysis of 2,5-disubstituted 1,3-oxathiolan-5-ones leads to various 1,3-disubstituted thiirans.[132]

The episulphide derivative of buta-1,2,3-trienes were obtained by the thiolation of alkylidenecyclopropanones with phosphorus pentasulphide in pyridine at 80 °C. The episulphide derivatives are partly converted into buta-1,2,3-trienes.[133,134]



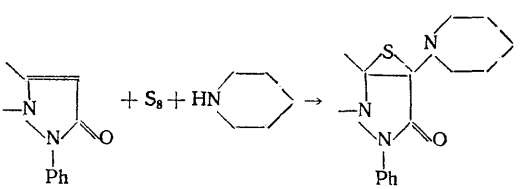
R = Bu^t.

3-Aryl-1,2-thiazolines are converted into thiiran and aryl cyanides on UV irradiation.[135]

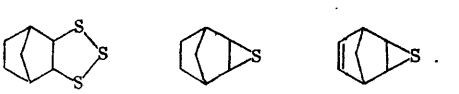


The behaviour of substituted 2*H*-1,3-oxathioles has been investigated under mass spectrometric electron impact conditions.[136] Their cyclodecomposition leads to the thiocarbonylides $RR'C{=}S{-}CBzR''$. Depending on the nature of R and R', the latter cyclise either into thiirans or into the initial oxathioles. The radical-ion reactions of dibenzoyldibromomethane with potassium xanthate[137] and of dibenzoylmethane with sulphur *NN*-bis-(arenesulphonyl)diimide[138] under mild conditions led to tetrabenzoylthiiran, which isomerises to 2,2,4-tribenzoyl-5-phenyl-1,3-oxathiole already during the formation process according to the results of two investigations.[136,139]

Publications have appeared on the syntheses of thiirans from alkenes and elemental sulphur. Irradiation of a mixture of norbornene and S_8 and CS_2 leads to trithiatricyclodecane (LI) and epithionorbornane (LII).[140] Norbornadiene gives rise to the episulphide (LIII) on heating with S_8 in dimethylformamide (DMF) and activation with NH_3.[141] The reaction of antipyrine with sulphur in the presence of cyclic amines leads to an aminothiiran.[142]

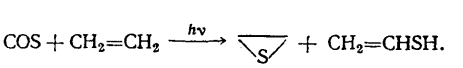


The synthesis of natural sesquiterpene episulphide derivatives of caryophyllene, isolated from the essential oil of hops, has been achieved. These compounds are formed on UV irradiation with mixtures of sesquiterpenes with S_8 in cyclohexane or on radiolysis of sesquiterpenes in the presence of phenyl isothiocyanate.[143]



(LI) (LII) (LIII)

New data have also been obtained on the photochemical reaction of COS with ethylene.[144]



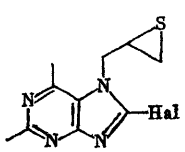
It has been shown that the formation of ethylenethiol is associated with the participation of excited $S(^1D_2)$ atoms. Recommendations concerning the control of the process have been developed.

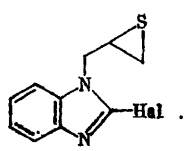
Calculations have been carried out for the $\dot{C}H_2CH_2\dot{S}$ species.[145] Their characteristic feature is the occurrence of the effective spin–orbital interactions of the unpaired electrons, which induces ready $T{-}S$ transitions and ensures the stereospecificity of the formation of the thiiran ring under mild conditions.

4. Reactions of thiirans without ring opening

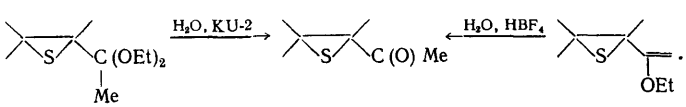
In the presence of alkalies, thioepichlorohydrin reacts in ether with mono-, di-, and tri-halogenoallyl alcohols, dichloropropanol,[28] alkylcellosolves,[29,30] and 3-(triorganosilyl)-substituted allyl[32] and propargyl[33,146] alcohols. Carboxylic acid salts react similarly with thioepichlorohydrin.[147] On treatment with 3-(trimethylsilyl)-propargyl alcohol, the Si—C≡C bond is cleaved and 2,3-epithio-1-propargyloxypropane is formed.[32]

The thiirans (III) have been obtained in the presence of bases under mild conditions from thioepichlorohydrin and alkyl-2-cyanoethylamines.[37] Lithio-*o*-carbaboranes form compounds (VII) in these reactions.[148] Thioepichlorohydrin reacts with sodium, potassium, and ammonium thiocyanates in alcohol to form 2,3-epithio-1-thiocyanatopropane with a small admixture of isothiocyanate, while the reaction with potassium diethyl phosphorothioate affords *OO*-diethyl thioglycidyl phosphorothioate.[149] The epithiopropanes (LIV) and (LV) have been obtained in aprotic media [DMF, dimethyl sulphoxide (DMSO)] by the reaction of thioepichlorohydrin with 8-halogenoxanthines and 2-halogenobenzimidazoles.[150]


(LIV)

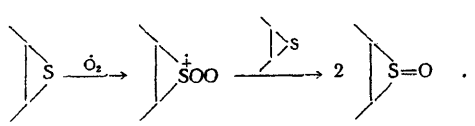

(LV)

The conditions governing the formation of acetylthiiran from acetylthiiran acetal and 2R-2-(α-ethoxyvinyl)thiiran have been investigated.[43]



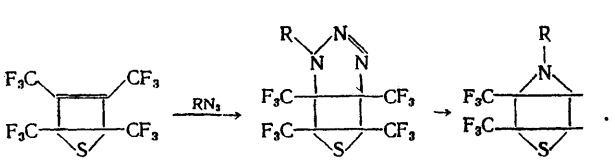
Formylthiiran is formed just as smoothly from its diethylacetal.[42]

The photochemical oxidation of alkylthiirans with oxygen in acetone, CH_3CN, $CHCl_3$, and CH_2Cl_2 leads to thiiran oxides in accordance with the scheme,[151]



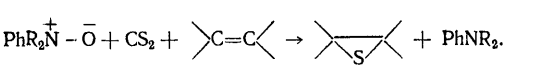
In alcohol, the thiiran ring is opened and the sulphur atom is oxidised. Diallyl-thiirans are indifferent to oxygen on UV irradiation.

The conversion of the stable "Dewar thiophen" into a valence isomer of 1,4-thiazine may serve as an example of the modification of thiirans at the multiple bond of a ring substituent.[152]



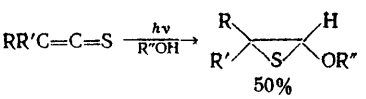
5. Other methods

A novel method of synthesis of thiirans was discovered in a study of the reaction of dimethylaniline oxide with CS_2 in the presence of alkenes.[153]

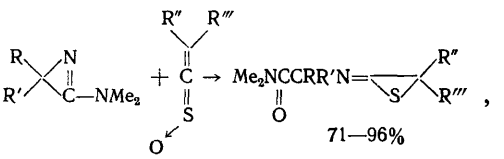


The yield increases with increase in the excess of CS_2 and the alkene. The thiolating agent is believed to be the oxathiiranthione formed from CS_2 and the *N*-oxide.

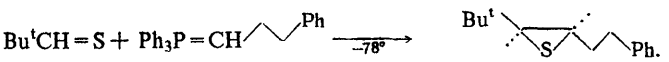
Alkoxythiirans are formed on UV irradiation of thioketens in benzene in the presence of alcohols.[154] The carbene RR'C—CS is believed to be a precursor of alkoxythiirans.



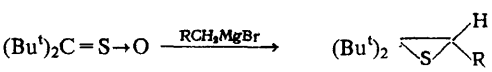
New methods of synthesis of thiiran imines are based on the reaction of dimethylaminoazirines with thioketen *S*-oxides.[155] It is believed that the reaction



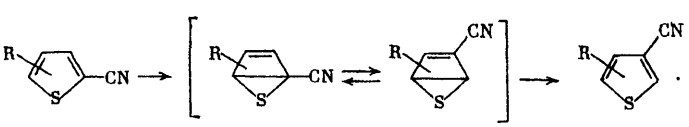
proceeds via a 1,3-dipolar addition mechanism. the formation of an epithio-compound in the reaction of pivaloylthioaldehyde with Wittig reagents has been explained by the formation and reactions of cyclic [2 + 2]adducts.[156]



Thiirans are the main products of the reactions of primary organomagnesium or organolithium compounds with the *S*-oxide of di(t-butyl) thioketone.[157]

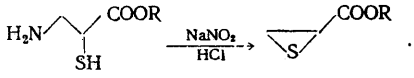


Bicyclic thiirans of the type of "Dewar thiophen" are apparently formed as intermediates in the photolysis of 2-cyanothiophens, which is the cause of their isomerisation to 3-cyanothiophens.[158,159]

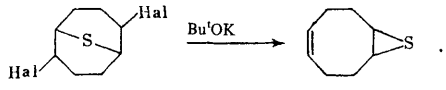


Thiirancarboxylic acids are formed stereoselectively on deamination of aminothiols.[160] The enantiomers of cysteine or its esters afford in this reaction epithioglycidates with the inverted

configuration. The enantiomers of 6-aminopencillanic acid are converted into 3,3-dimethylthioglycidic acid.

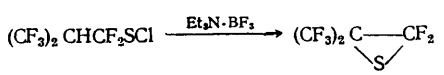


Dihalogeno-derivatives of thiabicyclooctanes and thiabicyclononanes are converted almost quantitatively into monoepithio-derivatives of cyclodienes on dehydrohalogenation by potassium t-butoxide.[161]

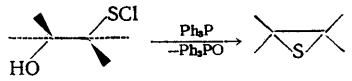


Epithiodiadamantylidene was obtained by the reaction of diadamantylidene with S_2Cl_2 in CH_2Cl_2 at 20 °C.[162–164] In the presence of SCl_2, the epithio-compound is chlorinated to 4-chloro-, 4,4'-dichloro-, and 4,4',8-trichloroepithiodiadamantylidenes.

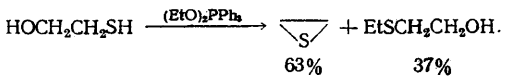
Epthio-compounds have been obtained[165,166] from sulphenyl chlorides. 2-Hydrooctafluoroisobutanesulphenyl chloride is dehydrochlorinated by the complex $NEt_3.BF_3$ to epithioperfluoroisobutane.[165]



2-Hydroxyalkanesulphenyl chlorides are converted stereospecifically into epithio-compounds on treatment with triphenylphosphine.[167]



The reaction of the monothio-derivative of ethylene glycol with diethoxytriphenylphosphorane in toluene leads to a mixture of thiiran and ethyl 2-hydroxyethyl sulphide.[168]



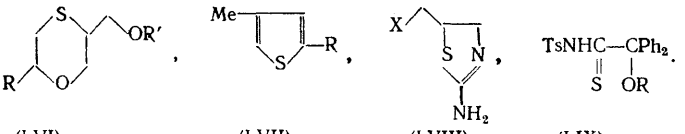
III. Reactivity

Extensive data on the reactivities of a wide variety of thiirans in reactions with hydroxy- and amino-compounds, thiols, CH acids, and various electrophiles as well as data on the behaviour of thiirans in desulphurisation and cyclisation reactions have accumulated during the last decade. There has been considerable expansion of available information about the intramolecular reactions of thiirans with functional group substituents. New quantitative characteristics of the principal types of reactions of thiirans have appeared.

1. Reactions with hydroxy-compounds

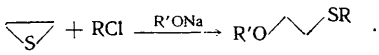
The polymerisation of thiirans in the presence of hydroxy-compounds and basic catalysts prevents the preparative use of this reaction.[1] It had been used earlier only for the synthesis of thietan-3-ol and its derivatives by the opening of the ring of thioepichlorohydrin by certain oxy-anions. This reaction (the thiiran–thietan rearrangement) is being investigated, as before, both for preparative purposes[4–12] and theoretically.[169] At the same time, new examples of the synthetic employment of the nucleophilic opening of the thiiran ring by hydroxy-compounds have appeared.

Thus the interaction of 1-(2-halogenoalkoxy)-2,3-epithiopropanes with alcohols in the presence of bases leads to 1,4-oxathianes (LVI).[29] Propargyl- or propyn-1-yl-thiirans isomerise to thiophens (LVII) on treatment with potassium t-butoxide.[52] Under the conditions of nucleophilic ring opening, *N*-2,3-epithiopropylcyanamide is quantitatively converted into 2-amino-1,3-thiazoline (LVIII).[82] Thiiran imines (XXXVI) react with alcohols under mild conditions to form the amides of α-alkoxy-substituted thiocarboxylic acids (LIX).[107,108] When ethylene sulphide is heated with phenyl acetate in the presence of tri-n-butylamine, 2-phenoxyethyl thioacetate is formed in a high yield.[170]



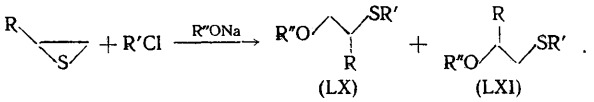
(LVI) (LVII) (LVIII) (LIX)

Another aspect is based on the competing reactions in thiiran–RONa–benzyl chloride systems.[171]



The study of such reactions has shown[172–182] that, in the presence of benzyl and allyl chlorides, monomeric products are formed in 50–80% yield from ethylene sulphide and sodium alkoxides derived from primary aliphatic alcohols, benzyl alcohol, and trifluoroethanol, and also sodium phenoxides. 2-R-Thiirans, including methylthiiran, butylthiiran, phenylthiiran, alkoxy- and aryloxymethylthiirans, and vinylthiiran react similarly in these systems.

It has been established that only alkoxy- and aryloxymethylthiirans interact regioselectively with alkoxy- and aryloxy-anions, mainly in accordance with Krasuskii's rule, i.e. with formation of products having the "normal" structure (LX). The reactions with other 2-R-thiirans afford mixtures of products containing also substances having the "anomalous" structure (LXI).[179–182]



(LX) (LXI)

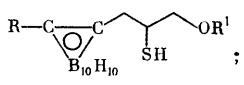
The mixture composition depends significantly on the nature of the oxy-anion and the ring substituent.

The kinetic characteristics and thermodynamic parameters of the reaction permit the conclusion that the reactions proceed via the "push-pull" (Ad_1) mechanism.[173,175–182] The rate-limiting stage in these reactions is the formation of the thiiran–hydroxy-compound ion pair which is facilitated by solvation by proton-donating solvents. The reactivity of this pair is higher than in the analogous reactions of oxirans, which is the reason for the increased tendency of thiirans to be polymerised by hydroxy-compounds. In all the cases investigated, large (in absolute magnitude) negative entropies for the activation of the "normal" opening of the thiiran ring compared with the "anomalous" opening are observed, which is also characteristic of the analogous reactions of oxirans.

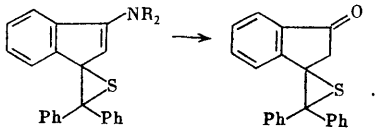
The polymerisation in the reactions of thiirans with hydroxy-compounds can also be suppressed under the conditions of acid catalysis. Thus, in the presence of sulphuric acid, 1,2-epithiodecane interacts with primary aliphatic alcohols to form mixtures of primary and secondary alkoxydecanethiols;[183,184] the isomer ratio depends on the nature of the alcohol and the amount of catalyst. With decrease in the solvating capacity of the solvent, the yield of the monomeric product falls. Tertiary alcohols are ineffective in these reactions in view of their low stability in the presence of acids.

In contrast to epithiodecane, carbaboranylthiirans (VII) react unambiguously with water and alcohols under the conditions of acid catalysis, forming the "normal" structure products (LXII).[71] Under the conditions of nucleophilic catalysis, these reactions lead to oligomers only.[185]

It is noteworthy that the acid-catalysed reactions of thiirans with hydroxy-compounds take place under comparatively severe conditions. Without affecting the thiiran ring, this made it possible to replace the enamine group of compound (LXIII) by the keto-group[104] and to obtain 16,17α-epithiopregnenolene from its acetate.[186] Some of the bicycloalkylidenethiirans are fairly resistant also to bases. This property has been used to remove with the aid of methanol the acetyl protecting group in the diacetates of epithiosecosteroids in the presence of Na_2CO_3.[121]



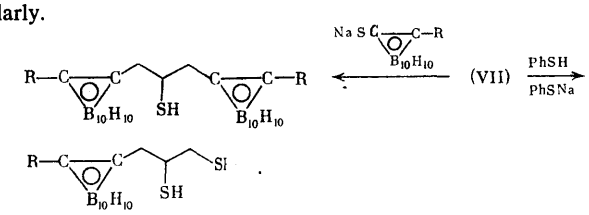
(LXII)



(LXIII)

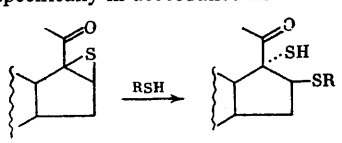
2. Reactions with thiols and thiones

There are few new data on the reactions of thiirans with thiols. The study of the properties of carbaboranylthiirans (VII) established that their interaction with thiophenol in the presence of sodium thiophenoxide in ethanol takes place unambiguously in accordance with Krasuskii's rule.[185] Sodium *o*-carbaboranyl-thiolates react similarly.



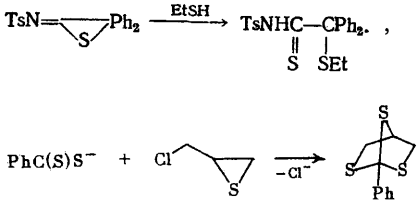
Under the same conditions, carbaboranylthiirans are converted into bismercaptans on reaction with sodium hydrogen sulphide[186] and into trithiocarbabonates on reaction with potassium methyl-xanthate.[72]

Interesting results have been obtained in the study of the reactions of the 16,17α-episulphide ring of 20-ketopregnanes and their hydrazones.[187,188] The reactions of the 3-acetate of 16,17α-epithio-pregnolone with phenylmethanethiol (under the conditions of electrophilic catalysis) or with thioloacetic acid take place stereospecifically in accordance with Krasuskii's rule.

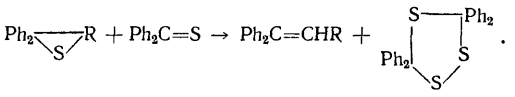


However, ethanethiol splits off sulphur from the epithio-compound under these conditions. The hydrazone of epithiopregnolone undergoes desulphurisation even by thioloacetic acid.

The results of the reactions of thiiran imines with ethanethiol[108] and of thioepichlorohydrin with aluminium dithiobenzoate[189] are of interest.



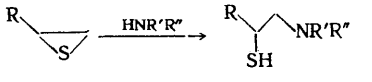
Data have been published on the reactions of thiirans with thiocarbonyl compounds. Di- and tri-substituted thiirans are desulphurised by thiobenzophenones under mild conditions with formation of alkenes and 1,2,4-trithiolans.[190]



Mono- and di-substituted thiolans react with carbon disulphide in solutions in tertiary amines at a high pressure and are converted into trithiocarbonates.[191] 1-(*N*-Carbazolyl)-2,3-epithiopropane readily forms a cyclic adduct with CS_2.[39] In the presence of zinc, cadmium, merury, and ammonium hydrogen sulphides, thiirans react with carbon disulphide and are converted into oligomeric polythio-carbonates.[192]

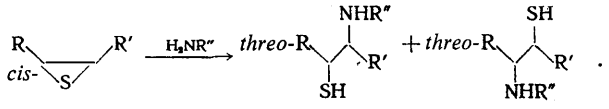
3. Reactions with amines

Reactions with amines constitute the most widely investigated branch of the chemistry of thiirans.[1] In addition to the known quantitative characteristics of the processes involving the opening of the ring in thiirans by amines[1] (Ref. 1, p. 219), a comparative study has been made of the kinetics of the reactions of epoxypropane and epithiopropane with dibutylamine.[193] The results of this study confirmed the qualitative idea that in aprotic media the thiiran ring is opened by dibutylamine more readily than the oxiran ring. The high regioselectivity of the opening of the epithiopropane ring by dibutylamine in conformity with Krasuskii's rule was established. This is a general feature of the reactions of 2-R-thiirans with amines.



The first data on the stereochemistry of this reaction have appeared. It has been shown that *cis*- and *trans*-2,3-dimethyl-thiirans are converted exclusively into *threo*- and *erythro*-aminothiols respectively on heating (90–100 °C) with primary amines (in 200% excess).[194] Mixtures of esters of the regioisomers of anilino-mercaptooctadecanoic acid having the *threo*-configuration have been obtained in the reactions of the methyl esters of *cis*-6,7- and *cis*-9,10-epithiooctadecanoic acids with aniline in the presence of Ag^+ as

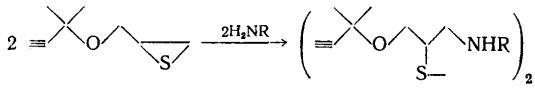
the catalyst; the *trans*-isomers give rise to the analogous products having the *erythro*-structure.[76] Thus the thiiran ring is opened by amines stereospecifically with inversion of the configuration:



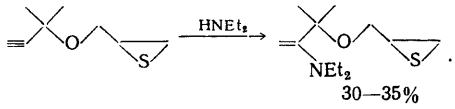
The influence of temperature, solvents, reactant ratio, and the presence of hydroxylated agents on the results of the reaction of 1,2-epithiodecane with secondary amines of different basicity has been investigated in detail.[195] The excess of the amine has a decisive influence on the yield of monomeric products, which indicates the participation of two molecules of the amine in the opening of the ring.

The regioselective formation of aminothiols with the "normal" structure has been established in the reactions of secondary amines with esters based on epithioglycidol. They include 1-triorganylsilylalkoxy(alkenyloxy)-2,3-dimethylthiirans,[32,33] polyhalogenoalkoxymethylthiirans, furfuryloxy- and t-butoxymethyl-thiirans,[31,34] and derivatives of *O*-(2,3-epithiopropyl)hydroxylamine.[196,197]

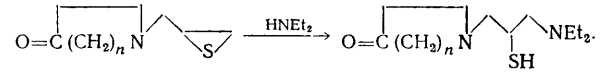
Alkynyloxymethylthiirans react with aliphatic primary amines even in the presence of their excess (100%) only under severe conditions (100–105 °C) with formation of disulphides.[198] Tryptamine, thyramine, and histamine react similarly.[199]



Under more severe conditions (130 °C), the disulphides formed combine with alkylamines via the triple bond. Dialkylamines do not enter into this reaction even in the presence of a large excess of the amine, while in the reaction catalysed by $Et_2O.BF_3$ they add to the triple bond.[200]

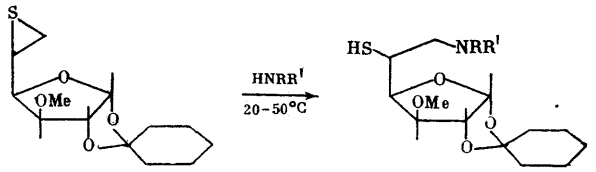


The reactions of *N*-(2,3-epithiopropyl)-substituted 2-pyrrolidinone and 2-piperidinone with diethylamine under severe conditions lead to products with the "normal" structure, which are partly oxidised to disulphides:[38]

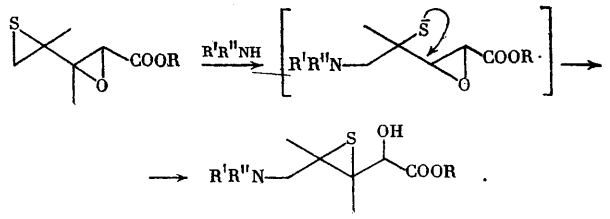


Ring opening via the Krasuskii mechanism has been established in reactions of amines with thiirans having electron-accepting ring substituents—trifluoromethylthiiran[75] and *o*-carbaboranylthiirans.[148,185,187]

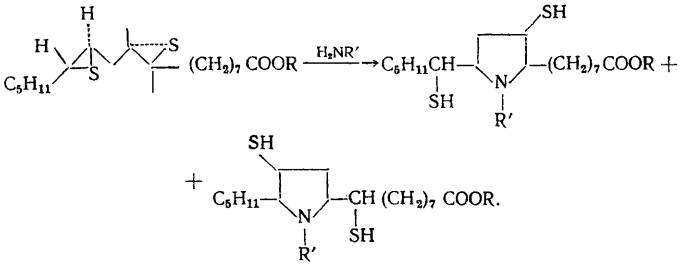
The amination of epithiocarbohydrates by primary and secondary amines and aminoacid esters takes place under unusually mild conditions, which made it possible to obtain aminomercaptoderivatives of glucofuranose,[201] isofuranose,[202] and sorbitol.[203]



The interaction of esters of 2,3-epoxy-4,5-epithiovaleric acids with secondary amines is accompanied by the 2,5-addition of the nucleophile and the 5,3-migration of the thiiran ring, which is a consequence of its "normal" opening and subsequent reaction of the aminothiolate formed.[46]

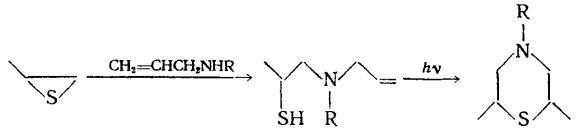


The reactions of primary amines with bisthiirans are accompanied by cyclisation. Thus the only products of the reaction of methyl-, isopropyl-, and benzyl-amines with the *threo*-isomer of *cis*-9,10-*cis*-12,13-diepithiooctadecanoic acid and its esters in aqueous alcohol in the presence of Ag^+ as the catalyst proved to be substituted mercaptopyrrolidines.[204–206]

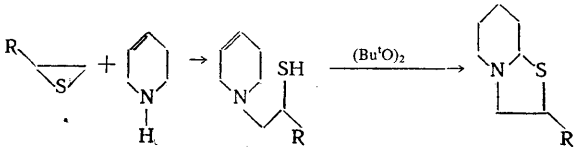


Aniline enters into this reaction with greater difficulty, affording substituted mercaptopyrrolidines with an admixture of aminomercaptothiirans.

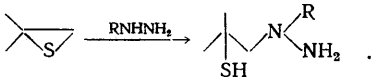
Allyl-, ethylallyl-, and benzylallyl-amines react with thiirans to form mainly the "normal" ring opening products, which cyclise to perhydro-1,4-thiazines on UV irradiation.[207]



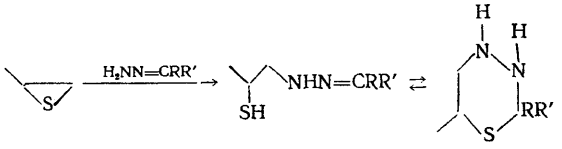
When 2-R-thiirans are heated in benzene with a twofold excess of tetrahydropyridine, secondary aminothiols are obtained in a high yield. They are converted into 7-thia-1-azobicyclo[4.3.0]nonanes under the conditions of a free-radical reaction.[208]



2-Mercaptoalkylation of alkylhydrazines by thiiran, methylthiiran, and epithioisobutane takes place at the substituted nitrogen atom, the ring being opened mainly in accordance with Krasuskii's rule.[209–211]



In benzene at 60 °C, thiiran, methylthiiran, and 2-epithiobutane interact with hydrazones[212,213] to form mainly the "normal" ring opening products, which cyclise reversibly to perhydro-1,3,4-thiadiazines.



The products of the "anomalous" ring opening and the products of the bis-2-mercaptoalkylation of the hydrazones are formed at the same time.

In the search for physiologically active substances, the mono-2-mercaptoethylation of σω-alkylenediamines[13] and the bis-2-mercaptoalkylation of *NN'*-dimethyl-σω-alkylenediamines[214] has been achieved; the products of the reaction of thiirans with *p*-aminophenylacetate esters have been obtained.[14] In the last case, the reaction takes place regioselectively in accordance with Krasuskii's rule.

Under the usual conditions for the 2-mercaptoalkylation of amines, thiiran interacts with macroporous styrene–divinylbenzene copolymers modified by amino-compounds.[215]

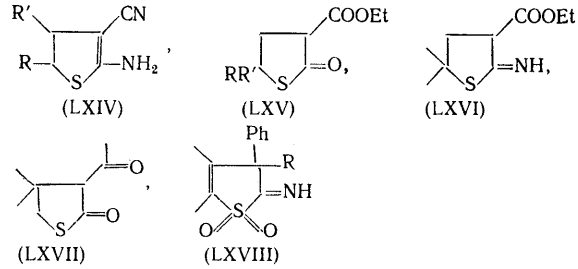
4. Reactions with CH acids

CH acids usually initiate the polymerisation of thiirans under the conditions of nucleophilic catalysis and 3-ethoxycarbonyl-2-imino-tetrahydrothiophens have been obtained earlier only in the reaction with ethyl cyanoacetate (Ref. 1, p. 201). The conditions for the formation of the products of the cyclocondensation of epithio-compounds with other CH acids and their salts have been found recently and the regioselectivity of these reactions has been investigated.

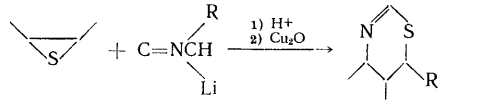
In the presence of NaH in DMSO, malonodinitrile interacts with thiiran, 2-methylthiiran, and 2-phenylthiiran, forming enaminonitriles of the dihydrothiophen series (LXIV) in 50–62% yield. The 2-methylthiiran ring is then opened in accordance with Krasuskii's rule, while that of 2-phenylthiiran is opened contrary to this rule.[216] An enaminonitrile was obtained from thiiran in diglyme in 23% yield,[217] while the product of the cyclocondensation of the enaminonitrile obtained from 2,2-dimethylthiiran in ethanol in the presence of EtONa of the catalyst was obtained in 62% yield.[218]

The reactions of thiirans with malonic ester in alcohol in the presence of EtONa lead to 3-ethoxycarbonyltetrahydrothiophen-2-ones (LXV) in 35–65% yield.[218] 2-Phenylthiiran is converted in the analogous reaction into a mixture of regioisomers (the "anomalous" ring opening product is the main component). 2,2-Dimethylthiiran reacts with cyanoacetic and acetoacetic esters, affording the "normal" ring opening products (LXVI) and (LXVII).[218]

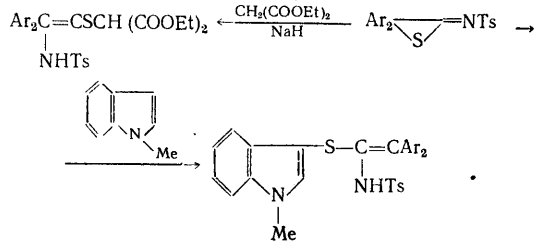
Substituted sodiophenylacetonitriles form the cyclocondensation products (LXVIII) with 2,3-dimethylthiirene 1,1-dioxide in tetrahydrofuran.[219]



The lithio-derivatives of isocyanides add to methylthiiran, epithiocyclohexane, and epithiocyclopentane, affording γ-mercaptoalkyl isocyanides, which cyclise to 4*H*-5,6-dihydro-1,3-thiazines.[220]



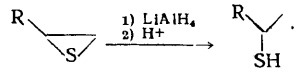
In the presence of NaH, tosyliminothiirans interact with malonic ester,[108] affording enaminosulphides. *N*-Methylindole interacts analogously.



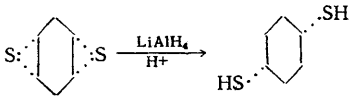
The attempt to involve diisopropylidenethiiran in the reaction with malonic ester in the presence of palladium diacetate as the catalyst was unsuccessful.[128] The product of this reaction was 1,1,4,4-tetramethylbutatriene.

5. Reactions with metal hydrides and organometallic compounds

The latest studies have confirmed the high regioselectivity of the reduction of thiirans by lithium tetrahydroaluminate to secondary thiols. Triorganylsilylalkoxy(alkenyloxy)methylthiirans,[32,33] trifluoromethylthiiran,[75] and also methyl- and phenyl-*o*-carbaboranylepithiopropanes[72] interact with $LiAlH_4$ exclusively in accordance with Krasuskii's rule.

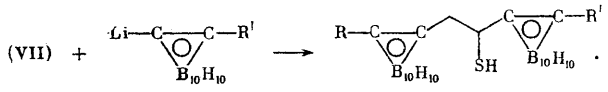


Together with a secondary thiol, an admixture of "anomalous" ring opening product is formed in the reaction of isopropyl-*o*-carbaboranylepithiopropane.[72] The reduction of *cis*-1,2,4,5-diepithiocyclohexane to *cis*-1,4-dimercaptocyclohexane is highly selective.[44]

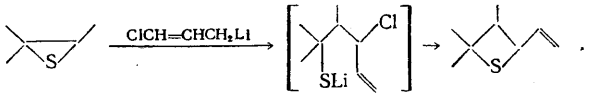


The elimination of sulphur from thiirans has been noted only in isolated instances. For example, the reduction of 4-chlorodiadamantylidenethiiran with $LiAlH_4$ yielded diadamantylidene and not a thiol.[221]

The characteristic features of the reactions of thiirans with organolithium compounds and Grignard reagents have not yet been established. The formation of monomeric products of the reactions of thiirans with organolithium compounds was first demonstrated by Kazantsev et al.[185] and by Ondona et al.[222] Thus carbaboranylthiirans (VII) react with lithio-*o*-carbaboranes to form secondary thiols.[185]

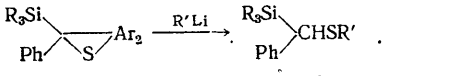


Butyllithium and ethylmagnesium bromide split off a sulphur atom from carbaboranylthiirans.[72,185] At temperatures in the range from −90 °C to −60 °C, substituted thiirans interact with 3-chloroallyllithium to form 2-vinylthietans.[222]

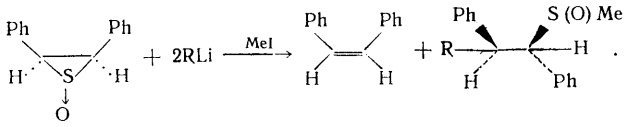


Thioepichlorohydrin is converted in this reaction into the 3-chloro-5,6-epithiohex-1-ene.

The opening of the ring in triorganosilylated triarylthiirans by methyl- and butyl-lithium is accompanied by the cleavage of the C−C bond.[106]

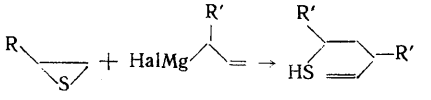


The reactions of butyl- and phenyl-lithium with *cis*- and *trans*-2,3-diphenylthiirans and their *S*-oxides[223] afford the desulphurisation and ring-opening products, which have been isolated as methylated derivatives. *trans*-2,3-Diphenylthiiran and its *S*-oxide are then converted quantitatively into *trans*-stilbene, while the ring opening products with the *threo*-configuration were obtained from the *cis*-isomers together with *cis*-stilbene.



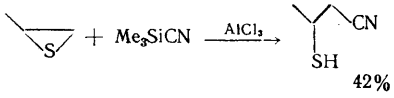
The stereospecificity of the desulphurisation has been explained by the formation and concerted decomposition of intermediate episulphuranes.

New examples of the regioselective interaction of thiirans with Grignard reagents have been described.[224–226] Alkenylmagnesium halides of the allyl type interact with various thiirans to form unsaturated thiols.[224–226]

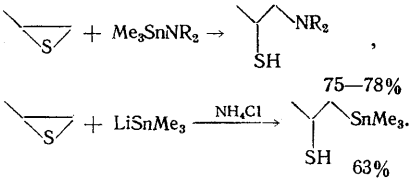


Diisopropylidenethiiran does not react with ethylmagnesium bromide.[129]

The reactions of thiirans with organic derivatives of Group IV elements have been investigated. Trimethylsilyl cyanide interacts with methylthiiran regioselectively in boiling dichloromethane in the presence of $AlCl_3$ as catalyst, affording silylated β-mercaptobutyronitrile together with propene.[227]

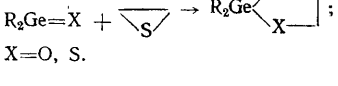


Dialkyl(trimethylstannyl)amides react with methylthiiran and epithiocyclohexane in the absence of the catalyst. In contrast to dialkyl(stannyl)amides, trimethylstannyllithium gives rise to the "normal" ring opening product.[228]

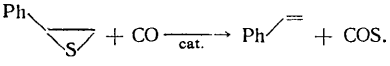


Epthiocyclohexane is partly converted into cyclohexene in this reaction.

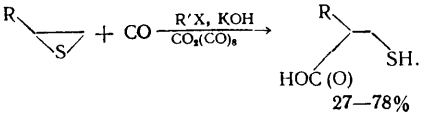
The complex of diethylgermylene and triethylamine interacts with thiiran at 130−150 °C, affording 1,2,5-germadithiolan and ethylene.[229,230] Diethylgermanethione, which undergoes [2 + 3]cycloaddition to thiiran, is believed to be an intermediate in this reaction. This has been confirmed by direct reactions of thiiran with dialkylgermanones and germanethiones.[231]



Metal carbonyls as well as variable valence metal complexes abstract sulphur from thiirans.[232] In the presence of carbon monoxide, rhodium and palladium complexes catalyse the desulphurisation reaction in accordance with the mechanism[233]

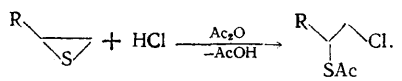


However, the reaction catalysed by $Co_2(CO)_8$ in benzene in the presence of methyl iodide or benzyl bromide and aqueous KOH under phase transfer conditions results in the formation of β-mercaptoalkanecarboxylic acids.[234]



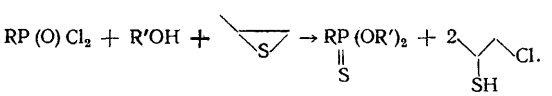
6. Reactions with electrophiles

It has been shown for a large number of examples that the reactions of thiirans with electrophiles are distinguished by a greater variety than had been believed previously. The interaction of carbaboranylthiirans (VII) with concentrated HCl at 0–10 °C resulted in the slow formation (over a period of 10 h) of the "normal" ring opening product. HBr and HI react similarly; in the latter case, the intermediate thiol is oxidised to the disulphide.[71,72,235] In contrast to HCl, HBr interacts with carbaboranylthiirans also in anhydrous media, which can be explained by the specific solvation of the sulphur atom by bromides. HCl in acetic anhydride interacts just as readily with these compounds as with methylthiiran.[70]

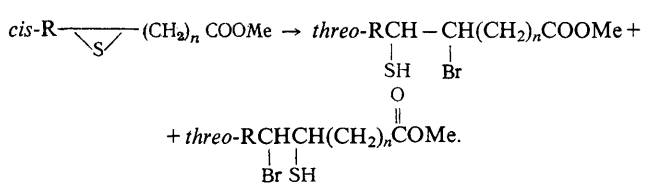


Similar features are characteristic of the reactions of hydrogen halides also with other electron-deficient thiirans, for example, with 3,4-epithiothiolan 1,1-dioxide;[73] in this case too, HCl reacts readily and unambiguously only in acetic anhydride. Under severe conditions, HCl interacts also with trifluoromethylthiiran, affording exclusively the product with the normal structure—a secondary halogenothiol.[75]

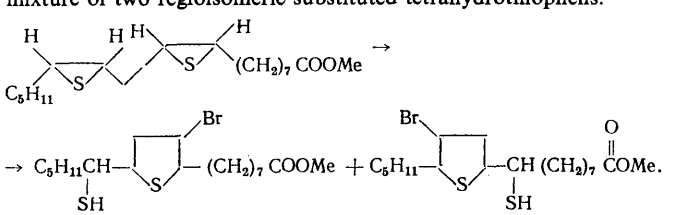
In the absence of electron-accepting substituents in the molecule, thiirans readily combine with HCl in non-polar media. Thus triorganosilylalkoxymethylthiirans[33] and 1-(*N*-phthalimido)-2,3-epithiopropane[236] are converted into secondary halogenothiols in $CHCl_3$ and CCl_4. Aliphatic 2-R-thiirans bind HCl so vigorously that they can be used successfully as hydrogen halide acceptors.[237]



The opening of the ring in thiirans by hydrogen halides is accompanied by the inversion of the configuration. A mixture of *threo*-isomers has been obtained from the esters of higher aliphatic *cis*-epithio-acids on interaction with HBr,[76] while the esters of the *trans*-epithioacids afforded a mixture of *erythro*-isomers.

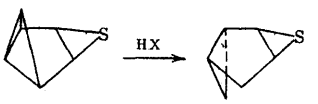


In a number of instances, the interaction of thiirans with hydrogen halides leads to unusual results. The esters of *cis*-9,10-*cis*-12,13-diepithiooctadecanoic acids react with HBr to form a 1:1 mixture of two regioisomeric substituted tetrahydrothiophens.[238]



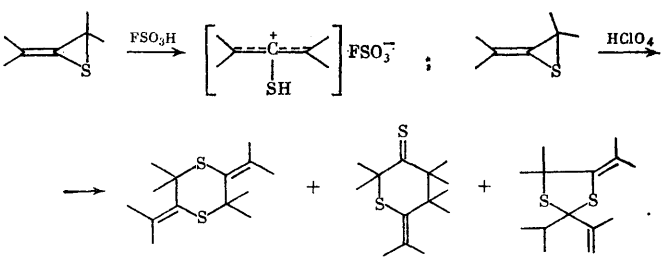
CCl_3COOH reacts similarly.

On treatment with HCl, epithioadamantylidene gives rise to diamantylidene.[221] The reaction of benzvalene sulphide with HCl and acetic acid is accompanied by a skeletal rearrangment.[85]



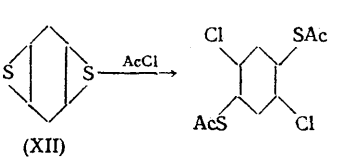
Carbaboranylthiirans (VII) are hydrolysed by 10% H_2SO_4 to mercaptoalkanols in accordance with Krasuskii's rule.[71] The usual thiirans do not polymerise under these conditions.

Tetramethylallene sulphide is protonated by FSO_3H to a stable carbonium ion.[239] However, 70% $HClO_4$ and BF_3 etherate induce its dimerisation.[126,239]



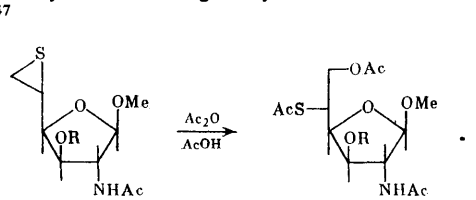
Carbazolylthiiran (VI) is polymerised by dilute inorganic or organic dicarboxylic acids,[240] but acetic acid affords the "normal" ring opening product in 65% yield. Addition in conformity with Krasuskii's rule has been noted also in the reaction of acetic acid with 16,17α-epithiopregnenolones and their hydrazones,[186,188] while the reaction with 1,2-epithiooctane is unambiguous.[241,242]

An uncertain type of ring opening has been observed in the reactions of acetyl chloride with higher 1,2-epithioalkanes[243] and alkylthiomethylthiirans.[244] Carbaboranylthiirans combine with acetyl and benzoyl chlorides in accordance with Krasuskii's rule.[72] Acetyl chloride reacts similarly at 100 °C with trifluoromethylthiiran.[75] The reaction of acetyl chloride with bisepithiocyclohexane (XII) leads to a symmetrical product.[41]

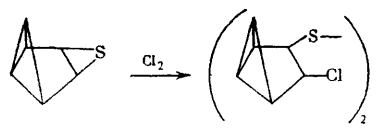


(XII)

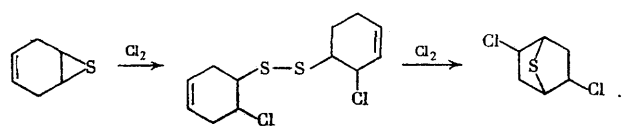
The interaction of higher 1,2-epithioalkanes with carboxylic acid anhydrides in the presence of tertiary amines takes place only under severe conditions and leads to mixtures of 1-acycloxy-2-acylthio-, 2-acyloxy-1-acylthio-, and 1,2-diacylthio-alkanes.[245,246] On the other hand, in acetic acid in the presence of sodium acetate as the catalyst, derivatives of 5,6-epithio-D-glucofuranose interact with acetic anhydride unambiguously in accordance with Krasuskii's rule.[247]



The ambiguity of the ring opening in methylthiiran by chlorine and 2-chloro- or 2-bromo-ethanesulphenyl chlorides (Ref. 1, p. 253) has been confirmed.[248] At the same time, *o*-carbaboranylthiirans (VII) interact unambiguously under mild conditions with chlorine, bromine, iodine,[40,72] and sulphuryl chloride[148] to form the disulphides. The reactions of phthalimidomethylthiiran with bromine[236] and of trifluoromethylthiiran with chlorine[75] are similar. Benzvalene sulphide interacts with chlorine like other thiirans.[86]



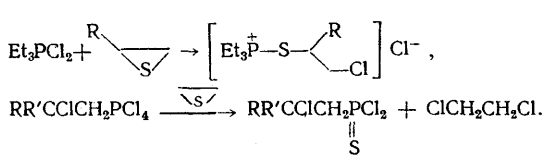
However, the monoepithio-derivatives of cycloalkadienes tend to rearrange under the influence of the halogens and sulphuryl chloride.[249]



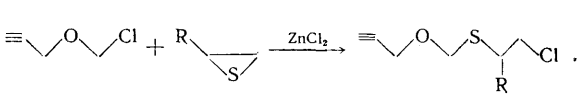
3,3-Ethylenedioxy-4,5-epithiocyclohept-1-ene reacts with halogens to form products corresponding to two possible routes to the opening of the ring.

The reaction of epithiodiamantylidene with SCl_2 leads to the chlorination of the adamantyl groups in the 4-position and then the 4'-position.[162] Methyl iodide abstracts sulphur from these compounds.[211] Refluxing of 4-chloroepithiodiamantylidene with formic acid leads to the substitution of the chlorine atom by the formate group, while the HCl evolved induces the desulphurisation of the epithio-compound formed.[221]

The reactions of 2-R-thiirans with dichlorotriethylphosphorane afforded the relatively stable triethyl-2-chloroalkylthiophosphonium chlorides.[250] Similar products of the reactions of 2-chloroalkyltetrachlorophosphoranes with thiiran decompose readily with evolution of dichloroethane.[251]



The reaction of chloromethyl propargyl ether with 2-R-thiirans in the presence of Friedel–Crafts catalysts results in the preferential formation of products with the "anomalous" structure.[252]

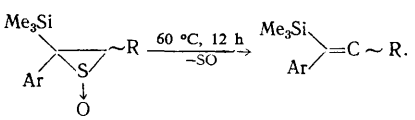


7. Desulphurisation of thiirans

New data refer mainly to the spontaneous or thermal desulphurisation and also to desulphurisation in the presence of metals, organometallic compounds, and trivalent phosphorus compounds.

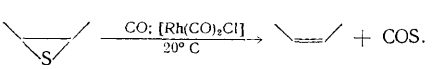
Allene sulphide is converted into allene already at –70 °C,[124,125] while 2,2,3-triphenylthiiran[101] and 2,2-diphenylthiiran[99] split off sulphur after 1 and 15 h respectively at 20 °C. 3-Dialkylaminoindenylidenethiirans (80 °C, 3 h),[104] *cis,trans*-divinylthiirans (90–100 °C),[53] the esters and amides of substituted thioglycidic acids (20–100 °C),[92,93,100,253] the esters of 1,2-epithioethylphosphonic acid,[77] spirothiirans (200–250 °C),[254] and *cis*- and *trans*-dideuteriothiirans (350 °C)[56] are converted into alkenes on heating. Spontaneous or thermal desulphurisation takes place stereospecifically,[53,56,93,253] but in the case of *cis*-2-R-3-R-thiirans it is accompanied by the partial formation of alkenes with the *trans*-configuration.[54]

Several examples of the thermal desulphurisation of thiiran *S*-oxides and *SS*-dioxides have been investigated. For example, the formation of substituted trimethylsilylalkenes from the corresponding *S*-oxides under mild conditions has been demonstrated.[255]



The classical desulphurisation of thiirans by copper bronze at 150–180 °C has been investigated for spirothiirans obtained by the reaction of diazo-compounds with thiopyrans,[102] dithionophthalimide,[103] and xanthones.[110,256] Alkoxythiirans[154] and higher thermal and internal epithioalkanes[257] react under mild conditions (40–90 °C); together with alkenes, alkanes are also formed to some extent under these conditions.

Higher alkenes[257] and secosteroids[121] have been obtained by refluxing the corresponding epithio-compounds with zinc in acetic acid. Thiirans are converted into alkenes on interaction with germylenes,[228] iron pentacarbonyl,[232] and tributyltin hydride in the presence of azobisisobutyronitrile.[257] Stereospecific desulphurisation is catalysed by rhodium complexes in the presence of carbon monoxide.[235]



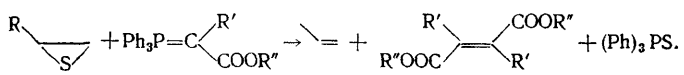
A wide variety of thiirans have been converted stereospecifically into alkenes on refluxing in dimethoxyethane in the presence of lithium.[55] Carbaboranylthiirans[72] and 2-R-3-R-thiirans[156] split off sulphur also on treatment with butyllithium. Butyl- and phenyllithium convert *cis*- and *trans*-2,3-diphenylthiirans or their *S*-oxides into alkenes.[223]

Triphenylphosphine has been used for the desulphurisation of 5-dialkylamino-3,4-epithio-2-hydroxyalkanecarboxylates,[36] a wide variety of 2-R- and 2-R-3-R-thiirans,[90] optically active thiirans,[91] triorganosilylthiirans,[105,106] Dewar's tetrakis(trifluoromethyl)-perhydro-1,4-thiazine,[152] carbaboranylthiirans,[258] and other epithiocompounds. The best desulphurising agents are sometimes PBu_3 and phosphites. Thus, dispirothiirans,[123] tetramethylallene sulphide,[126] and diisopropylidenethiiran[129] are converted into the corresponding alkenes on interaction with PBu_3 and phosphorous tris(dialkylamides). The oxime of 1-acetyl-1-methylthiiran[77] and thiiran imines[155] are readily converted into the oxime of isopropenyl methyl ketone and keten imines respectively on reaction with PBu_3.

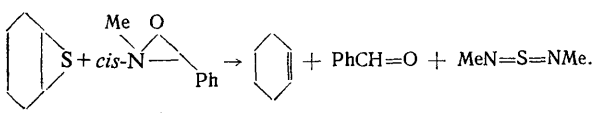
Trialkyl phosphites have been used to synthesise di-, tri-, and tetra-alkylethylenes,[90] *N*-allylpyrimidines,[97] alkylidenepyrazolines,[109] cyclohexylidenecyclohexanes,[122] etc. from thiirans.

New examples of the nucleophilic desulphurisation of thiirans are provided by the conversions into alkenes of triorganosilylated thiirans on reaction with trialkylammonium fluorides[105,106] and by the reactions of carbaboranylthiirans with Grignard reagents.[186] The electrophilic desulphurisation of epithiodiamantylidene has been achieved with methyl iodide.[221] The homolytic elimination of sulphur occurs on the interaction of thiirans with thioketones.[190]

Alkenes are formed from thiiran on reaction of the latter with selenonium ylides (partly)[259] and with phosphonium ylides (quantitatively).[260]

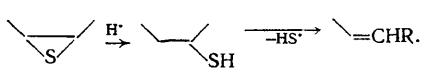


At 20 °C, thiiran, epithiocyclohexane, *cis*- and *trans*-2,3-dimethylthiiran and epithiosteroids are desulphurised quantitatively by oxaziridines.[261]



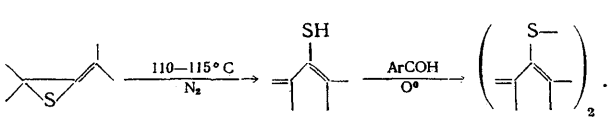
The reaction is stereospecific and is the best method for converting epithio-compounds into alkenes.

cis-2,3-Dimethylthiiran is desulphurised in the gas phase by atomic hydrogen.[262] The quantitative characteristics of such reactions have been obtained for thiiran itself.[263]



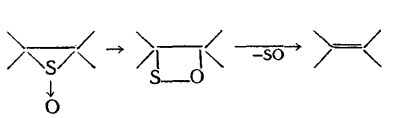
8. Other homolytic reactions

Tetramethylallene sulphide is converted on thermolysis into a 1,3-diene-3-thiol.[264]



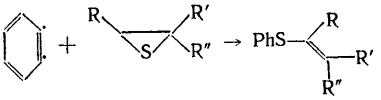
A similar shift of the hydrogen atom takes place also on thermolysis of thiiran with formation of ethylenethiol.[144,265]

The interaction of epithiodiadamantylidene with singlet oxygen leads to desulphurisation and the formation of an *S*-oxide, dioxetan, and an epoxide.[266] 1,2,3-Oxadithiolan-2-thione undergoes similar reactions under the conditions of vacuum thermolysis.[267] It is suggested that *S*-oxides are formed as intermediates.

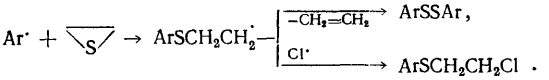


The formation of the *S*-oxide of diisopropylidenethiiran from an epithio-compound and *m*-chloroperbenzoic acid is accompanied by desulphurisation.[128] However, only the *S*-oxide has been obtained from dideuteriothiiran.[56]

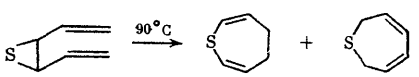
Dehydrobenzene reacts unambiguously with thiirans to form alkenyl phenyl sulphides.[268]



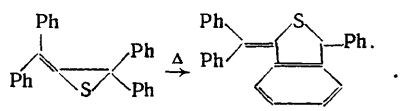
Aryl radicals (produced from ArN_2Cl in the presence of CuCl) react with thiiran to form primary radical species, which are stabilised either by eliminating ethylene or by combining with a chlorine atom.[269]



The homolytic reactions of thiirans are sometimes accompanied by rearrangements. The thermolysis of *cis*-divinylthiiran leads to a mixture of 2,7- and 4,5-dihydrothiepins, while the thermolysis of *trans*-divinylthiiran affords 2,7- and 2,3-dihydrothiepins.[53]



Tetraarylallene sulphides are converted into thiophen derivatives.[115]



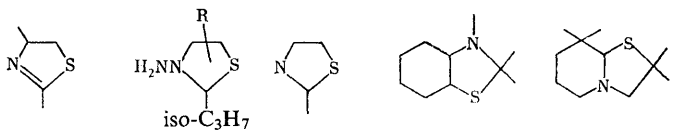
Treatment of α-methylthioglycidamides with amines leads to substituted 1,2,5,6,9,10-hexathiacyclododecanes.[88]

9. Cycloaddition reactions

The earlier ideas concerning the cycloaddition of thiirans to nitriles in the presence of strong acids were tested in 1978 on a large number of examples.[270] The high regioselectivity of these reactions, leading to thiazolines with the "normal" structure (LXIX), was demonstrated. The [2 + 3]cycloaddition of thiirans to the C=N bond in aldehyde hydrazones was described for the first time by Shevchenko and Potekhin.[212] Isobutyraldehyde hydrazone reacts with thiiran, methylthiiran, and 2,2-dimethylthiiran to form 3-amino-thiazolidines;[213] asymmetric thiirans afford a 1:1 mixture of regioisomers of compound (LXX).

The unusually easy (20°, 5 h) cycloaddition of thiiran to the C=N bond in alkaloids belonging to the C_{20} diterpenoid series has been described;[271] in the presence of an excess of the thiiran, cyclic adducts are formed almost quantitatively. The cycloaddition of thiirans to azomethines has been studied systematically,[207,272–274] the *N*-alkyl- and *N*-aryl-imines of aromatic aldehydes and acetone, pyrrolines, tetrahydropyridines, and dihydroquinolines have been made to react with thiiran, methylthiiran, 2,2-dimethylthiiran, and epithiocyclohexane. The ring opening in conformity with Krasuskii's rule results in the formation of a mixture of (*Z*)- and (*E*)-isomers of thiazolidines of the type (LXXI), (LXXII), and

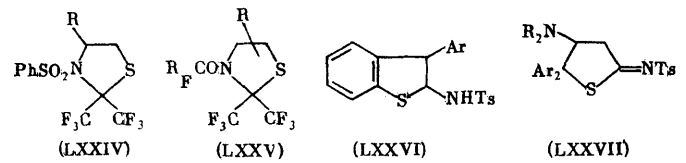
(LXXIII). The diethylacetal of formylthiiran reacts similarly with Schiff bases.[275]



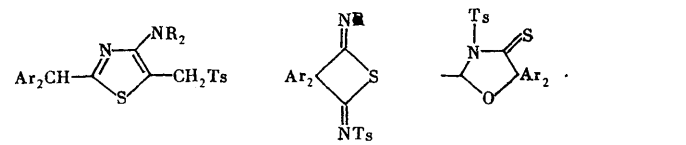
(LXIX) (LXX) (LXXI) (LXXII) (LXXIII)

The highly electrophilic hexafluoroacetone benzenesulphonylimine reacts with thiirans to form the cyclic adducts (LXXIV) only after the preliminary formation of $n\pi$-complexes (–60 °C).[276] The more electrophilic hexafluoroacetone polyfluoroacylimines vigorously open the ring in thiiran and methylthiiran even at –78 °C, which leads to a mixture of the regioisomers of compound (LXXV).[277]

The iminothiirans (XXXVI), obtained from diaryldiazoalkanes and arenesulphonyl isothiocyanates, enter vigorously into the cycloaddition reaction.[107,108,278,279] By virtue of their ready conversion into the acyclic dipolar state, they are converted into 2,3-dihydrobenzothiophens (LXXVI) even in boiling chloroform. At 0 °C, they react with enamines to form 2-iminoperhydrothiophens (LXXVII), with ynamines to form thiazoles (LXXVIII), and with isonitriles to form diiminothietans (LXXIX). They react with aldehydes at 20 °C to form oxazolidinethiones (LXXX). The reactions are highly regiospecific and stereospecific.



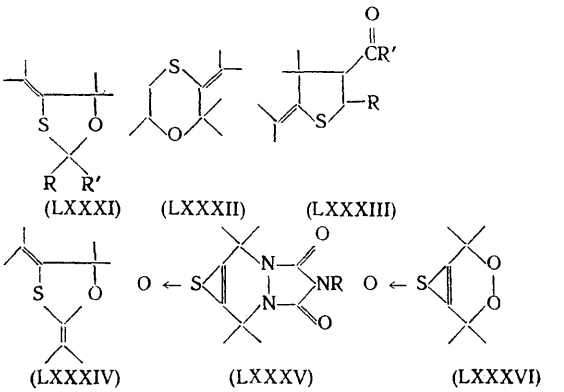
(LXXIV) (LXXV) (LXXVI) (LXXVII)



(LXXVIII) (LXXIX) (LXXX)

New types of cycloaddition reactions have been discovered in the study of the reactions of allene sulphides with carbonyl compounds and oxirans.[280,281] Tetramethylallene sulphide interacts with aldehydes and ketones on heating (110–115 °C) or in the presence of an electrophilic catalyst with formation of 1,3-oxathiolans (LXXXI). The analogous reaction with oxirans leads to the cyclic [3 + 3]adduct (LXXXII), while the reaction with αβ-unsaturated ketones affords acylthiophanes (LXXXIII). Diphenylketen gives rise to the oxathiolan (LXXXIV).

The *S*-oxide of diisopropylidenethiiran enters into Diels–Alder reactions with electron-accepting dienophiles at 20 °C. Thus the *S*-oxide reacts with 1,2,4-triazolidinediones to form the cyclic [4 + 2]adduct (LXXXV).[282] Photochemical oxidation with oxygen in the presence of tetraphenylporphyrin also leads to the cyclic [4 + 2]adduct (LXXXVI). The latter proved to be an active dienophile which readily enters into cycloaddition reactions with cyclodienes.[283]



(LXXXI) (LXXXII) (LXXXIII)

(LXXXIV) (LXXXV) (LXXXVI)

Intramolecular cyclisations are characteristic of thermal reactions of a wide variety of tetraallene sulphides[115] and divinylthiirans.[53] The high-temperature reactions of the latter usually lead to mixtures of 4,5-dihydrothiepins, 2-vinylthiophen, and desulphurisation products. 3-Phenyl-2-vinylthiiran is converted under these conditions into a mixture of 2-phenylthiophen and 2-phenyl-2,3-dihydrothiophen.[284]

The formation of cyclic [3 + 2]adducts has been noted in the homolytic opening of the thiiran ring in the presence of aromatic compounds. For example, benzothiophen has been obtained by the thermolysis of thiiran in chlorobenzene.[285]

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