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The Structure and Methods of Synthesis of Thiirans

A.V.Fokin and A.F.Kolomiets

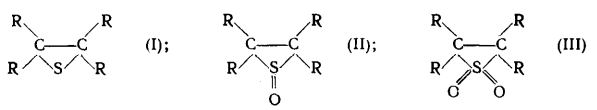
The data presented in the review confirm the earlier results concerning a structural similarity between the two-carbon skeleton of the thiiran ring and the double bond of alkenes.
The available data on the syntheses and structures of thiirans and alkene episulphoxides and episulphones are treated systematically. The methods for the formation of the thiiran ring are classified and synthetic procedures based on homolytic, anionotropic, and cationotropic closure of thiiran rings and on thiiran reactions occurring without the opening of the ring are discussed.
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I. INTRODUCTION

Thiirans (alkylene sulphides or epithioalkanes) are saturated sulphur-containing three-membered heterocyclic compounds with structure (I). The thiiran 1-oxides (II) and 1,1-dioxides (III) can also be included in this group.



(I); (II); (III)

Until recently thiirans were believed to be of purely theoretical interest, their chemistry being investigated to elucidate the nature of three-membered heterocyclic compounds, but in the last few years the attitude towards these substances changed radically. The accumulated information about the properties and reactivities of thiirans made a significant contribution to theoretical organic chemistry and demonstrated the wide scope of their applications in syntheses of polymeric substances, physiologically active compounds, detergents, oil additives, etc.

More than 400 studies have now been made on the properties and methods of synthesis of thiirans. Almost half of these have been discussed in previous reviews [1-9]. The considerable advances achieved in the chemistry of thiirans during the last decade led us to undertake a new survey of the available information about this interesting branch of organic chemistry.

In contrast to previous reviews on thiirans, in the present article attention has been concentrated on a systematic arrangement of the data. The available information about the structures of thiirans is discussed critically, the known methods of thiiran synthesis are classified, and the mechanisms of the closure of thiiran rings are considered. In order to elucidate in greater detail certain problems, analogies have been drawn between thiirans and their heteroanalogues—oxirans and aziridines.

The limited size of the review precluded a detailed description of all the problems involved in the topic under consideration. The present state of thiiran chemistry is described on the basis of publications during the last two decades. Earlier communications are quoted only when necessary to illustrate certain postulates.

II. THE STRUCTURE OF THIIRANS

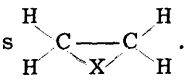
The problems concerning the structure of three-membered cyclic compounds have been the subject of a lively discussion begun by Walsh [10] in 1947, who considered Zimakov's concepts [11] in relation to the characteristics of the structure of oxiran. In the course of the discussion and subsequent studies, significant arguments were adduced, demonstrating the structural similarity between cyclopropane [12] and particularly its heteroanalogues on the one hand and ethylenic hydrocarbons on the other.

One of the first pieces of evidence confirming certain structural analogies between cyclopropane, oxiran, thiiran, and alkenes was obtained by Linnett [13]. The force constants of the C–H bonds in methylene groups, which he calculated from Raman and infrared spectra, proved to be 5 for cyclic compounds and 5.1 for ethylene. The closeness of these values and their considerable difference from the constants of the C–H bonds in the methylene groups of paraffins (4.6) indicate, according to the author, a greater similarity between the valence states of the carbon atoms in cyclopropane and its heteroanalogues to those in ethylenic compounds compared with the corresponding states in paraffins. This conclusion was confirmed by subsequent studies on the structures of cyclopropane heteroanalogues.

The results of electron diffraction studies on aziridine [14,15], oxiran, and thiiran [16] (Table 1) suggest that the transformation of an acyclic compound into a three-membered heterocycle is accompanied by a rearrangement of the hybrid states of the atoms forming the ring. The C–C bond lengths in all these compounds are similar and intermediate between the C–C bond length in diamond (1.544 Å) and the C=C bond length in ethylene (1.344 Å). It is interesting to note that the distance between the carbon atoms in cyclopropane heteroanalogues is close to the length of the central bond in butadiene (1.483 Å), which can be regarded, according to Dewar's ideas [17], as a simple sp^2–sp^2 σ bond. The C–H bond lengths in cyclopropane heteroanalogues are similar to the corresponding bond lengths in ethylene (1.086 Å), while the HCH angle exceeds by 6.5–6.9° the tetrahedral angle and approaches the HCH angle in ethylene. The lengths of the bonds

between the carbon atoms of the ring and the heteroatom are equal or slightly greater than the lengths of the corresponding bonds in acyclic amines, ethers, and sulphides.

The above data on the structures of cyclopropane heteroanalogues suggest that their molecules contain two types of *endo*-bonds. The two-carbon skeleton has an enhanced *s* character compared with the saturated C–C bond. According to its fundamental parameters, this bond approaches the σ bond in ethylene. The remaining two *endo*-bonds are formed from the p electrons of the heteroatom and the partly hybridised p electrons of the carbon atoms. This results in a type of overlapping of atomic orbitals which is intermediate between the lateral π-bonding and terminal σ-bonding overlapping.

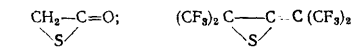
The principal parameters of the molecules .

Parameter	X		
	NH	O	S
Bond length, Å			
C–C	1.480	1.467	1.492
C–H	1.083	1.082	1.078
C–X	1.488	1.436	1.819
HCH angle	116°41′	116°41′	116°00′
CXC angle	—	61°24′	65°48′

The electronic state of the heteroatoms in aziridine, oxiran, and thiiran can be inferred only from certain indirect data. The studies of the ability of three-, four-, and five-membered heterocycles to form a hydrogen bond with phenol [18], of their capacity for complex formation with iodine [19], and of their heats of solution in chloroform [20] indicate an enhanced *s* character of the free electrons of the heteroatom in three-membered heterocycles compared with four- and five-membered heterocyclic compounds and acyclic amines, ethers, and sulphides. This is also indicated by the chemical shifts of the α- and β-CH_2 groups in the NMR spectra of cyclopropane heteroanalogues [21,22]. Thus the formation of a three-membered heterocycle entails a change in the electronic states not only of carbon atoms but also of the heteroatom in the ring.

The enhanced *s* character of the lone electron pairs of the heteroatoms is evidence for the presence of an unusual conjugated system in molecules of cyclopropane heteroanalogues. It is quite likely that the sharp differences between the ring strain energies of cyclopropane on the one hand (25 kcal $mole^{-1}$ [23]) and aziridine, oxiran, and thiiran (14, 13, and 9 kcal $mole^{-1}$ respectively) on the other are due to the stabilisation of the cyclic state in heterocyclic compounds by the π-electrons of the heteroatoms.

The above features of the structures of cyclopropane heteroanalogues are shown most clearly in the series of thiiran compounds owing to the greater covalent radius of the sulphur atom compared with those of the nitrogen and oxygen atoms and the high lability of its $3p$ electrons. The enhanced sp^2–sp^2 character of the C–C bond in thiirans has been confirmed, apart from the data quoted above, by a study of the structure of propylene sulphide [2-methylthiiran] [24]. The CH_3–CH bond length (1.513 Å) is smaller than the C–C bond length in diamond by an amount equal to the difference between the effective covalent radii of the carbon atom in the sp^3- and sp^2-hybrid states, which suggests that the bond is of the sp^3–sp^2 type. The existence of 2-thiiranone [25] and 3-hexafluoroisopropylidene-2,2-bistrifluoromethylthiiran [26],



may be regarded as one of the pieces of evidence confirming the sp^2 hybrid state of the carbon atoms in the thiiran ring.

The enhanced *s* character of the C–C bond in thiirans is due to the pronounced p character of the C–S bond. In the ethylene sulphide [thiiran]–ethylene sulphoxide–ethylene sulphone series the inclusion of the sulphur p electrons in additional valence bonds lowers the stability of the thiiran ring and alters the nature of the C–C bonds. The C–C bond length calculated from microwave spectra of ethylene sulphone [27] proved to be 1.586 ± 0.01 Å. This suggests that the carbon atoms of the thiiran ring in ethylene sulphone are in the sp^3 hybrid state.

The pronounced p character of the C–S bond is responsible for the pseudo-unsaturated character and the electrophilic properties of thiirans, which has been confirmed by spectroscopic studies on phenylthiirans substituted in the *para*-position [28]. It is quite likely that vacant $3d$ orbitals of the sulphur atom contribute to the π-electron density of the thiiran ring, because a satisfactory agreement has been achieved between experimental and calculated spectroscopic characteristics when account was taken of not only $3s$ and $3p$ but also $3d$ levels of this element [29].

The enhanced pseudo-unsaturated character of the thiiran ring is responsible for its greater stability compared with the oxiran ring, which has been confirmed by a comparative study of the behaviour of p-methoxyphenyloxiran and p-methoxyphenylthiiran under solvolysis conditions [30]. The greater stability of the thiiran ring compared with the oxiran ring is also indicated by lower strain energy of the thiiran ring (relative to the oxiran ring), determined from the difference between the heat of formation and the sum of the individual bond energies [32], and by the lower strain entropy and enthalpy of thiiran compared with oxiran [30] (59.19 e.u. and 38.44 kcal $mole^{-1}$ for oxiran and 21.47 e.u. and 17.62 kcal $mole^{-1}$ for thiiran).

The thiiran molecule can be represented, like those of aziridine and oxiran, by an asymmetric rotator with the symmetry plane perpendicular to the plane of the C–C ring. For this reasons, its 2,3-disubstituted derivatives exist as two geometrical isomers (*cis*- and *trans*-). The internally compensated *cis*-isomers of the symmetrical 2,3-disubstituted thiirans are optically inactive. Monosubstituted thiirans, the *trans*-isomers, and the *cis*-isomers of 2,3-disubstituted thiirans can be obtained in an optically pure state [31–35].

III. METHODS FOR THE SYNTHESIS OF THIIRAN COMPOUNDS

The reactions of acyclic or certain cyclic compounds leading to the formation of three-membered sulphur-containing rings are most frequently used to synthesise thiirans. However, methods based on reactions of thiirane derivatives without ring opening have also been used successfully in many instances.

1. METHODS BASED ON THE HOMOLYTIC CLOSURE OF THIIRAN RINGS

a. Addition of Sulphur to Alkenes

The early attempts to add atomic sulphur formed in the pyrolysis of diethyl tetrasulphide to ethylene, propene, and cyclohexene were relatively ineffective [36]. The yield of thiiran derivatives did not exceed several per cent in view of the low yield of atomic sulphur in the reaction

$$R{-}CH{=}CH_2 + C_2H_5(S)_4C_2H_5 \xrightarrow{150^\circ} R{-}\underset{\diagdown S \diagup}{CH{-}CH_2}$$

Best results were obtained using carbon oxide sulphide as a source of atomic sulphur [37-39]. Irradiation of a mixture of carbon oxide sulphide in ethylene or propene with ultraviolet light (255–229 nm) at 25°C leads to the formation of the corresponding thiirans in a yield of 60–100% relative to the olefin which has reacted. However, the degree of conversion of alkenes in such reactions is very low. 1,2-Epithiobutene [2-ethylthiiran], *cis*- and *trans*-butylene sulphides, and isobutylene sulphide [2,2-dimethylthiiran] were obtained in low yields under the same conditions. Only butadiene reacts anomalously under the conditions of photolytic sulphur addition, giving rise to vinyldithiacyclobutane and thiophen [40].

Under photolysis conditions, hexafluorocyclobutene is readily acted upon by atomic sulphur [41]. The resulting perfluorocyclobutylene sulphide is unstable and has a half-life of about 1 min at 20°C. Tetrafluoroethylene reacts at 445° with elemental sulphur to form a mixture of tetra-, tri-, and mono-sulphides [42,43]. Tetrafluorothiiran was obtained under these conditions in a yield of 2%.

The formation of thiirans on reaction with sulphur under photolysis conditions is a typical free-radical process. The sulphur atom in both the singlet and triplet states enters readily into this reaction [38], which proceeds with a low activation energy [39]. Under the reaction conditions, the formation of the thiiran is accompanied by its photolytic decomposition, which is the reason for the low degree of conversion of alkenes in this reaction.

$$R{-}CH{=}CH_2 + S^* \rightarrow R{-}\underset{\diagdown S \diagup}{CH{-}CH_2} \xrightarrow{S} R{-}CH{=}CH_2 + S_2$$

A careful study [43] has shown that the high-temperature reaction of tetrafluoroethylene with sulphur proceeds via a stage involving the formation of difluorocarbene:

$$CF_2{=}CF_2 \xrightarrow{>400^\circ} :CF_2 \xrightarrow{S} CF_2{=}S \xrightarrow{:CF_2} \underset{\diagdown S \diagup}{CF_2{-}CF_2}$$

b. Condensation of Sulphur and Its Compounds with Diazoalkanes

This reaction was historically the first process whereby it was possible to obtain thiirans as individual compounds. Before its discovery, the formation of thiirans in reactions was inferred only from the evolved polyalkylene sulphide [44,45] and it was believed that these substances do not exist in a monomeric state [45].

In 1916–1920 Staudinger and coworkers [46-48] reported the formation of thiirans in the reaction between diazoalkanes and aromatic thioketones, thiophosgene, and thiobenzoyl chloride:

$$RR'CN_2 + R''R'''C{=}S \rightarrow \underset{\diagdown S \diagup}{RR'C{-}CR''R'''}$$

The reactions proceed smoothly at room temperature and the final products are isolated in high yields after the evolution of nitrogen ceases.

The scope of Staudinger's method for the synthesis of thiirans and also some of the limitations in their applications have been determined in studies by Schonberg and coworkers [49-56]. According to their data, thiobenzophenones, thioxanthene, and other aromatic cyclic thioketones react unambiguously only with diaryldiazomethanes. The reactions with diazomethane, diazoethane, and ethoxycarbonyldiazomethane result in the formation of 1,3-dithiolans:

$$Ar_2C{=}S + R{-}CHN_2 \rightarrow \begin{array}{c} Ar_2C{-}CAr_2 \\ | \quad\quad | \\ S \quad\quad S \\ \diagdown CH \diagup \\ | \\ R \end{array}$$

Thiirans have also been obtained by the reaction of diaryldiazoalkanes with other thiono-compounds, including diphenyl trithiocarbonate, the chlorides of phenyldithiocarbonic and phenylthiocarbonic acids, and xanthogen sulphide:

$$Ar_2CN_2 + S{=}\underset{\diagdown Y \diagup}{\overset{\diagup X \diagdown}{C}} \rightarrow Ar_2C\underset{\diagdown S \diagup}{\overset{\diagup X \diagdown}{-C}}$$

(X=SC_6H_5; Cl; SC(S)OR; OC_6H_5; Y=SC_6H_5; OC_6H_5; OR)

The reaction of diazoethane with thiocarbonic acid derivatives is similar to that of diaryldiazomethanes [52]. However, in this case too diazomethane reacts anomalously with formation of 1,3-dithiolan derivatives.

Aliphatic thioketones have recently been successfully introduced into the reaction with diazoalkanes [57]. In this case the reaction involving diazomethane yielded the normal condensation products—2,2-disubstituted thiirans:

$$RR'C{=}S + CH_2N_2 \rightarrow \underset{\diagdown S \diagup}{RRC{-}CH_2}$$

Cycloalkenethiones react with diazoalkanes to form a complex mixture of products from which thiirans, dithiolans, and alkenes were isolated [58]. The reactions of diazomethane [59], diazoethane, and dimethyldiazomethane [60] with thioketones and thio- and dithio-carboxylates led to the isolation, together with thiirans, of olefins and 1,2,3- and 1,3,4-thiadiazolins. In certain cases, for example in the reaction between fluorenethione and diphenyldiazomethane [64], the only products were alkenes.

In contrast to aromatic thioketones [65], hexafluorothioacetone readily forms 2,2-bis(trifluoromethyl)thiirans not only on reaction with diphenyldiazomethane but also with ethoxycarbonyldiazomethane [61]. The fluoride of perfluorothiopropionic acid also reacts with diazoalkanes, but the resulting thiirans readily undergo spontaneous sulphur elimination and the final outcome of such reactions is the formation of alkenes [62]:

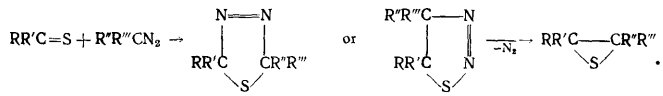
$$CF_3CF_2C(S)F + (C_6H_5)_2CN_2 \rightarrow \underset{\diagdown S \diagup}{CF_3CF_2CF{-}C(C_6H_5)_2} \xrightarrow{-S} CF_3CF_2CF{=}C(C_6H_5)_2$$

Thiocarbonyl fluoride enters into exchange reactions with diphenyldiazomethane [43,63], which leads to the formation of tetraphenylthiiran:

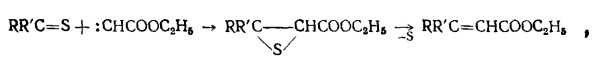
$$2(C_6H_5)_2CN_2 + CF_2{=}S \rightarrow \underset{\diagdown S \diagup}{(C_6H_5)_2C{-}C(C_6H_5)_2}$$

The mechanism of the complex reactions in thiono-compound–diazoalkane systems has not been investigated thoroughly. The hypothesis that the diazoalkane initially

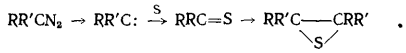
undergoes the Pechmann condensation with the thiono-compound to form 1,2,3- or 1,3,4-thiadiazolin, whose decomposition with liberation of nitrogen is accompanied by a free-radical closure of the thiiran ring at the C–C or C–S bond, is quite likely:



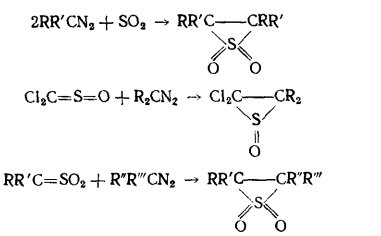
All the reactions in such systems can also be accounted for on the hypothesis of the initial formation of carbenes in the reaction mixture. The addition of the latter to the C=S bond can lead to the formation of both a thiiran and a 1,3-dithiolan. The latter mechanism of the formation of thiirans from thiono-compounds and diazoalkanes is confirmed by the reactions of thioketones with ethoxycarbonylcarbene [65]:



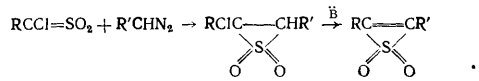
and also by the reactions of diazoalkanes with sulphur [64,66], which take place readily under the usual conditions of the above syntheses, where the formation of a carbene is the most likely process:



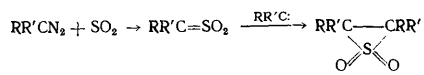
The ability to condense with coordination-unsaturated sulphur compounds is a common property of diazoalkanes. Apart from thiono-compounds and sulphur, sulphur dioxide [67–76] and sulphenes [77–80] react smoothly with diazoalkanes:



These reactions do not always proceed unambiguously. In certain cases alkenes [71] or derivatives of 1,3,4-thiodiazines are the side products of these processes [70,79]. 3-Alkyl-2-halogenothiiran 1,1-dioxides are converted under the reaction conditions into thiiren 1,1-dioxides:

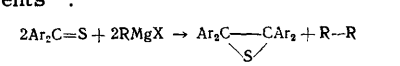


The mechanism involving the preliminary formation of carbenes is regarded as the most likely pathway to the formation of the thiiran 1,1-dioxide ring [76]:

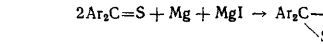


c. Condensation of Thiones with Carbenes

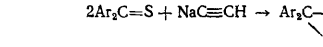
In 1927 Schonberg et al. reported the formation of tetra-arylthiirans in reactions of thiobenzophenones with Grignard reagents [81]:



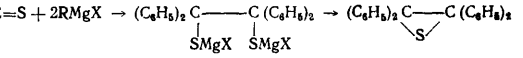
The results of this reaction is independent of the nature of the organomagnesium compound: thioketones react readily with alkyl- or aryl-magnesium bromides or iodides and are converted into thiirans in high yields. Similar results were obtained on treating thioketones with metallic magnesium in the presence of magnesium iodide [82]:



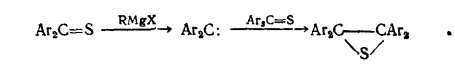
Later the formation of thiirans was observed on treating thioketones with sodium acetylide [83]:



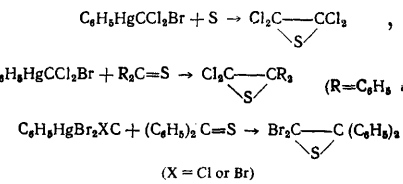
Moreau [84] believes that dithiobenzopinacol is an intermediate in the reaction between thiobenzophenone and Grignard reagents:



However, a recent investigation of these reactions [85] led to the conclusion that the primary step is the elimination of sulphur from the thioketone with formation of a carbene:

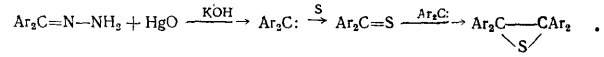


The condensation of carbenes with sulphur and thiones have been widely investigated by Seyferth et al. [86], who used various phenyl(trihalogenomethyl)mercury compounds as a source of carbenes. The bromodichloro-, dibromochloro-, and tribromo-methyl derivatives react smoothly with sulphur, thiophosgene, and thiobenzophenone, forming halogenothiirans:



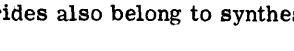
Only phenyl(trifluoromethyl)mercury fails to form a thiiran in the reaction with thiobenzophenone [87].

The marked ability of carbenes to react with elemental sulphur and thiones has been used to develop a simple preparative method for the synthesis of tetra-arylthiirans [88,89]. It consists in treating ketone hydrazones with mercury(II) oxide in the presence of potassium hydroxide and elemental sulphur:



The conversion of phenylmethanesulphonyl chloride into 2,3-diphenylthiiran on heating with triethylamine in methylene chloride or ether probably also involves the formation of a carbene [90].

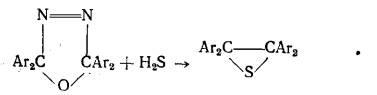
The possibility of synthesising polyfluorothiirans by pyrolytic reactions of fluoro-compounds with formation of difluorocarbene in the presence of sulphur and its compounds has been demonstrated in a number of studies. These syntheses include the high-temperature combination of tetrafluoroethylene with sulphur [43] and the reactions of 2,2,3-trifluoro-2-trifluoromethyloxiran with thiocarbonyl fluoride, thiocarbonyl chloride fluoride, and perfluorothioacyl fluorides also belong to syntheses of this type [49,91–94]:



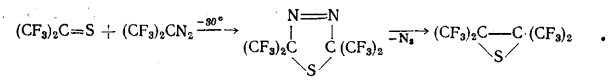
The yield of polyfluorothiirans under these conditions is usually low owing to the occurrence of side reactions involving the final products, in which they undergo sulphur elimination and isomerisation.

d. Syntheses of Thiirans by the Pyrolysis of Heterocyclic Compounds

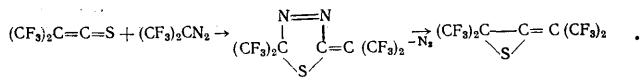
There are at present few examples of these reactions. In 1939 Schonberg and Barakat [95] showed that thiirans are formed in high yields on heating oxadiazines in an atmosphere of hydrogen sulphide:



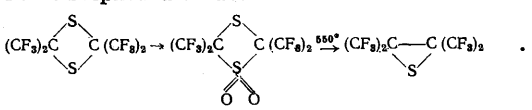
Middleton [26] obtained from perfluorothioacetone and bis(trifluoromethyl)diazomethane under mild conditions 2,2,5,5-tetra(trifluoromethyl)-1,3,4-thiadiazine, which he converted into tetra(trifluoromethyl)thiiran by pyrolysis:



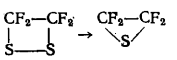
Bis(trifluoromethyl)thioketen reacts similarly to hexafluorothioacetone. The first example of thiirans whose ring is linked to the substituent by a C=C bond was obtained in this way:



Middleton also developed a method for the preparation of perfluoro-derivatives of tetra-alkylthiirans from thioketone dimers [96]. By oxidising the latter with chromium trioxide in nitric acid, he obtained sulphones which he converted into thiirans by pyrolysis over platinum in an atmosphere of sulphur dioxide:



Tetrafluorothi-iran was obtained together with other products also in the pyrolysis of tetrafluorodithiacyclobutane [94]:

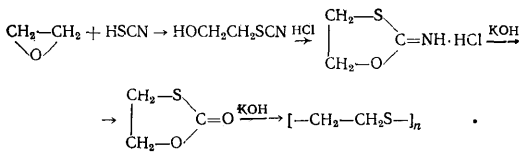


There is no doubt that the above syntheses of thiirans have a free-radical mechanism. In many of these, except the last, a homolytic closure of the thiiran ring with formation of a C–C bond takes place.

2. REACTIONS INVOLVING THE ANIONOTROPIC SUBSTITUTION OF THE OXYGEN ATOM IN OXIRANS BY A SULPHUR ATOM

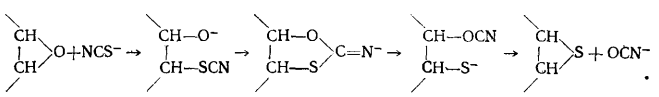
The syntheses of thiirans by the reaction of their oxygen analogues with alkali metal thiocyanates and thiourea have now become classical and are recommended for use on a preparative scale as the most convenient procedures of this kind [97].

The history of the devlopment of this method has been described in very great detail in Weissberger's review [7] and one need only note that all the stages of the conversion of oxiran into thiiran in the reaction of the former with thiocyanates were first described in 1937 by Sergeev and Kolychev [98]. Having obtained 2-thiocyanatoethanol by the reaction of oxiran with thiocyanic acid, the authors converted it almost quantitatively into the hydrochloride of ethylene monothiocarbonate imine [the hydrochloride of 2-imino-1,3-oxathiolan]. The latter was converted on treatment with an equivalent amount of alkali into ethylene monothiocarbonate [2-oxo-1,3-oxathiolan] and with an excess of alkali into poly(ethylene sulphide).



On the basis of the results of Sergeev and Kolychev [98], Ettlinger [99] proposed a mechanism for the reaction of oxirans with alkali metal thiocyanates whose validity was proved rigorously by van Tamelen [100] and independently by Price and Kirk [31].

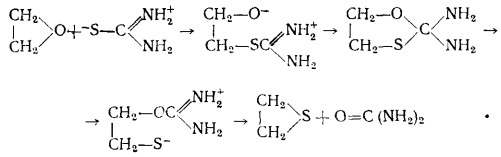
Ettlinger believes that the formation of thiirans in these reactions involves the nucleophilic opening of the oxiran ring by the thiocyanate anion, the isomerisation of the resulting alkoxide anion via an intermediate cyclic state into a thiolate anion, and the conversion of the latter into the thiiran with elimination of the cyanate anion:



According to this mechanism, the conversion of the oxiran ring into a thiiran ring should involve two Walden inversions in the *trans*-opening and *trans*-closure of the ring. Only oxirans derived from acyclic and unstrained cycloalkenes can be expected to give rise to thiirans. Those derived from strained cycloalkenes should not react, because the formation of an intermediate bicyclic ion with two strained rings by *trans*-closure is impossible.

Van Tamelen showed that cyclohexenylene oxide {cyclohexeno[*b*]oxiran} reacts with potassium thiocyanate, 2-thiocyanatocyclohexanol, and the hydrochloride of cyclohexenylene monothiocarbonate imine {the hydrochloride of 2-iminocyclohexeno[*d*]1,3-oxathiolan} and is smoothly converted into cyclohexenylene sulphide {cyclohexeno[*b*]thiiran} in the presence of bases. Cyclopentenylene sulphide {cyclopenteno[*b*]thiiran} is not formed from the corresponding oxiran and potassium thiocyanate. Price and Kirk showed that an intermediate iminoether is formed in the reaction between 2-methyloxiran and potassium thiocyanate, having isolated it in the form of the 4-nitrobenzoate. Moreover they obtained L(–)-2,3-dimethylthiiran by the reaction of D(+)-2,3-dimethyloxiran with potassium thiocyanate. All these findings are consistent with Ettlinger's ideas concerning the mechanism of the conversion of oxirans into thiirans.

A similar mechanism for the formation of thiirans in the reaction of oxirans with thiourea was proposed by Culvenor et al.[101]:



Bordwel and Andersen[102] believe that the transition state in this process is formed from a neutral molecule of *S*-(2-hydroxyalkyl)isothiourea and not from the 2-alkoxyisothiuronium ion. They base this view on the observation that high yields of thiirans are obtained only in media with a pH close to 7.

The mechanisms proposed by Ettlinger and Culvenor for the conversion of oxirans into thiirans were confirmed further by recent studies on the reactions of potassium thiocyanate and thiourea with optically active 2-phenyloxiran, 2-methyl-3-phenyloxiran, and 2,3-diphenyloxiran[35]. It was shown that the conversion of the above compounds into thiirans entails the inversion of the configuration of the initial molecule at both carbon atoms of the ring, which can only be understood when account is taken of the formation of cyclic transition states in the reaction.

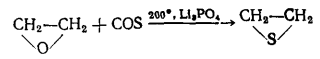
The scope of the synthesis of thiirans from oxirans by reaction of the latter with alkali metal thiocyanates or thiourea is very great. Thiiran and 2-methylthiiran[103-105], the *cis*- and *trans*-isomers of 2,3-dimethylthiiran[31,34], 2,3-dimethylthiiran[103], 2-hexylthiiran[106], 2-diethoxymethylthiiran[107], 2-vinylthiiran[108], cyclohexeno[*b*]thiiran and its derivatives[103,108], 2-chloromethylthiiran[103], alkoxy- and aryloxy-methylthiirans[109-113], alkylthiomethyl- and dialkylaminomethyl-thiirans[100,113], 2-phenylthiiran and its ring-substituted derivatives[28,35,114,115], esters of epithiodienecarboxylic acids [thiiranylalkenecarboxylic acids][116], 4-piperidinylthiirans[33], and other compounds have been obtained by this method.

The extensive studies on these reactions by Culvenor et al.[108] showed that only thiirans with electronegative groups attached to the thiiran ring cannot be obtained by this method because of the ease of elimination of sulphur in the course of their formation. However, later investigations established that under certain conditions of synthesis even thiirans which readily lose sulphur can be obtained from oxirans. For example, *cis*- and *trans*-2,3-diphenylthiirans were obtained in yields up to 90%[117] under the conditions of the Bordwel synthesis by the initial condensation of the corresponding oxirans with thiourea sulphate and subsequent cautious alkaline treatment of the resulting isothiuronium salts.

The yields of thiirans in the reactions of oxirans with alkali metal thiocyanate of thiourea are 30–80% and depend significantly on the process conditions. The reactions are usually carried out at 0–20°C under homogeneous conditions, using water, lower alcohols[101-103,108], and mixtures of alcohol and acetic acid[118] as solvents. According to patent data[119], a higher yield of thiirans is achieved when anhydrous polar solvents are used.

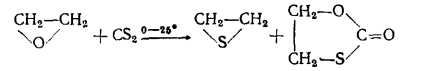
Ammonium thiocyanate, aryl- and diaryl-thioureas, thiocarboxylic acid amides, and certain thiocarboxylic acids have been used instead of alkali metal thiocyanates and thiourea[24,103]. The reactions with these substances take place under the conditions of the synthesis of thiirans from oxirans by reaction with thiourea or alkali metal thiocyanates.

Industrial methods for the synthesis of thiirans from their oxygen analogues and readily available sulphur-containing compounds, such as carbon oxide sulphide and carbon disulphide, are now being developed. Durden et al.[120] showed that at 150°C oxiran forms a copolymer with carbon oxide sulphide in the presence of bases. However, when these substances are brought into contact over a basic catalyst under more severe conditions (at about 200°C), thiiran is formed. The best catalyst for these reactions proved to be trilithium phosphate:



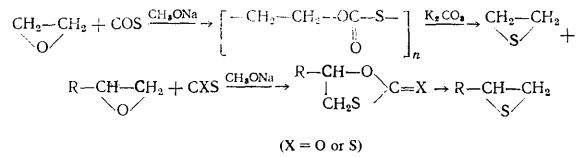
According to patent data, the formation of thiirans from oxirans and carbon oxide sulphide or carbon disulphide in the vapour phase is catalysed by sodium fluoride, its mixtures with other sodium halides, the halides of other alkali and alkaline earth metals, alkaline earth metal oxides, and alkali metal sulphides[121-123]. The yield of low-boiling thiirans reaches 90% in relation to the oxiran which has reacted.

Thiiran can be obtained in yields up to 80% from oxiran and carbon disulphide in the presence of a mixed catalyst consisting of partly hydrated lithium chloride and triethylsulphonium iodide[124,125]. Ethylene monothiocarbonate-[2-oxo-1,3-oxathiolan] is a side product:



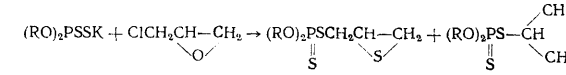
Somewhat less satisfactory results were obtained when the reaction was catalysed by lithium chloride in the presence of hydrogen sulphide[126]. The main products in the presence of these catalysts are ethylene mono- and dithiocarbonates [2-oxo-1,3-oxathiolan and 2-oxo-1,3-dithiolan] and thiiran is formed in yields up to 20%.

When the catalyst is sodium methoxide, the above reactions give rise to polymeric substances[127] or alkylene mono- and di-thiocarbonates [alkyl derivatives of 2-oxo-1,3-oxathiolan or 2-oxo-1,3-dithiolan][128,129], which can be converted into thiirans on heating with alkaline agents:



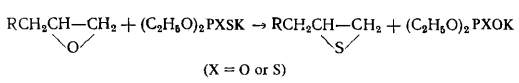
(X = O or S)

Interesting reactions involving the conversion of 2-chloromethyloxiran into derivatives of 2-methylthiiran have been described by Schroder[130]. According to his data, the reactions of 2-chloromethyloxiran with an excess of salts of *OO*-dialkylphosphorodithioic acid in water lead to *OO*-dialkyl *S*-thi-iranylmethyl phosphorodithioates. These data were confirmed by Nuretdinova[131], who also showed that small amounts of thietan derivatives are formed in the reactions together with thiirans:



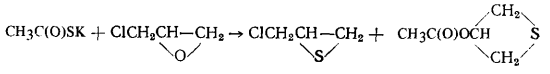
Arbuzov and Nuretdinova[132,133] studied the reactions of 2-chloromethyloxiran, 2-methyloxiran, glycidyl phenyl ether [2-phenoxymethyloxiran], and *OO*-diethylphosphonomethyloxiran with thiolic acid salts. Potassium salts of

phosphorothioic and phosphorodithioic acids react smoothly with oxirans and the corresponding thiirans were isolated in yields of 40–55%:

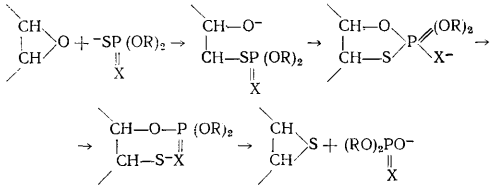


(X = O or S)

On reaction with the triethylammonium salt of *OO*-diethylphosphorodithioic acid, 2-chloromethyloxiran is also converted into 2-chloromethylthiiran. However, the reaction with thioacetic acid salts gives rise to a mixture of 2-chloromethylthiiran and 3-acetoxythietan:



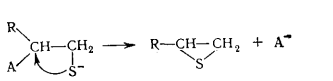
The mechanism of the conversion of oxirans into thiirans by the reactions with thiolic acid salts is satisfactorily consistent with the scheme devised by Ettlinger and Culvenor:



The validity of this scheme is also confirmed by the susceptibility of *S*-(2-hydroxyethyl) esters of thiocarboxylic and phosphorothioic acids [134] to cleavage by bases with formation of thiirans or their polymers. The formation of thiirans in the acid-catalysed reaction of oxirans with phosphine sulphides [135] also proceeds in accordance with Culvenor's mechanism

The marked influence of the polarity of the solvent must be regarded as a characteristic feature of the above methods of synthesis of thiirans from oxirans. In an aqueous homogeneous medium the process is usually exothermic. Heat is required for the reaction in less polar solvents. This is due primarily to the specific features of the anionotropic reactions in ionic alkoxide–thiolate rearrangements and in the closure of the thiiran ring. The driving force in the first process is provided by the high energy of the thioacyl linkage. The favourable effect of the polar solvent is in this case evident, as in other instances of the nucleophilic substitution at coordination-unsaturated carbon and phosphorus atoms.

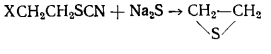
The completion of the stage involving the formation of thiiran rings from oxiran rings is very similar in all the cases considered. The conversion of the thiolate anion into thiiran can be regarded as anionotropic ring closure with elimination of the weaker nucleophile (the alkoxide anion):



The anionotropic closure of the thiiran ring is promoted by the comparatively low enthalpy associated with the thiiran ring strain, the low capacity for solvation and hence the high reactivity of the thiolate anion, and the marked influence of the solvolysis of the eliminated alkoxide anions.

3. THE ANIONOTROPIC FORMATION OF THIIRANS FROM 2-SUBSTITUTED ALKANETHIOLS AND THEIR DERIVATIVES

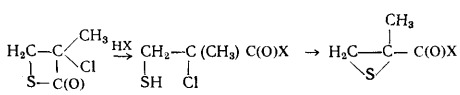
Historically the first example of these reactions is the syntheses of thiirans by Delepine's method [136–140], which were described soon after Staudinger's reports of the syntheses of tetra-arylthiirans. Delepine's method made it possible to obtain for the first time the lowest thiirans. The syntheses are based on the reaction of vicinal dithiocyanato- and halogenothiocyanato-alkanes with sodium sulphide:



Thiiran and 2-methylthiiran [136–141], tetramethylthiiran [142], thi-iranylalkanecarboxylic acids [143], and cyclohexeno[*b*]thiiran and its derivatives [144] were obtained by this method. The reactions are usually carried out in lower alcohols, aqueous alcohol, or water. The usual alkaline agents can be used instead of sodium sulphide [143,145]. Thi-iranylalkanecarboxylic acids are synthesised by treating the corresponding vicinal dithiocyanato-derivatives with sodium hydroxide [143]. The yield of the lowest thiirans in syntheses by Delepine's method is usually low owing to their polymerisation in the course of their formation. However, substances which are relatively stable under the conditions of the syntheses were obtained in virtually quantitative yields [142]. Delepine's method can be of practical interest for the conversion of higher olefins into thiirans in view of the availability of effective methods for the formation of vicinal chlorothiocyanato-alkenes.

The syntheses of thiirans from 2-halogenoalkanethiols, analogous to the halogenohydrin syntheses, were published for the first time in 1939. [146–148] A high yield of thiiran (up to 98%) was obtained under relatively mild conditions by adding alkali to chloroethanethiol, keeping the pH of the medium at about 7.5–9.5. Cyclohexeno[*b*]thiiran and cyclopenteno[*b*]thiiran (yield up to 80%), [100] as well as 2-mercaptomethylthiiran and 2-mercaptomethyl-2-methylthiiran [149] were obtained by this method under similar conditions.

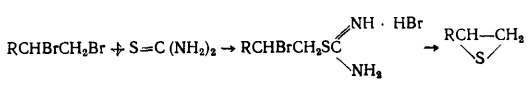
The reaction has been widely used by Knunyants and coworkers [150–156] in the syntheses of thioglycidic acids and their esters and amides. Numerous attempts to obtain these compounds by the reaction of glycidic acid derivatives with potassium thiocyanate or thiourea [104,157], by treating vicinal dithiolacetates with bases [158,159], and by the reaction of thioketones with chloroacetates [160] proved to be unsuccessful. The simplest examples of compounds of this series were obtained for the first time in good yields by treating the thiolactone of α-chloroisobutyric acid with ammonia and amines [150], with a mixture of alcohol and triethylamine [151], or with a dilute solution of alkali [152]. The reactions involves the preliminary opening of the thiolactone ring:



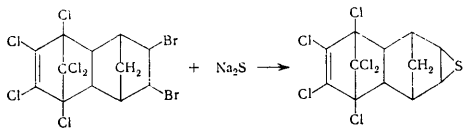
(X=OCH$_3$; OH; NRR')

Similar compounds have also been synthesised in yields up to 90% by mild alkaline treatment of derivatives of α-chloro-β-mercaptocarboxylic acids [153–156] obtained by the hydrolysis of the corresponding acyl derivatives.

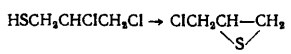
2-Halogenoalkylisothiuronium salts, formed by the reaction of vicinal dihalogenoalkanes with thiourea, react similarly to 2-halogenoalkanethiols [161]:



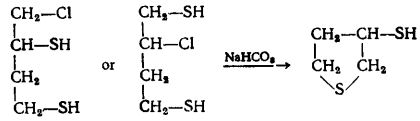
The conversion of vicinal dihalogenoalkanes into thiirans by reaction with sodium sulphide probably involves the formation of 2-halogenoalkanethiols [162]:



The mild conditions in the formation of the thiiran ring in the alkaline treatment of 2-halogenoalkanethiols make it possible to obtain thiirans containing highly reactive groups, for example 2-chloromethylthiiran [163]:

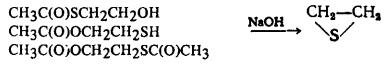


The reactions of 2-halogenoalkanethiols usually proceed unambiguously and the yield of products exceeds 70%. An anomalous reaction was observed only in the cyclisation of 3-chloro-1,4-dimercaptobutane and 4-chloro-1,3-dimercaptobutane [149], where 3-mercaptothiolan was isolated instead of the expected 2-(2-mercaptoethyl)thiiran:

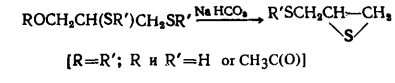


Thus the scope of the synthesis of thiirans from 2-halogenoalkanethiols is very great. The method makes it possible to obtain thiirans derived from strained cycloalkenes and thioglycidic acids, which are not formed in other synthesis.

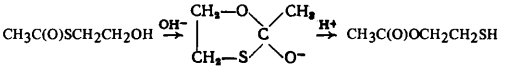
The first reports of the syntheses of thiirans from *O*-acetyl, *S*-acetyl, and *OS*-diacetyl derivatives of 2-mercaptoalkanols were published in 1949: [164-166]



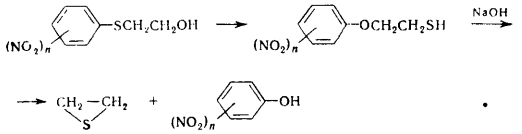
Partly or fully acylated 2,3-dimercaptopropanol was converted by this method into 2-mercaptomethylthiiran or into 2-acetylthiothiiran:



After analysing the above studies [164-166], Culvenor et al. [101] concluded that the formation of thiirans in these and similar instances known at the time is a consequence of the high capacity of 2-substituted thiols for isomerisation. They believe that the conversion of acylthioalkanols into thiirans is due to their marked ability to undergo anionotropic reactions:

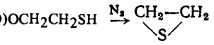


Hence it followed that a wide variety of mercaptoalkanol derivatives of the type $RSCH_2CH_2OH$, in which R is an electronegative group with a coordination-unsaturated central atom, can be converted into thiirans. This was in fact confirmed by Culvenor et al. [101] for the reaction of 2-hydroxyethyl nitrophenyl sulphides with bases:



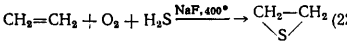
Culvenor's ideas stimulated extensive studies on the above reactions and were confirmed subsequently. Ethylene monothiocarbonates were decomposed by alkali [167], and thiiran could be synthesised in 70–80% yield by treating them with sodium methoxide. Cyclopenteno- and cyclohexeno-[*b*]thiirans were obtained in high yields from *trans*-2-acetylthiocyclopentyl acetate and *trans*-2-acetylthiocyclohexanol [168]. The same compounds were obtained [169] by the alkaline decomposition of *trans*-2-acetylthiocycloalkyl toluene-*p*-sulphonates. Doyle et al. [149] investigated the syntheses of thiirans from the triacetates of the dimercapto-derivatives of isobutyl, pentyl, hexyl, and decyl alcohols. Fully acylated 6-mercaptoglucose was converted into thiiran by treatment with sodium methoxide [170]. Similar compounds were also obtained by the alkaline decomposition of *S*-acyl-*O*-tosyl derivatives of carbohydrates [172-174]. The synthesis of thiirans from *O*-(2-mercaptoalkyl) esters of *O*-alkyl- and *O*-arylcarbonic and arylcarbamic acids and from *S*-(2-hydroxyalkyl)esters of *O*-alkylthiocarbonic and arylthiocarbamic acids has been patented [171]. The best yields of thiiran (67–80%) was obtained from the 2-mercaptoalkyl esters by treating the latter with sodium methoxide. When aqueous alkalis are used, the yield depends on the nature of the thiirans formed and varies from 25 to 85%.

A catalytic method for the conversion of 2-mercaptoalkyl acetates into thiirans was developed recently [175]:

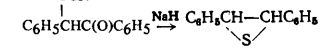


The esters are supplied to the reaction zone in a mixture with xylene in an atmosphere of nitrogen. The catalyst is based on aluminium with added sodium, iron, and silicon oxides. The degree of conversion of 2-mercaptoethyl acetate is 85% and the yield of thiiran reaches 70.5%.

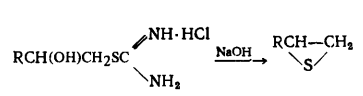
According to Harding et al. [165], 2-methylthiiran is obtained in low yield when 1,2-dimercaptopropane is treated with alkali. However, under the usual conditions 2-mercaptoalkanols are not converted into thiirans. A high-temperature alkaline cyclisation of monothioethylene glycol probably occurs when thiiran is obtained from ethylene, hydrogen sulphide, and oxygen [176]:



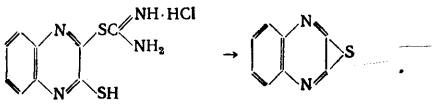
Like *S*-acyl derivatives of mercaptoalkanols, 2-thiocyanatoethanol [98] and 2-thiocyanatocyclohexanol [100] can be converted into thiirans. Decyl thiocyanate reacts similarly in the presence of sodium hydride [177] and a 2-hydroxylalkylisothiuronium salt:



or on treatment with alkali [178,179]:

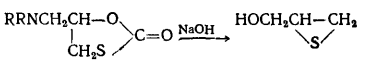


The hydrochloride of 3-isothiuronium-2-mercaptoquinoxaline is converted into thiiran even on crystallisation from dimethylformamide [180]:

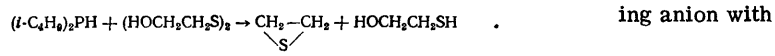


In the presence of bases thiirans are formed readily not only from thiocyanatoalkanols but also from their acyl derivatives [181].

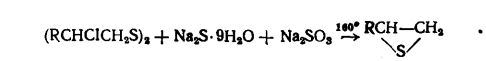
The derivatives of thiocyanatoalkanols, formed when cyclic alkylene carbonates are cleaved by alkali metal thiocyanates, undergo a spontaneous transformation into thiirans [182-184]. The mechanism of these reactions is analogous to that of the formation of thiirans from oxirans. The yield of thiirans reaches 65%. Cyclic alkylene monothiocarbonates [alkyl derivatives of 2-oxo-1,3-oxathiolan] are converted into thiirans in the presence of bases at 200°C. [185,186] Treatment of *NN*-dialkylaminomethyl derivatives of cyclic ethylene monothiocarbonates [2-oxo-1,3-oxathiolans] with alkali leads to the formation of 2-hydroxymethylthiiran [187]:



The last groups of reactions to be considered comprises those of 2-substituted polythio-compounds. The reduction of di-(2-hydroxyethyl) disulphide with di-isobutylphosphine results in the formation of thiiran together with ethylene monothioglycol [188]:

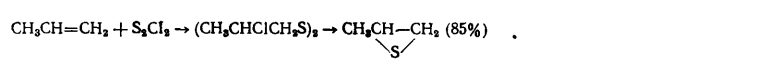


Substituted thiirans have been obtained by the reduction of di-(2-chloroalkyl) disulphides with a mixture of sodium sulphide and sulphite [189]:



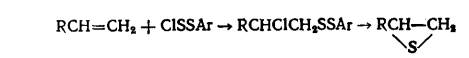
The yield of 2-methylthiiran in this reaction reaches 77%.

A method has been patented for the synthesis of 2-methylthiiran from propene and sulphur monochloride [190]. Di-(2-chloropropyl) disulphide is first obtained in the presence of Friedel–Crafts catalysts and is then cyclised at 80–90°C over a mixture of sodium sulphide and carbonate:



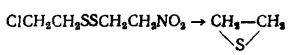
A similar method was used to synthesise bisepithioalkanes from diene hydrocarbons [191]. The reduction of polymeric disulphides to thiirans was achieved in this case with the aid of aluminium in water.

Stereospecific syntheses of thiirans from alkenes have been achieved by the initial condensation of the latter with arenesulphenyl chlorides and the subsequent decomposition of the resulting aryl 2-chloroalkyl disulphides with sodamide or sodium sulphide [192,193]:



Cyclohexeno[*b*]thiiran, *cis*- and *trans*-2,3-dimethylthiiran [192], and thiirans derived from norbornenes [193] were obtained in this way in yields up to 70%.

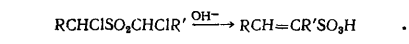
Thiiran was also obtained in the decomposition of 2-chloroethyl 2-nitroethyl disulphide in the presence of potassium benzoate [194]:



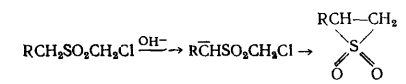
The above transformations of vicinal dithiocyanato- and halogenothiocyanato-alkanes, 2-halogenoalkanethiols, acyl derivatives of 2-mercaptoalkanols, 2-substituted dialkyl disulphides, and 1,2-dimercaptoalkanes into thiirans take place under conditions promoting the formation of 2-substituted thiolate anions. The anionotropic cyclisation of the latter takes place under mild or severe conditions depending on the nature of the substituent in the anion. The anionotropic formation of the thiiran ring takes place most readily in reactions of 2-halogenoalkanethiols.

4. ANIONOTROPIC REACTIONS OF DERIVATIVES OF α-HALOGENOSULPHIDES

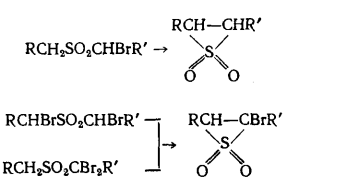
In 1940 Ramberg and Backlung [195] described a rearrangement of α-halogenosulphones accompanied by the elimination of sulphur dioxide and the formation of alkenes. αα-Dihalogenosulphones are converted into alkenyl sulphonates in these reactions:



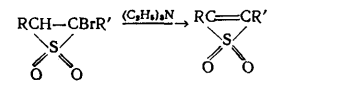
Somewhat later it was suggested on the basis of kinetic studies of these reactions [196] that the primary step in them is the elimination of a proton and cyclisation of the resulting anion with formation of a thiiran 1,1-dioxide:



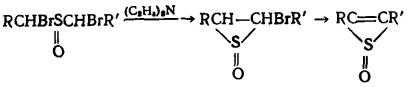
An experimental confirmation of the mechanism of the Ramberg–Backlung rearrangement was obtained by Neureiter and Bordwell [73,75], Paquette and coworkers [197-203], and Carpino and coworkers [204-206], who showed that, when a mixture of α-halogeno-, αα-dihalogeno-, and αα′-dihalogeno-sulphones is heated with triethylamine under mild conditions, the hydrogen halide is split off and thiiran 1,1-dioxides are formed:



Halogenothiiran 1,1-dioxides undergo further reactions under the above process conditions with formation of thiiren 1,1-dioxides:



α-Halogenosulphoxides undergo cyclisation reactions similar to those of α-halogenosulphones [206]:



Syntheses of thiirans from non-oxidised α-halogenosulphides under the conditions of anionotropic reactions have not been described.

5. THE FORMATION OF THIIRANS AS A RESULT OF CATIONOTROPIC REACTIONS OF ACYCLIC COMPOUNDS

Reactions involving cationotropic closure of thiiran rings have been little investigated. However, the data already available on these problems show that the practical applications of such syntheses are promising.

A method for the pyrolytic decomposition of 2,3-dimercaptopropanol to 2-mercaptomethylthiiran, which is of merely historical interest as the first attempt at the synthesis of thiirans by cationotropic reactions, was patented in 1948: [207]

$$HOCH_2CH(SH)CH_2SH \xrightarrow[-H_2O]{} HSCH_2CH\!-\!CH_2 \quad (S)$$

Better results were obtained in the pyrolysis of mercaptoalkanols in the presence of acids. Ethylene monothioglycol is converted into thiiran over potassium hydrogen sulphate at a temperature as low as 120°C. [208] The pyrolytic decomposition of ethylene monothioglycol in the monobutyl ether of triethylene glycol in the presence of t-dodecyl mercaptan [7,7-dimethyloctanethiol] and sulphuric acid leads to the formation of thiiran in 92.3% yield [209]. The initial cleavage of the C–OH bond with formation of the carbonium ion, which cyclises with elimination of a proton, is most likely in these reactions:

$$HOCH_2CH_2SH \xrightarrow[-HO^-]{} \overset{+}{C}H_2\!-\!CH_2SH \xrightarrow[-H^+]{} CH_2\!-\!CH_2 \quad (S)$$

This mechanism of the closure of the three-membered ring, involving the elimination of a cation, may be called cationotropic.

A few other reactions involving the formation of thiiran rings, which can be classified as cationotropic, are also known. Petrov and Sokol'skii [210] described the formation of 2-methylthiiran from chloromethyl ethyl sulphide in anhydrous hydrofluoric acid. Bearing in mind the ease of the heterolytic dissociation of the C–Cl bond in chloromethyl sulphides, the initial compound presumably dissociates with formation of a carbonium ion. The latter undergoes cationotropic cyclisation, facilitated by the $+I$ effect of the methyl group:

$$CH_3\!-\!CH_2\!-\!S\!-\!CH_2Cl \xrightarrow[-Cl^-]{} CH_3\!-\!\overset{H}{\underset{}{CH}}\!-\!\overset{+}{S}\!-\!CH_2 \xrightarrow[-H^+]{} CH_3\!-\!CH\!<\!\begin{matrix}CH_2\\S\end{matrix}$$

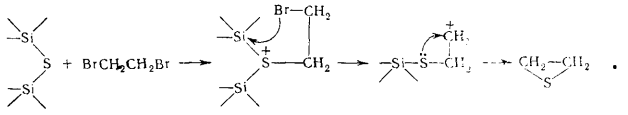
In this case cationotropic reactions do not involve the sulphur atom and the thiiran ring is formed from the carbon skeleton. There are similar reactions between $\alpha\alpha'$-dibromosulphoxides and phosphorus tris(dimethylamide) [211], which most probably involve the preliminary formation of an adduct of the quasiphosphonium type:

$$RCHBrSCHBrR' \;\underset{O}{\overset{\|}{}} + [(CH_3)_2N]_3P \rightarrow RCH\!-\!CHR' \;\underset{O}{\overset{\|}{}} + [(CH_3)_2N]_3PBr_2$$

The unusual reactions of compounds containing both sulphur and silicon with alkyl halides can be regarded as another example of processes of this kind [212]. On heating with dibromoethane, hexamethylcyclotrisilthiane decomposes by the reaction

$$[(CH_3)_2Si]_3S_3 + BrCH_2CH_2Br \rightarrow \underset{S}{CH_2\!-\!CH_2} + (CH_3)_2SiBr_2$$

The reactions in this system involving a preliminary alkylation of the sulphur atom can be attributed to the low strength of the Si–S bond and the high affinity between silicon and halogen atoms. The cationotropic transformations in this reaction involve the sulphur atom:



Reactions involving the cationotropic formation of episulphonium salts are of the same type. In a study by Gladshtein and Soborovskii [213] the methiodide of thiiran was obtained by treating the 2-thiocyanatoethyl ester of dimethylcarbamic acid with methyl iodide. The sulphonium salt formed initially in this reaction decomposes on heating to 100°C with decarboxylation and in the presence of methyl iodide undergoes further reactions:

$$(CH_3)_2NC(O)OCH_2CH_2SCN + CH_3I \rightarrow (CH_3)_2NC(O)OCH_2CH_2S\underset{I}{\overset{CH_3}{<}}CN \xrightarrow[-CO_2]{100^\circ}$$

$$\rightarrow (CH_3)_2NCH_2CH_2S\underset{I}{\overset{CH_3}{<}}CN \rightarrow CH_2\!-\!CH_2 \;\underset{CH_3}{\overset{}{S^+}} \; I^- + (CH_3)_2NCN$$

Judging from the properties quoted by Gladshtein and Soborovskii [213], the structure $(CH_3)_2NCH_2CH_2SCH_3.ICN$ may be attributed to the decarboxylation product. Its conversion into the episulphonium salt is due to the cleavage of the C–N bond by iodine cyanide:

$$(CH_3)_2NCH_2CH_2SCH_3 + ICN \rightarrow \overset{+}{C}H_2\!-\!CH_2 \;\underset{CH_3}{\overset{}{S}} \rightarrow CH_2\!-\!CH_2 \;\underset{CH_3}{\overset{}{S^+}}$$

Knunyants and coworkers [214] described an elegant method for the preparation of episulphonium salts by the reaction of the amides of β-chloro-α-methylthioalkanecarboxylic acids with silver toluene-p-sulphonate. The reactions take place readily in solution in acetonitrile:

$$ClCRR'CR''C(O)NHR''' \rightarrow RR'C\!-\!\!-\!\!-\!CR''C(O)NHR'''$$
$$\quad\quad SCH_3 \qquad\qquad\quad S^+ \quad CH_3$$

They proceed via a stage involving the formation of a carbonium ion, which rearranges to the sulphonium ion.

The above examples demonstrate the ready formation of thiiran rings by cationotropic reactions of 2-substituted thiol derivatives. The cationotropic closure of the thiiran ring can be achieved by the formation of the two-carbon skeleton or the C–S bond of the ring.

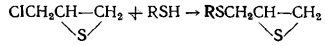
6. THE REACTIONS OF THIIRANS WITH RETENTION OF THE THIIRAN RING

There have been only a few syntheses of thiirans by this procedure. It has been shown in a patent [215] and in another report [113] that 2-acylthiomethylthiirans can be obtained by the selective acylation of 2-mercaptomethylthiiran:

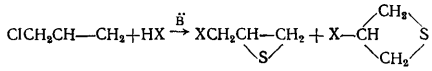
$$HSCH_2CH\!-\!CH_2 \;(S) \xrightarrow{(CH_3CO)_2O} CH_3C(O)SCH_2CH\!-\!CH_2 \;(S)$$

The electrophilic opening of the thiiran ring by acid anhydrides and chlorides takes place under more severe conditions, which makes it possible to obtain high yields of products formed by the acylation of the mercapto-group.

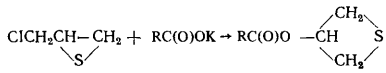
A wide variety of 2-methylthiiran derivatives have also been obtained by the nucleophilic substitution of the halogen atom in 2-halogenomethylthiirans. Unambiguous reactions occur only when 2-chloromethylthiiran reacts with thiophenols [216-219] and aliphatic thiols [220-223]. 2-Alkyl(aryl)methylthiirans are usually synthesised in aqueous media, using sodium and potassium hydroxides as the condensing agents:



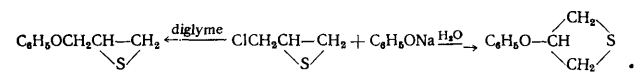
The reactions of 2-halogenomethylthiirans with phenols, alcohols, carboxylic acids, thiolocarboxylic acids, and *OO*-dialkylphosphorodithiolic acids are accompanied by side reactions as a result of the thiiran–thietan rearrangement:



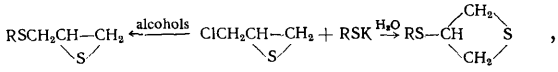
Under certain conditions, the side reaction can predominate and may even be the only one occurring. For example, the reaction of 2-chloromethylthiiran with potassium acetate in acetic acid results in the formation of 3-acetoxythietan and not a thiiran derivative [109]. 3-Acyloxythietans have also been obtained in a similar reaction of 2-chloromethylthiiran with sodium or potassium methacrylate, carbonate, chloroacetate, and benzoate in aqueous solutions [224,225]:



The mode of these reactions depends in many cases on the nature of the solvent employed. According to Sander [226], sodium phenoxides react with 2-chloromethylthiiran in diglyme to form 2-phenoxymethylthiirans, while in an aqueous medium the products are 3-aryloxythietans:



A similar behaviour was demonstrated by Arbuzov and coworkers [225,227-234] in reactions of *OO*-dialkylphosphorodithioate and thioacetate salts with 2-chloromethylthiiran. In aqueous solutions they observed the isomerisation of the thiiran ring to the thietan ring, while in anhydrous alcohols the main products were 2-acylthiomethylthiirans:

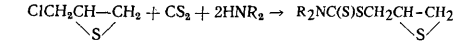


where R = CH_3CO or $(C_6H_5O)_2P(S)$. Similar results are presented in a patent [232].

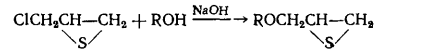
The course of the thiiran–thietan rearrangement depends to some extent also on the nature of the reactants employed. In the reaction between 2-chloromethylthiiran and thioacetates the thietan derivative is formed in a greater amount than in the reaction with *OO*-diethylphosphorodithioate [225]. As the electrophilic properties of the initial thiiran are enhanced, its tendency to isomerise in the reaction increases [228]. 2-Bromomethylthiiran is readily converted into a thietan derivative even under anhydrous conditions, while 2-acetoxymethylthiiran forms thiiran derivatives on reactions with salts of thiolic acids even in aqueous media.

The available information suggests that the thiiran–thietan rearrangement proceeds at the stage involving the formation of an ion pair. Unambiguous transformations with retention of the thiiran ring presuppose the creation of conditions for the formation of an ion pair, the recombination of which to an uncharged molecule takes place before the isomerisation of the cation. The loosening of the ion pair by the solvation shell promotes the isomerisation of the thiiran ring to the thietan ring.

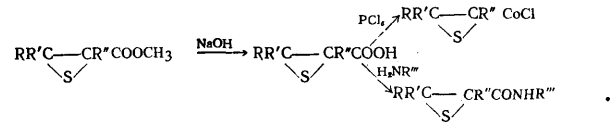
The three-membered ring of 2-chloromethylthiiran constitutes a weaker electrophilic centre than the carbon atom of the 2-methyl group. As a result, it is possible to obtain a wide variety of 2-methylthiiran derivatives from 2-chloromethylthiiran in complex systems and in the presence of nucleophiles, for examples [233,234]:



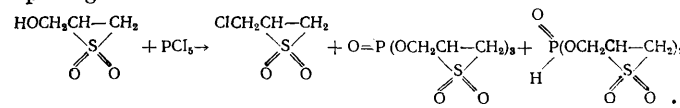
In the presence of aqueous alkali 2-chloromethylthiiran reacts with alcohols to form 2-alkoxymethylthiirans in yields up to 40% : [235]



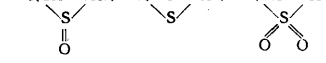
Despite the relatively high susceptibility of the thiiran ring to cleavage, thiirans could not be made to undergo a wide variety of reactions. Knunyants and coworkers [152,153] described reactions of thioglycidic acids and their derivatives which do not involve ring opening. They showed that methyl esters of epithioglycidic acids are hydrolysed under mild conditions by dilute alkalis. The thioglycidic acids obtained in this way could be converted under mild conditions into acid chlorides and amides:



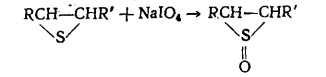
The reactions of 2-hydroxymethylthiiran 1,1-dioxide with phosphorus pentachloride also proceed without ring opening [187]:



The reactions of thiirans involving a change in the valence state of the sulphur atom constitute a special group. Mild oxidation of thiiran with hydrogen peroxide or perbenzoic acid leads to the formation of polyethylenesulphone [poly(thiiran 1,1-dioxide)] [71]. However, 2,3-diphenylthiiran is converted smoothly into thiiran 1-oxide or 1,1-dioxide in the presence of hydrogen peroxide or 3-chlorobenzoic acid [177,211]:



Thiiran 1-oxides and their homologues are obtained in high yields only on mild oxidation with sodium periodate in methanol [236]:



Thus the possibility in principle of the synthesis of thiiran compounds by reactions involving the substituents at the carbon atoms of the thiiran ring and the oxidation of the sulphur atom has now been established.

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The available data on the chemistry of thiirans are much less extensive than those for their nitrogen- and oxygen-containing heteroanalogues. However, the number of reactions leading to the closure of thiiran rings which have now been investigated is not less then the number of tested methods for the synthesis of oxiran, aziridine, and their homologues.

The available information about the syntheses of thiirans embraces virtually all possible types of methods for the homolytic and heterolytic formation of ring *endo*-bonds. Syntheses of thiirans involving the formation of their two-carbon skeleton via a homolytic mechanism and also via anionotropic and cationotropic cyclisation have been described. Methods based on the homolytic, anionotropic, and cationotropic closure of thiiran rings at the C–S bond have been widely investigated.

Numerous procedures for the preparation of thiirans are formally similar to the syntheses of aziridines and oxirans. For example reactions involving the anionotropic closure of thiiran rings at the C–S bond resemble the Gabriel–Wenker syntheses of aziridines and the chlorohydrin syntheses of oxiran and its homologues. Also similar are the methods for the synthesis of *N*-, *O*-, and *S*-heteroanalogues of cyclopropane based on the condensation of imines, carbonyl compounds, and thiocarbonyl compounds with carbenes, the pyrolysis of nitrogen-containing heterocyclic compounds, and cationotropic transformations of acyclic compounds. Thiirans are formed more readily in such reactions than oxirans and aziridines and the reactions themselves are more general. This is undoubtedly because of the smaller strain in thiiran rings and the characteristics of the electronic structure and behaviour of the sulphur atom.

The greater ease of formation of thiiran rings on energy grounds compared with oxirans is clearly shown in the reactions of derivatives of 2-mercaptoalkanols. The formation of three-membered heterocycles from ethylene carbonate and monothiocarbonate [2-oxo-1,3-dioxolan and 2-oxo-1,3-oxathiolan] takes place under virtually identical conditions (200°C). In the latter case the only product is thiiran. Thiiran and not oxiran is also formed from 2-mercaptoethanol and its acyl derivatives under the conditions of the anionotropic and cationotropic ring closure.

The methods for the synthesis of thiirans discussed in the review suggest a great scope for the synthesis of these compounds from simple readily available substances. From this point of view, there is no doubt that further development of thiiran chemistry can serve as one of the rational ways of solving problems which are at present important, namely that of the utilisation of sulphur and its simple compounds. On the other hand, the great synthetic possibilities in the series of thiiran compounds lead to good prospects for theoretical research. It is sufficient to mention that the discovery of the formation of thiiran compounds containing a ring formed at the double bonds of alkenes or in a chain of conjugated double bonds [26,180] is of general theoretical interest. The chemistry of thiirans with a halogen attached to the ring suggests ways for the investigation of the simplest heteroaromatic compounds with three-membered rings [206]. The syntheses and reactions of thiiran derivatives are of interest for modern stereochemistry.

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