Translated from *Uspekhi Khimii*, **57**, 1131-1169 (1988) U.D.C. 547.818.59.1.07; 547.736.732, 547.665.07, 269, 1+547, 279, 523; 223

Reactions of Saturated Cyclic Sulphides

E.N.Karaulova

The latest advances in the chemistry of saturated cyclic sulphides, mainly with 3-10-membered rings and their derivatives are examined. The results of studies concerning the introduction of functional groups into the sulphides and the conversion of the sulphides into acyclic compounds are surveyed.
The bibliography includes 198 references.

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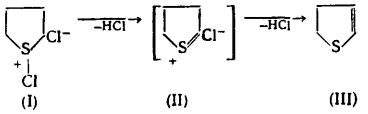
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I. INTRODUCTION

During the last 10–15 years the reactions of cyclic sulphides such as sigmatropic rearrangements and reactions with ring opening have found extensive applications in synthetic organic chemistry. New data have been obtained on "traditional" reactions—complex formation and oxidation. The synthesis and the reactions of sulphonium salts have developed vigorously. They are promising for use in the chemistry of dyes and as fungicides and flocculants. Zwitter-ions based on arylthioniacycloalkane salts have found applications as monomers for the preparation of polymers stable in water and acids. The review covers the literature up to 1986, mainly during the last 10 years. Earlier data are described in monographs[1,2] and other reviews.[3-5]

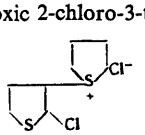
II. COMPLEXES INVOLVING CYCLIC SULPHIDES

Thiolan reacts with chlorine to form the 1:1 complex (I), which is stable in methanol only at a low temperature.[6] On raising the temperature of the complex (I), Pummerer's reaction takes place with the tentative formation of the carbosulphonium ion (II), which undergoes further reactions:[7]



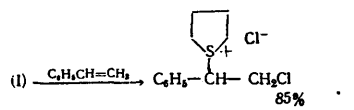
(I) (II) (III)

The dihydrothiophen (III) formed under these conditions adds to the complex (I), affording the toxic 2-chloro-3-thiolanylthiolanium chloride (IV):



(IV)

Hydrogen chloride retards the decomposition of the complex (I), possibly inhibiting the formation of compound (II). The complex (I) reacts with unsaturated compounds giving rise to sulphonium salts; the reaction proceeds effectively with styrene:[7]



The charge-transfer complexes formed by thiolan, thiane, and 1,4-dithiane with iodine absorb in the far IR at the following frequencies respectively: 158, 200 cm^{-1}; 157, 214 cm^{-1}; 165 cm^{-1}, while the complexes of the same sulphides with iodine bromide absorb at 186–188 and 222–228 cm^{-1}.[8]

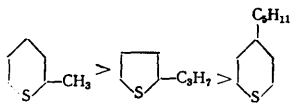
Saturated cyclic sulphides form donor–acceptor complexes with participation of a hydrogen bond with hydroxyl-containing compounds. When they are absorbed on silica and alumina, thiolan and thiane form hydrogen bonds with the hydroxy-groups of the sorbents and there is also an interaction with the electron-accepting centres on the alumina surface.[9] The thermodynamic characteristics of the complexes of thiolan with phenols have been determined: $\Delta H = -3 \pm 0.2$ kcal mol^{-1} and $\Delta S = -9.4$ kcal mol^{-1} K^{-1} for the hydrogen bond in the thiolan–phenol complex, while for the complex of thiolan with resorcinol we have $\Delta H_1 = -4.6 \pm 0.8$ kcal mol^{-1} and $\Delta S_1 = -13$ kcal mol^{-1} K^{-1}.[10]

The ability of sulphides, including cyclic sulphides, to form complexes with mercury(II) acetate has served as the basis of the acidimetric method for the quantitative potentiometric determination of sulphides.[11]

The stability of thiolan complexes (and also *d*-biotin complexes) with biologically important metal ions (Mg^{2+}, Ca^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) and also with Ag^+ in 50% alcohol, 96% dimethylformamide (DMF), and 98% dimethyl sulphoxide (DMSO) or D_2O) is extremely low; with increase in the concentration of water, the interaction of the sulphides with all the ions except Ag^+ increases.[12]

In order to model the capacity of petroleum sulphides for extraction from K_2ReOCl_5 solution, 13 complexes of 2-propylthiolan, 2-methylthiane, and 4-pentylthiane having the composition $L_2Re(=O)Cl_3$, where L = thiacycloalkane, have been obtained.[13] They have the structure of a flattened octahedron, where the chlorine atoms and one of the ligands are located in the equatorial

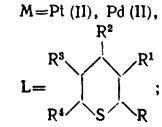
plane, while the oxygen and the second sulphide molecule occupy the vertices of the octahedron. The energy of formation of the complexes and their thermal stability diminish in the sequence of ligands



Acido-complexes with bivalent platinum and palladium salts have been obtained from aryl- and alkyl-substituted thianes, thiadecalins, and perhydrothioxanthenes:[14,15]

$$2L + K_2MCl_4 \xrightarrow{\text{alcohol}} ML_2Cl_2$$

M=Pt (II), Pd (II),



$R=R^4=C_6H_5$, $R=R^4=C_4H_5$, $R^2=CH_3$; $R=R^3=R^4=C_6H_5$; $R=C_6H_5$, $R^3R^4=(CH_2)_4$; $R=R^3=C_6H_5$, $R^3R^4=(CH_2)_4$; $RR^1=R^3R^4=(CH_2)_4$; $RR^1=R^3R^4=(CH_2)_4$, $R^3=CH_3$; $RR^1=R^3R^4=(CH_2)_4$, $R^3=C_6H_5$.

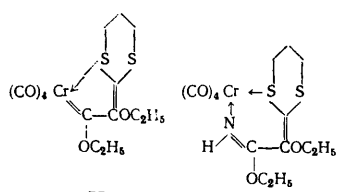
On crystallisation from benzene, the last two compounds give rise to $PtL_2Cl_2.C_6H_6$ and $PtL_2Cl_2.2C_6H_6$ respectively. The complexes exhibit a moderate antimicrobial activity; the complexes of bicyclic and tricyclic sulphides show a more appreciable antiphage activity.[14] The complexes of PdL_2Br_2 having the *trans*-configuration have been obtained in 83–94% yields from PdL_2Cl_2 and KBr in aqueous acetone;[15] the complexes PtL_2X_2 have been obtained in aqueous dioxan:

$$L + K_2PtCl_4 + KX \xrightarrow{\text{aqueous dioxan}} PtL_2X_2 ;$$

X = Br, I; L = 2,6-diphenyl, 4-methyl-2,6-diphenyl-, or 2,4,6-diphenylthiane.

The complex of palladium chrloide with 4-methyl-2,5-diphenylthiane has been used[16] as the catalyst in the dehydrohalogenation of 3,4-dichlorobut-1-ene.

The chelates (V) and (VI) have been obtained from 1,3-dithiane:[17]



(V) (VI)

The formation of complexes by macrocyclic sulphides, especially thiacrown-ethers, has been investigated in recent years (for a review of the complexes between sulphides and transition metals, see Murray and Hartly[18]). Complexes of 1,4,7-trithiacyclononane with univalent copper, nickel, and cobalt tetrafluoroborates have been obtained; the metal atom in these complexes is at the centre of a slightly deformed octahedron. The complexes of 1,4,8,11,tetrathiacyclotetradecane (VII) with rhodium and cobalt salts, i.e. $[Rh(VII)X_2]^+$ and $[Co(VII)X_2]^+$, where X = Cl, Br, NCS, NO, or $1/2Cr_2O_4$, have been investigated. The cobalt complexes are obtained in three ways: from a bivalent cobalt salt with a non-coordinating anion and the sulphide, this step being followed by the reaction of the resulting complex with a coordinating anion and oxidation with air; from a cobalt salt, the sulphide, and an anion accompanied by oxidation in a single stage; in a complex with tervalent cobalt by exchange with a more strongly coordinating anion.[20]

The rhodium complexes have the *cis*-structure. The magnetic moments, molecular conductivities, and absorption IR and visible spectra have been measured for the complexes enumerated above.[20]

The cation $[Rh(VII)]^+$ has been obtained[21] by reducing the rhodium complexes and its capacity for coordination to various anions and electrophiles has been investigated. The cation $[Rh(VII)]^+$ enters into oxidative addition reactions, for example, with acetyl chloride, which involves an increase in the coordination number of rhodium and in its oxidation state (up to Rh^{2+}).

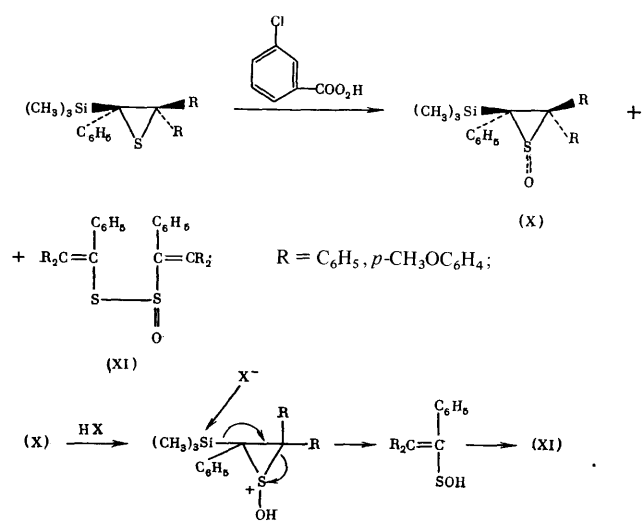
The extracting capacity of the thiacrown-ether (VII) in relation to the cations Na^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Te^+, Ag^+, Pd^{2+}, Cd^{2+}, and Hg^{2+} (anions—perchlorate, picrate, and tetraphenylborate) has been investigated.[22] Only copper is extracted quantitatively. The complexes of pentathia-15-crown-5-(1,4,7,10,13-pentathiacyclopentadecane) (VIII) with univalent and bivalent copper have been obtained.[23] The electrolytic reduction of the $[Cu(VIII)]^{2+}$ complex in a nitrogen atmosphere leads to $Cu[(VIII)]^+$. Both complexes are monomeric in the crystalline state.

The complex with Cu^{2+} has a square-pyramidal geometry with the copper atom located 0.41 Å above the basal plane, which is made up of four electron-donating sulphur atoms, the fifth sulphur atom being coordinated at the vertex but deviating by 12.8° from the perpendicular. The Cu^+ complex has the structure of a distorted tretrahedron, close to the geometry of the complex with Cu^{2+} but with the exception that one of the C–S bonds in the basal plane is impaired. In both complexes, the perchlorate anions are not coordinated.

The complex of 1,4,7,10,13,16-hexathiacyclo-octadecane (hexathia-8-crown-6) (IX) with nickel picrate (1 : 1) is obtained[24] by refluxing in acetone. The octahedral complex $[Ni(IX)]^{2+}$ has a star structure: the nickel ion is at the centre of symmetry and the thiacrown ether surrounds it.

III. OXIDATION OF THE SULPHIDES

The oxidation of thiirans and substituted phenylthiiran oxides by peroxide compounds has been discussed in a monograph.[2] When *cis*-2,3-diphenylthiiran is oxidised with perbenzoic acid, the *anti*-sulphoxide is formed exclusively.[25] When silylated thirrans are subjected to similar oxidation, they give rise to ring opening products together with the sulphoxide (with the *anti*-disposition of the S=O group relative to the silyl group), possibly as a result of the acid-catalysed conversion of the sulphoxide (X) into an unstable sulphenic acid, which dimerises with simultaneous dehydration:[26]

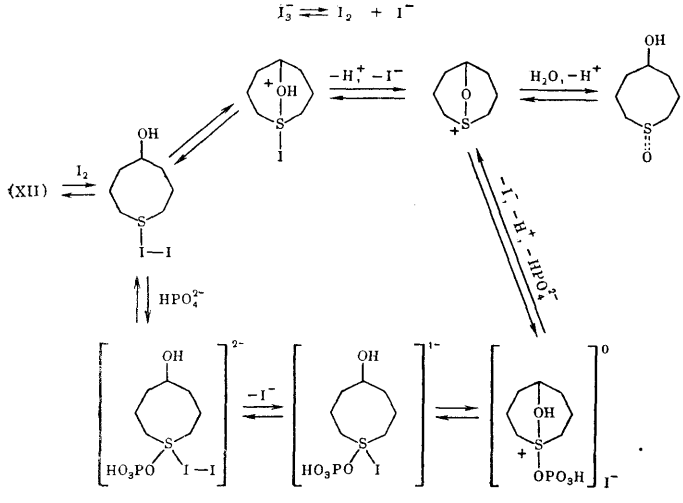


(X) (XI)

The alternative homolytic opening of the ring in compound (X) is not, however, ruled out.

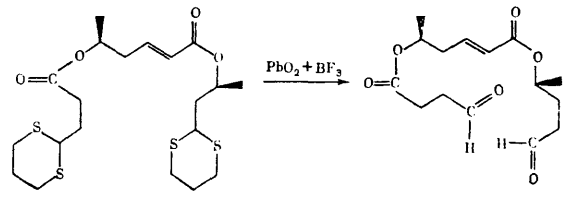
Tetrafluoromethyl-1,3-dithietan is oxidised by chromium trioxide or nitric acid to the monosulphone.[2]

Thiolan is converted into cyclobutane when it is ozonised in oxygen.[27] The oxidation of thiolan to the sulphoxide by gaseous oxygen is catalysed by petroleum metalloporphyrins, most effectively by vanadyl-porphyrins.[28] When thiolan and thiane are oxidised with atmospheric oxygen in the presence of copper(II) dichloride (in isopropyl alcohol at 130 °C and 50 atm),[29] sulphoxides are formed in 50–70% yields and a selectivity of 70–80%; 2-hexytlthiolan is not oxidised under these conditions. Thiolan and thiane are oxidised to the sulphones by refluxing with a solution of copper(II) permanganate or a mixture of potassium permanganate and copper(II) sulphate pentahydrate.[30] 2,5-Dichloromethylthiolan and 2-chloromethyl-5-chlorothiane were oxidised to the sulphoxides with t-butyl hydroperoxide in the presence of $MoCl_5$;[31] 1,3,5,7-tetramethyl-2,4,6,8-tetrathia-adamantane was oxidised in the same way (in benzene) to the 2-oxide in 55% yield.[32] The oxidation of 4-hydroxythiane, 4-hydroxy-4-methylthiane, and 5-hydroxythiacyclo-octane (XII) with iodine in aqueous methanol in the presence of phosphate buffer takes place with participation of the *trans*-annular interaction of the hydroxyl with sulphur;[33] in the case of the sulphide (XII), the bridged intermediate 9-oxa-1-thioniabicyclo[3.3.1]nonane tri-iodide was isolated (not shown in the scheme below) whose oxidation leads to hydroxysulphoxides with a great preponderance of the stereoisomers having the OH and S=O groups in the *trans*-positions (in excess of 92%). Under these conditions, the sulphide–iodine complex is initially formed from the tri-iodide and then decomposes via two pathways, the main pathway depending on the buffer and its reverse process being of second order with respect to the iodide:

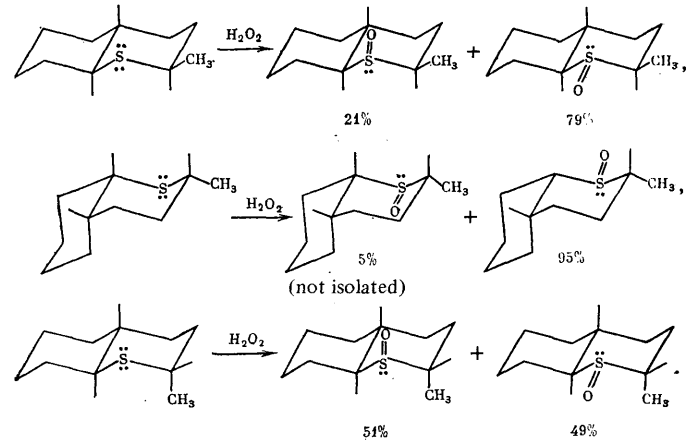


The electrochemical oxidation of 4-(*p*-chlorophenyl)thiane in aqueous acetone or acetonitrile in the presence of bromides, for example, $(C_4H_9)_4NBr$, affords[34] isomeric sulphoxides in 80% yield (under the conditions of kinetic control, about 90% of the *trans*-isomer is formed and at equilibrium there is 80% of the *cis*-isomer). One of the sulphur atoms in 2-(α-tetrahydrofuryl)-1,3-dithiane is oxidised by sodium periodate,[34] the yield of the sulphoxide being 70%.

Treatment of 5-(*o*-carboxyphenylamino)-2-phenyl- and 5-(*o*-carboxyphenylthio)-2-phenyl-1,3-dithianes with hydrogen peroxide in acetic acid[36] gave rise to the corresponding bis-sulphones. Extensive oxidation hydrolysis of 1,3-dithianes has been used[37] in one of the stages of the synthesis of gramicidin:



The oxidation of the stereoisomers of 3-methyl-2-thiabicyclo[4.4.0]-decane with hydrogen peroxide in acetic acid[38] led to the isolation of the stereoisomeric sulphoxides:



The oxidation of thiadecalins and thiabicyclo[4.3.0]nonanes has also been discussed in the review.[5]

4-Thiahomoadamantane was oxidised[39] with *m*-chloroperbenzoic acid to the sulphone in 54% yield. 2-*exo*-Hydroxy-4-thiahomo-adamantane (XIII) was oxidised[39] with pyridinium chlorochromate to the corresponding ketone in 48% yield; together with the ketone, 3-thiatricyclo[5.3.1.$0^{4,9}$]undec-5-ene is formed as a result of skeletal rearrangement (with participation of the episulphonium ion).

It is appropriate to consider also the oxidation of petroleum sulphides, since saturated cyclic sulphides predominate among them.[1] The oxidation of the petroleum sulphides to sulphoxides is the principal method of converting them into derivatives with functional groups. In the liquid-phase oxidation with atmospheric oxygen in the presence of copper chloride in isopropyl alcohol (heating under pressure),[40] the degree of conversion of the petroleum sulphides does not exceed 90% and the maximum selectivity is then 80% (for a yield of about 70 mole %). When the concentrate of petroleum sulphide is oxidised with oxygen in the presence of copper phenoxide, the formation of sulphoxides is inhibited by the competing reaction involving the oxidation of the hydrocarbons present in the concentrate.[41] The oxidation of petroleum sulphides to the sulphoxides directly in petroleum distillates can be usefully performed with t-pentyl. t-butyl, and cumenyl hydroxperoxides;[42,43] the highest conversions are obtained in oxidation catalysed by molybdenum compounds in the presence of carboxylic acids.[43] Molybdenum naphthenate has been recommended[44] as the catalyst for the oxidation of petroleum sulphides to the sulphoxides with hydrogen peroxide.

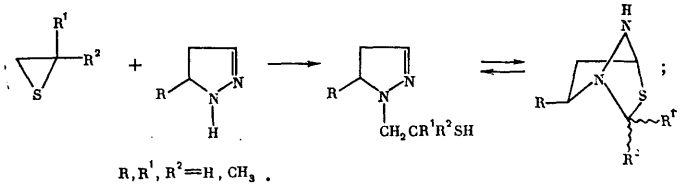
The concentrates of petroleum sulphides have been oxidised to the sulphoxides with a mixture of air and nitrogen dioxide.[45] The method can be regarded as successful, since a complex mixture of

nitrogen-containing products is formed together with the sulphoxides.

IV. REACTIONS WITH OPENING OF THE HETEROCYCLE

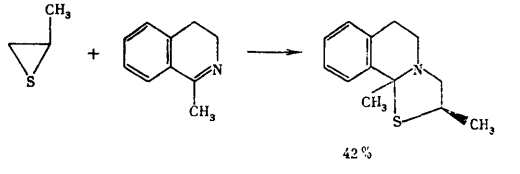
1. The Effect of Nucleophiles

When thiiran and its methyl-substituted derivatives react with unsaturated cyclic nitrogen-containing bases, the thiiran ring is opened in accordance with Krasuskii's rule.[46,47] The reaction with 2-pyrazolines results in the formation of 1-(2-mercaptoalkyl)-2-pyrazolines, which are capable of isomerising reversibly to 4-thia-1,8-diazabicyclo[3.2.1]octanes.[46] A mixture of diastereoisomeric mercaptoalkylation products in comparable amounts is formed from 5-methyl-2-pyrazoline:



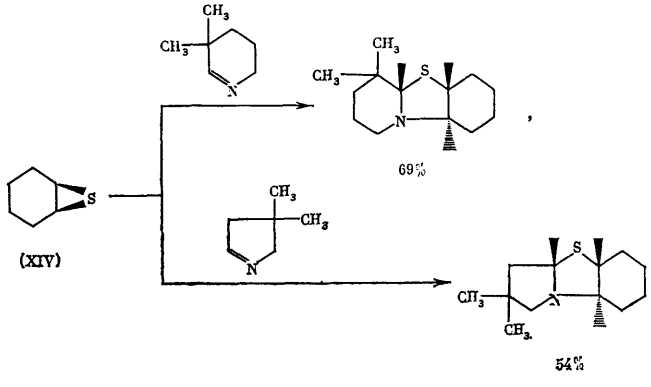
R, R', R² = H, CH₃ .

The reaction with 2,3,4,5-tetrahydropyridines and 1-pyrrolines affords the corresponding perhydrothiazolo[2,3-*a*]pyridines and perhydropyrrolo-[2,1-*b*]thiazoles.[47] In the case of methylthiiran, compounds with the *cis*-disposition of the angular substituent and the methyl group are formed:



42%

In the reaction involving epithiocyclohexane (XIV), the opening of the thiiran ring is accompanied by the inversion of the configuration:[47]

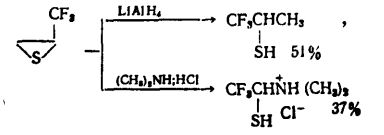


(XIV)

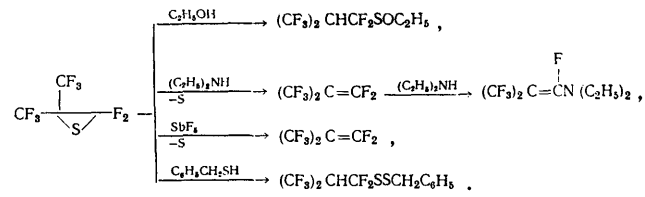
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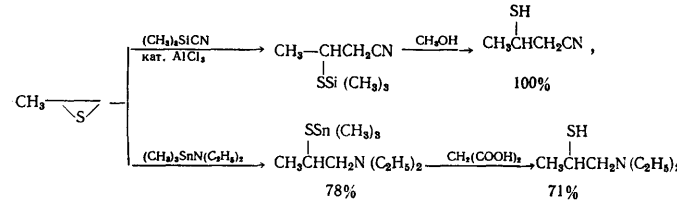
The aminomercaptans $C_4H_9OCH_2CH(SH)CH_2NRR^1$ (R = R^1 = C_4H_9; R = C_6H_5, R' = CH_3) have been synthesised[48] by treating butoxymethylthiiran with amines. Nucleophiles act analogously on trifluoromethylthiiran:[49]



In contrast to this, in the case of perfluorothiiran the attack by the nucleophile is directed to the sulphur atom:[50]

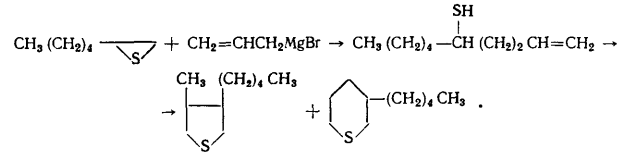


Regioselective opening of the thiiran ring occurs on treatment of organic derivatives of Group IVB elements,[51] such as $(CH_3)_3SnNR_2$ and $(CH_3)_3SiCN$. The subsequent alcoholysis or acidolysis of the reaction products leads to β-amino- or β-cyano-thiols:

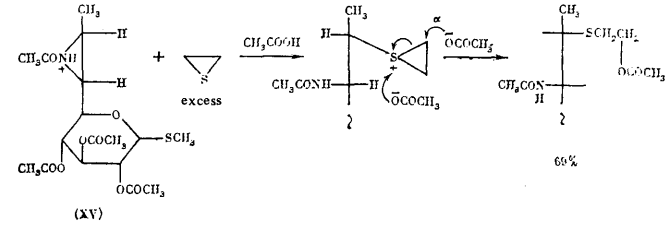


78% 71%

The reaction of thiirans [including epithiocyclohexane (XIV)] with alkenylmagnesium bromides is of great synthetic importance. It yields alkenethiols, whose subsequent cyclisation leads to five-membered and six-membered thiacycloalkanes,[52–54]† for example:[52]



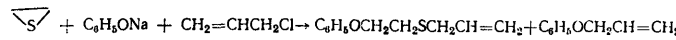
Treatment of tetra-acetylepimine (XV), a derivative of the antibiotic linocomycin, with thiiran in acetic acid affords the 7-(2-acetoxyethyl)thio-derivative:[55]



(XV)

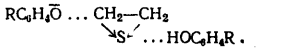
69%

The opening of the thiiran ring by phenols under the conditions of base catalysis leads to the polymerisation of the thiiran; in order to suppress it, a powerful electrophile (allyl chloride) is introduced:[2,56–59]

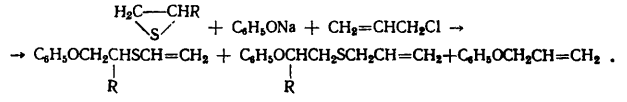


† For a detailed description see Karaulova's review.[4]

The study of the kinetics of the reaction led to the conclusion[56] that its mechanism involves the formation of complexes of sodium phenoxide with thiirans. In the case of substituted phenoxides RC_6H_4ONa (R = *p*-CH_3, *p*-OCH_3, *m*-CH_3, *p*-F, *p*-Cl, *p*-I, or *m*-Cl), the rate of ring opening diminishes as the electron-accepting properties of the substituent are enhanced, but the rate increases as the acidity of the phenol is reduced (by introducing electron-donating substituents).[57] The ring opening is achieved as a result of the joint action of the nucleophile and the proton donor:

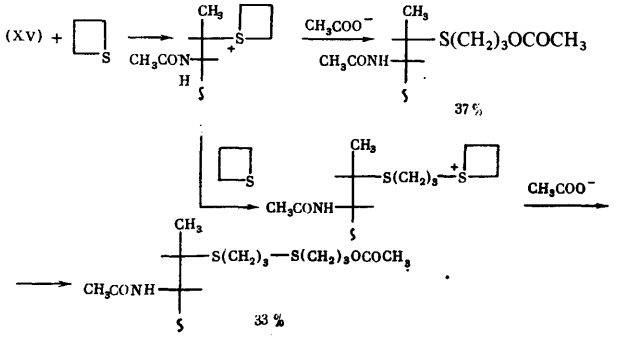


In the reaction of substituted thiirans, the mode of opening of the thiiran ring varies as a function of the electronic character of the substituent:[58]



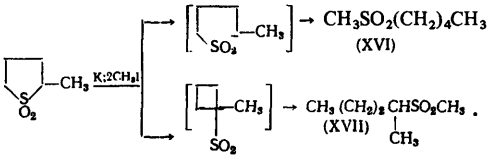
For substituents whose electronic effect is transmitted via the inductive mechanism, products corresponding to the opening of the ring in accordance with Krasuskii's rule predominate (R = CH_3, 75%; R = CH_2OCH_3, 96%; R = C_4H_9, 75%). For substituents containing a π-electron system, anomalous reaction products predominate (R = C_6H_5, 80%; R = CH=CH_2, 90%). The reaction with disubstituted thiirans proceeds analogously;[59] in highly polar aprotic solvents, the rate and regioselectivity of the reaction increase sharply.[59]

Thietan in acetic acid reacts with the tetra-acetylepimine (XV) via two pathways:[55] the formation of the 7-(3-acetoxypropyl)thio-derivative is accompanied by the interaction with a second thietan molecule:

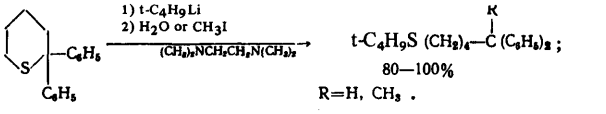


Thiolan and thiane react with compound (XV) only via the first pathway[55]—the 7-(4-acetoxybutyl)thio-derivative (yield 71%) and the 7-(5-acetoxypentyl)thio-derivative (yield 11%) are formed respectively.

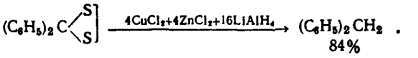
Colloidal potassium (obtained by dispersing potassium in toluene by exposure to ultrasound) is an effective reagent for the clevage of the C–S bond.[60] Its effect on sulphone derivative from thietan, thiolan, 2-alkylthiolans, and thiane has been investigated. The yields of alkyl methyl sulphones are 84–94%. It has been shown for 2-methylthiodioxide that the reaction is regioselective–cleavage of the C–S bond takes place mainly at the substituted carbon atom [we have the ratio (XVI):(XVII) = 10:1]:



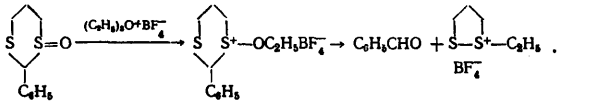
The ring of 2,2-diphenylthiane is ruptured analogously on treatment with t-butyl-lithium:[61]



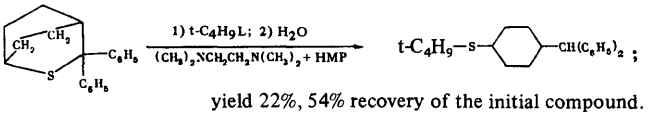
The reductive cleavage of the C–S bond at C(2) in 2,2-diphenyl-1,3-dithiolan takes place on treatment with lithium tetrahydroaluminate in combination with copper and zinc chlorides:[62]



Intramolecular decomposition has been observed[63] on treatment of 2-phenyl-1,3-dithiane-1-oxide with triethyloxonium tetrafluoroborate:[63]



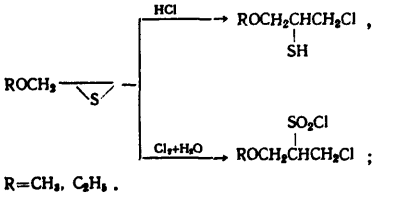
The rupture of the C–S bond in the 3,3-diphenyl-2-thiabicyclo-[2.2.2]octane on treatment with t-butyl-lithium proceeds with difficulty:[61]



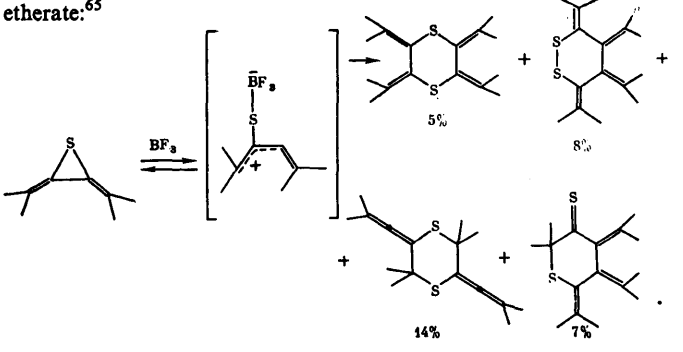
yield 22%, 54% recovery of the initial compound.

2. The Effect of Electrophiles

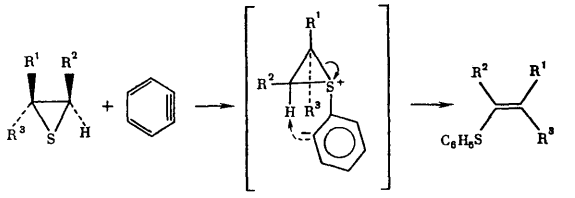
2-Alkoxymethylthiirans react with hydrochloric acid at low temperatures or with chlorine in accordance with Krasuskii's rule:[64]



Diallene episulphide ("thiiranoradialene") produces (together with polymers) dithia[6]radialenes on treatment with boron trifluoride etherate:[65]



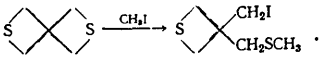
Thiiran as well as methyl 2,2-dimethyl-, hexyl-, phenyl-, and 2,3-diphenyl-thiirans, epithiocyclohexane, and epithiocyclo-octane react with 1,2-dehydrobenzene, which is a powerful electrophile, to form phenyl vinyl sulphides in 71–90% yields:[66]



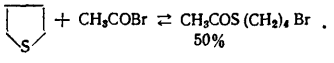
The anionic component of the intermediate betaine acts as a base and abstracts the acid hydrogen from the three-membered ring with the simultaneous formation of a C–C bond and the dissociation of the C–S bond. The reaction is stereospecific: *cis-* and *trans*-phenylthiostilbenes are formed from *cis- and trans*-2,3-diphenylthiirans respectively.

Trifluoromethylthiiran is attacked by electrophiles (Cl_2, HCL, CH_3COCl) at the sulphur atom. The products are respectively 3-chloro-1,1,1-trifluoropropane-2-sulphonyl chloride (yield 72%), 3-chloro-1,1,1-trifluoropropane-2-thiol (yield 69%), and its acetate (yield 38%).[49]

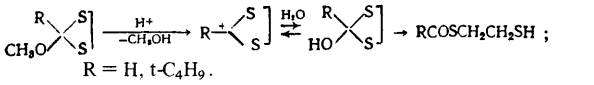
The dithiaspiroheptane ring is opened by methyl iodide:[67]



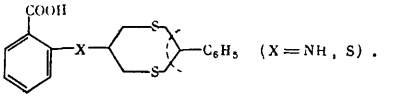
Thiolan is cleaved reversibly by acetyl bromide on refluxing:[68]



The kinetics and mechanism of the hydrolysis of 2-methoxy-1,3-dithiolans in acid media have been investigated.[69] The reaction proceeds in three stages and leads to 2-mercaptoethyl thiocarboxylates:



On treatment with mercury(II) chloride, derivatives, of 2-phenyl-1,3-dithiane split off the C_6H_5CH fragment and are converted into the mercaptides of 2-substituted propane-1,3-dithiols:[36]



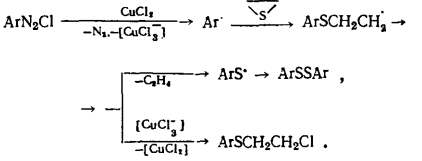
On treatment with chlorine, 2,4,6-trichloro-1,3,5-trithiane is cleaved, affording $CHCl_2–S–CHCl_2$ and $CHCl_2SCl$.[70]

3. Radical Reactions

Episulphides are rapidly desulphurised on heating with *NN*-bis-(trimethylsilyl)aminodimethylphosphine and are converted in a quantitative yield into the corresponding alkenes and the phosphine sulphide.[71] Here there is a possibility of the homolytic cleavage of the heterobond:[2]

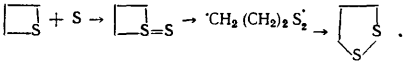


The homolytic cleavage of thiiran takes place on treatment with arenediazonium chlorides in the presence of $CuCl_2$:[72]



The reaction of thiiran with toluene-*p*-diazonium chloride afforded[72] β-chloroethyl *p*-tolyl sulphide in 50% yield relative to the *p*-toluidine employed.

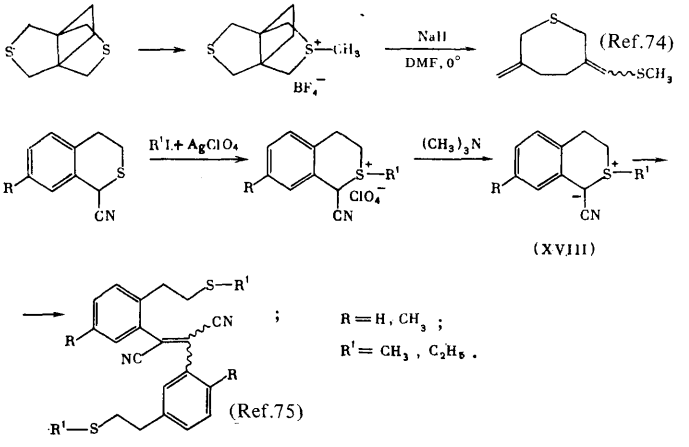
Metastable sulphur is obtained by the photolysis of gaseous COS. Under these conditions, the reaction involving thietan yields 1,2-dithiolan and ethylene in comparable amounmts as the main products.[73] The proposed mechanism of the formation of 1,2-dithiolan is as follows:



V. REARRANGEMENTS WITH CHANGE IN THE NUMBER OF MEMBERS IN THE RING

In recent years, studies on the sigmatropic rearrangements of sulphides, especially semiaromatic sulphides,‡ have been carried out widely. Such rearrangements frequently lead to a change in the number of members in the ring or to the opening of the latter[74,75] (see, for example, Scheme 1).

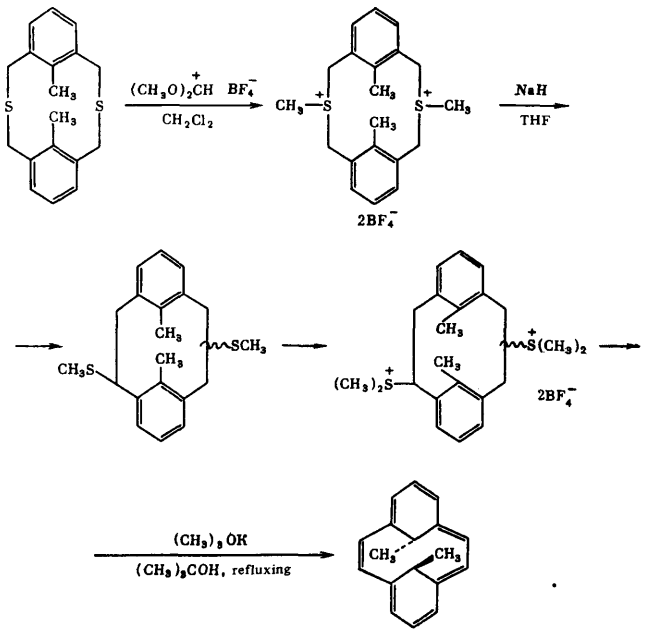
Scheme 1



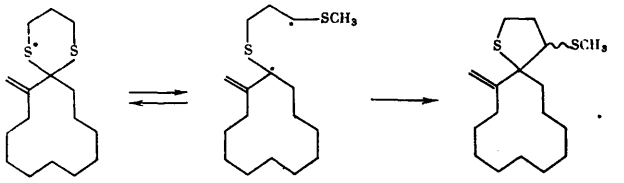
The Stevens rearrangement involves reactions of sulphonium ylides—the cyclic sulphide is initially converted into the sulphonium salt and is then acted upon by a strong base, whereupon an acyclic sulphide linkage is produced. The Stevens rearrangement is frequently used in the synthesis of cyclophanes; with its aid, a cyclic

‡ "Semiaromatic sulphides" are polycyclic sulphides where at least one carbon atom involved solely in a σ-bond, is linked to the sulphur atom.

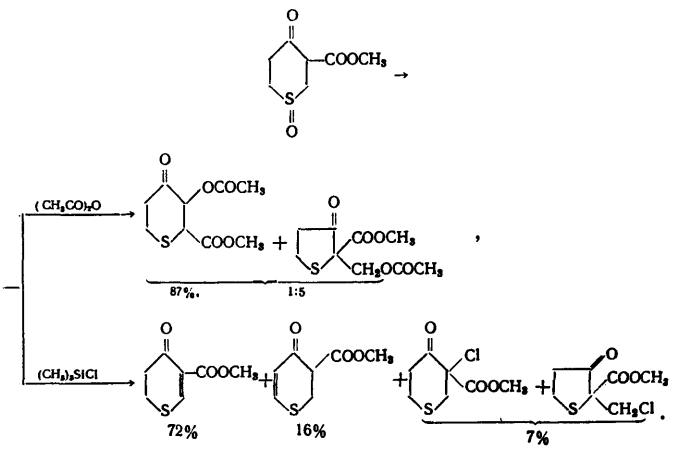
sulphide linkage is replaced (in several steps) by the C=C double bond.[76-78] A convenient methylating agent for the synthesis of the sulphonium salts is dimethoxycarbonium fluoroborate:[76]



The Stevens rearrangement can also lead to the contraction of the heterocycle:[79]

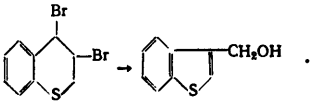


The ring contraction in cyclic sulphides can occur under the conditions of various reactions. Thus the contraction of the six-membered ring is observed on electron impact mass-spectrometry[80] and in the Pummerer rearrangement—both under standard conditions (when the sulphoxide is treated with acetic anhydride) and on reaction with chlorotrimethylsilane:[81]

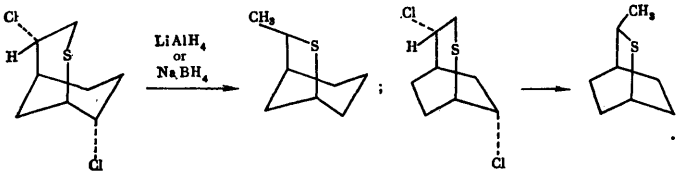


Thiane isomerises to 2-methylthiolan in the temperature range 250–350 °C in the presence of acid catalysts, among which Al_2O_3 is the most selective.[82] Thiane and thiacycloheptane initially isomerise over charcoal treated with nitric acid at 400–500 °C, producing respectively 2-methyl- and 2-ethyl-thiolans, which are then dehydrogenated (via an ionic mechanism) with the preferential formation of thiophens.[83]

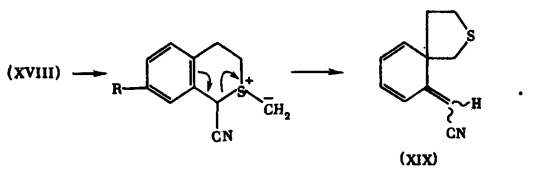
The hydrolysis of bromothiachromans and bromodihydronaphthothiopyrans in aqueous acetone with added potassium hydroxide gives rise to benzo- and naphtho-thiophens respectively,[84] for example:



The reductive dechlorination of the adducts of 4-vinylcyclohexene with sulphur dichloride (dichlorothiabicycloalkanes) is accompanied by skeletal rearrangements—redistribution of the carbon bonds between the rings or the contraction of the heterocycle:[85]



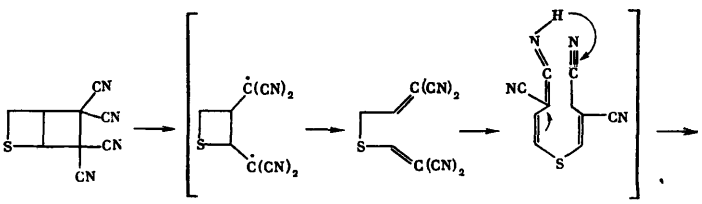
The ylides (XVIII), R′ = CH_3 isomerise in protic solvents (ethanol, methanol) with ring contraction and the formation of the spiro-compound (XIX)[75]—there is initial isomerisation to a methylide, which then undergoes a [2,3]sigmatropic rearrangement (despite the breakdown of aromaticity):

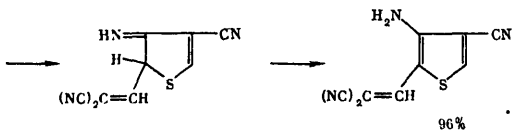


The expansion of the thiiran ring is observed in reactions of epithiohalogenohydrins with nucleophiles.[2] This involves a thiiran–thietan rearrangement. The mechanism includes a cationotropic transformation:

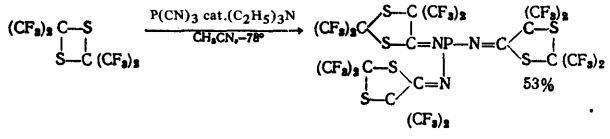


When a solution of 5,5,6,6-tetracyano-2-thiabicyclo[2.2.0]hexane in benzene is refluxed, an arrangement takes place with expansion of the thietan ring and the formation of 3-amino-4-cytano-2-(2,2-dicyanovinyl)thiophen.[86] A radical mechanism involving the opening of both rings with subsequent ring expansion in the acyclic intermediate to form iminodihydrothiophen and tautomerisation of the latter has been proposed:[86]

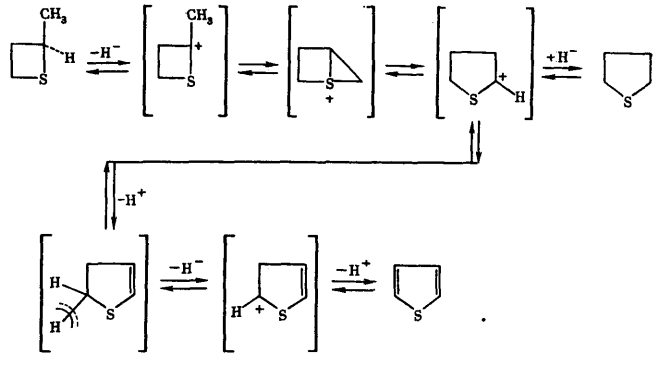




In the interaction of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietan with $P(CN)_3$ or $As(CN)_3$, the latter react in the isonitrile form, a carbon atom is "inserted" in the dithiethan rings, and 1,3-dithiolan derivatives are formed:[87]

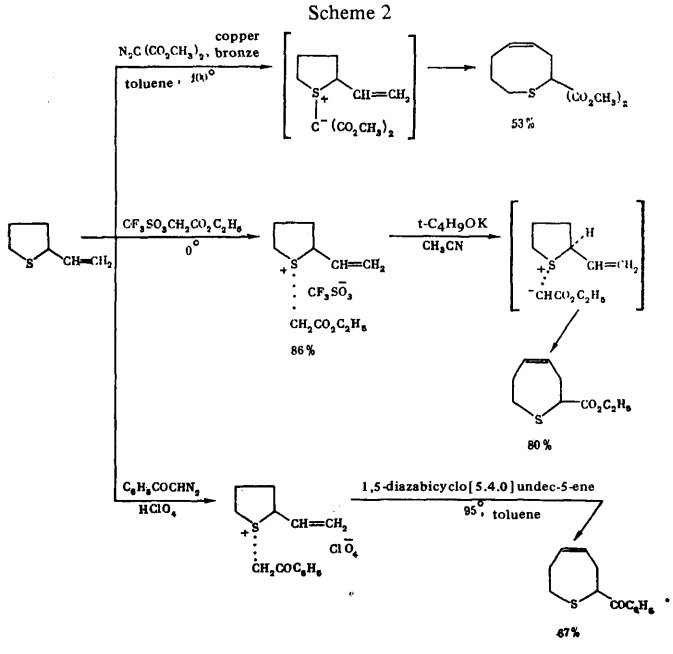


2-Methylthietan isomerises to thiolane on treatment with hydride ion acceptors—triphenylmethyl fluoroborate, chloranil, chlorotriphenylmethane—in the presence of $SnCl_4$,[88] whereupon a thiophen is also formed:



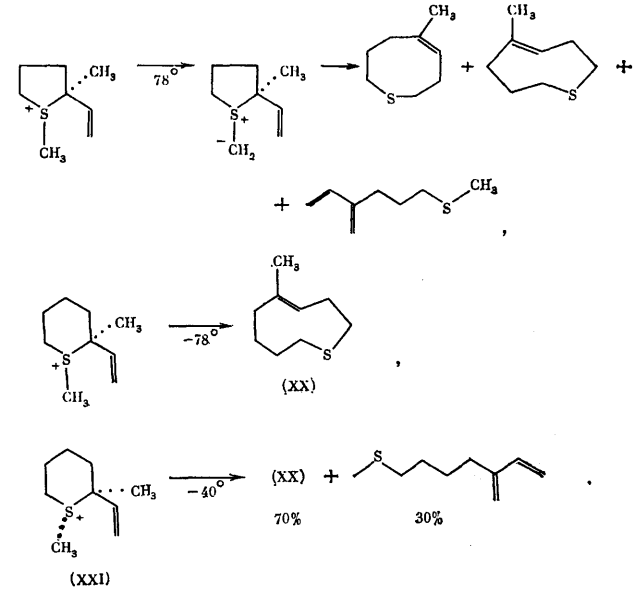
Thiacyclo-octane derivatives are obtained from vinylthiolan. The reaction is of the type of a [2,3]sigmatropic shift and proceeds via an ylide formation stage[89] (see Scheme 2).

Scheme 2

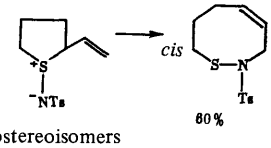


An analogous [2,3]sigmatropic ring expansion has been investigated for the salts of various 2-vinylthiacycloalkanes.[79,90-93] It has been noted that reactions involving 1,2-dimethyl-2-vinyl-substituted thiolanium and thianium hexafluorophosphates (on treatment with potassium t-butoxide) are stereoselective but not stereospecific[90] (see Scheme 3).

Scheme 3

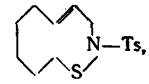


The reaction involving the stereoisomer (XXI) does not take place at −78 °C. The stereochemistry of the ring expansion in the [3,2]sigmatropic rearrangements of sulphonium ylides can depend on the way in which the ylides are formed and on the initial sulphonium salt.[91] On heating *N*-(toluene-*p*-sulphonylimino)-derivatives of 2-vinylthiolan and 2-vinylthiane in xylene, the ring expansion also takes place as a result of the insertion of the nitrogen atom:[92]



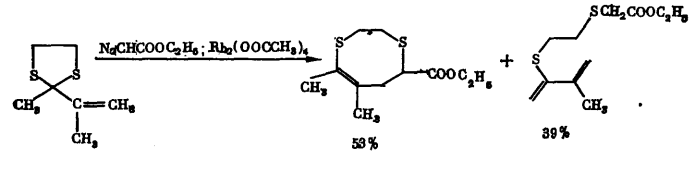
diostereoisomers

It has been suggested[91] that initially there is pyramidal inversion to the *cis*-diastereoisomer, which then rearranges. On treatment with chloramine-T in methanol at room temperature, 2-vinylthiacycloheptane immediately affords the product of the rearrangement

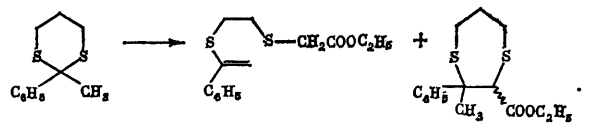


which has the *trans*-configuration.[92]

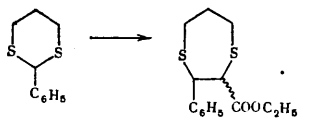
The rearrangement of 2-vinyl-1,3-dithiolans and 2-vinyl-1,3-dithianes was carried out by treatment with diazoacetic ester and rhodium tetra-acetate (the catalyst of the formation of ylides[93]) or copper sulphate,[79] for example:



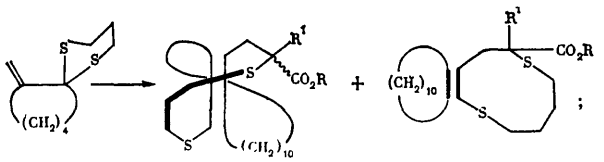
In the reaction involving 2-phenyl-1,3-dithianes under the same conditions, a [1,2]sigmatropic rearrangement takes place:[93]



The diastereoisomer ratio for the insertion product is 15, the isomer where the phenyl and ethoxycarbonyl groups are in the *trans*-positions predominating:

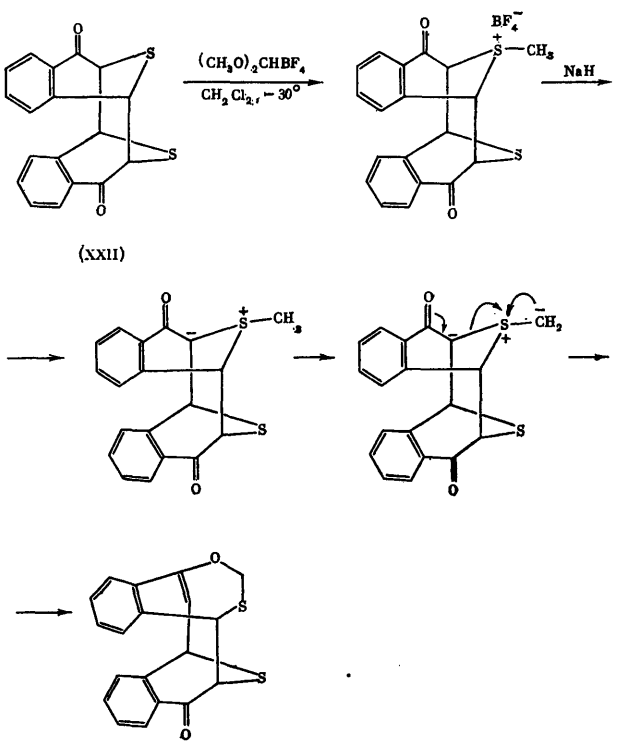


"Betweenanes" have been synthesised using ethyl diazoacetate or diazomalonate via a [2,3]sigmatropic rearrangement:[79]



$R=C_2H_5$, $R^1=H$; $R=CH_3$, $R^1=CO_2CH_3$.

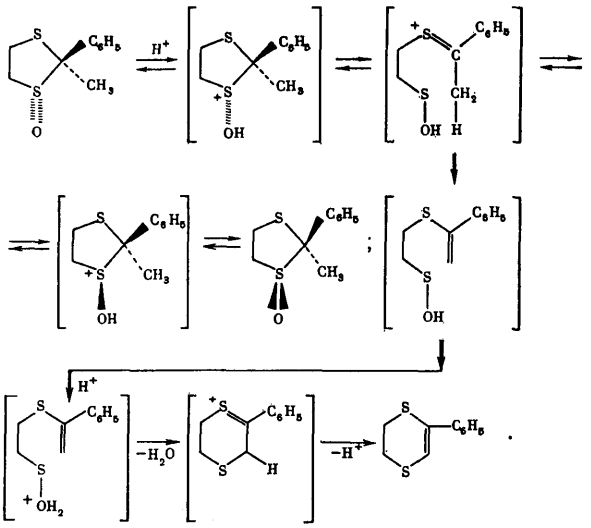
In the [2,3]sigmatropic rearrangement of the "semiaromatic" bis-sulphide (XXII), ring expansion occurred as a result of the incorporation of an oxygen atom:[94]



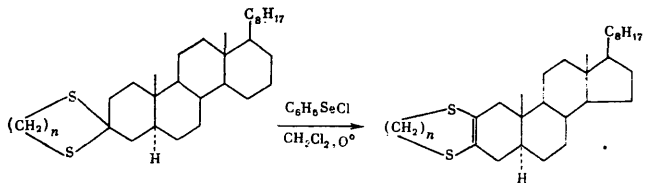
(XXII)

On heating, 2,5-di(chloromethyl)thiolan isomerises irreversibly to 2-chloromethyl-5-chlorothiane and an analogous isomerisation has been observed on heating an aqueous acetone solution of 2,5-di-(hydroxymethyl)thiolan and also on oxidation of 2,5-di(chloro-methyl)thiolan with *t*-butyl hydroperoxide in the presence of $MoCl_5$.[31]

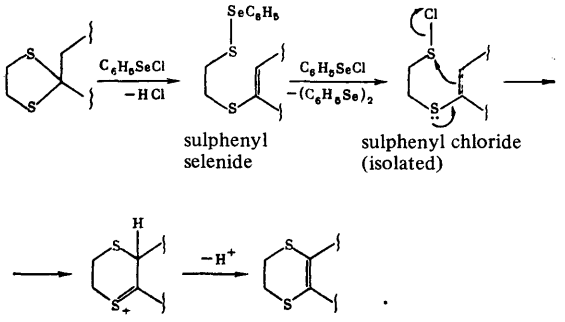
Both *cis*- and *trans*-2-methyl-2-phenyl-1,3-dithiolan monoxides are converted in a quantitative yield into 2-phenyl-1,4-dithiacyclohexene on treatment with acetic anhydride of toluene-*p*-sulphonic acid.[95] The ring expansion reaction is non-stereospecific. On initial protonation with toluene-*p*-sulphonic acid or on acylation with acetic anhydride, intermediate sulphonium ions are formed and then the C–S bond in the sulphoxide is broken and a carbosulphonium intermediate is produced, which then loses a proton; the subsequent ring closure is acid catalysed:



The expansion of the rings of 1,3-dithiolans and 1,3-dithianes takes place on treatment with benzeneselenyl chloride.[96] This reaction has been used to synthesise steroid dihydro-1,4-dithiines and dihydro-1,4-dithiepins:



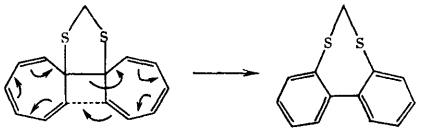
The reaction proceeds with participation of a cationic intermediate:



sulphenyl selenide

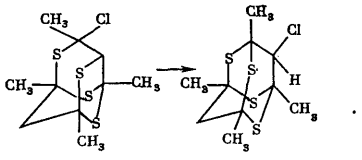
sulphenyl chloride (isolated)

The dispirodithiolan (XXIII) slowly rearranges at room temperature;[97] under these conditions, 14 electrons participate in the orbital symmetry-allowed [7,7]sigmatropic shift:

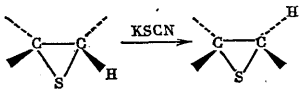


(XXIII)

On treatment with HCl in ether and on storage, the tetrathiahomoadamantane derivative (XXIV) undergoes skeletal isomerisation with expansion of one of the rings, the contraction of the other, and the formation of a tetrathia-adamantane derivative:[32]



Isomerisation without change in the skeleton, namely the epimerisation of episulphides, occurs on treatment with potassium thiocyanate in aqueous solution on heating:[98,99]



The yields in such stereoisomerisation are 10–30% for 5α,6α-epithiopregnanolone.[98] The interconversions of the *cis*- and *trans*-isomers of 3-hydroxy-1,2-epithiocyclohexanol are observed under these conditions; 3-acetoxy-1,2-epithiocyclohexanol isomerises analogously.[99]

The five- and six-membered cyclic sulphonium salts with a methyl substituent in the ring racemise on heating or, in a special case, undergo epimerisation, which apparently proceeds via the pyramidal inversion at the sulphur atom.[100] On treatment with butyl-lithium in tetrahydrofuran, 2α-phenyl-*cis*-1-thiadecalin 1,1-dioxide isomerises to 2β-phenyl-*trans*-1-thiadecalin 1,1-dioxide.[101] The inversion of the configuration on metallation involves the C(2) and C(9) atoms. During deuterium exchange, the configuration at C(2) in the initial 2α-phenyl-*cis*-sulphone is inverted and [2-D]-2β-phenyl-*cis*-1-thiadecalin 1,1-dioxide is formed.[101]

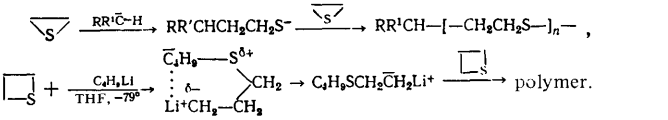
2-Methylthiaindan isomerises over $ZnCl_2/Al_2O_3$ to 3-methylthiaindan to the extent of 20%; the process may proceed with participation of a carbonium ion.[102]

VI. POLYMERISATION OF CYCLIC SULPHIDES

During the 1960's and especially 1970's, the polymerisation of thiirans and thietans became the subject of numerous investigations (see the relevant reviews[2,103,104]). Practical applications were proposed for a number of thiiran and thietan polymers and copolymers (see, for example, the patent literature in the book of Fokin and Kolomiets[2]).

In order to polymerise thiolans and thianes, the latter are initially converted into sulphonium salts (see below).

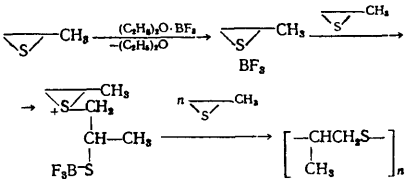
In the anionic polymerisation of cyclic sulphides, the primary condensation product has more pronounced nucleophilic properties than the initial nucleophile,[2,104] for example:



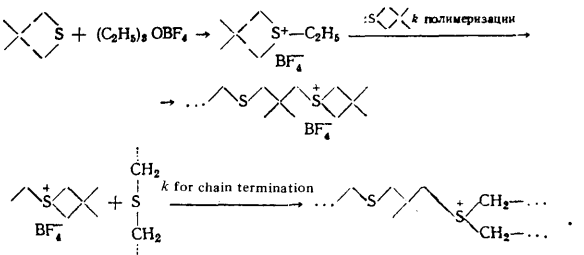
A wide variety of initiators, for example ethyl-lithium, lithium ethanethiolate, 1,4-dilithio-1,1,4,4-tetraphenylbutane,[105] and the potassium salts of aromatic nitriles and ketones[106] are used in the anionic polymerisation of thiirans and thietans. The same initiators are used in the synthesis of block copolymers of dienes with thiirans and thietans.[107,108]

4-Amino-1,2-dithiolane polymerises on heating in chloroform solution.[109]

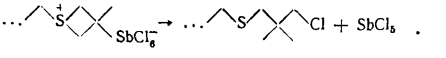
The cationic polymerisation of thiirans and thietans is usually initiated by onium compounds and proceeds via the formation of a zwitter-ion:[104]



Triethyloxonium fluoroborate[110–114] as well as 1-ethyl-3,3-dimethylthietanium fluoroborate,[110] triethyloxonium hexachloroantimonate,[115] triethyloxonium hexafluorophosphate, perchloric acid, and methyl fluorosulphonate[116] are used as catalysts of the polymerisation of thiirans and thietans. The kinetics and mechanism of the cationic polymerisation of thietans are similar to those described above[114]— chain propagation takes place as a consequence of the nucleophilic attack by the monomer directed to the α-carbon atom of the cyclic sulphonium ion. Polymerisation stops as a consequence of the reaction between the reactive chain end and the sulphur atom in the chain already formed, whereupon an unstrained sulphonium ion incapable of reinitiating the polymerisation is produced:



On initiation with the aid of $(C_2H_5)_3OSbCl_6$, chain termination is facilitated by the fact that the growing chain interacts with the counterion, forming an alkyl chloride:[115]

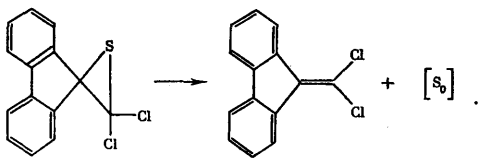


On treatment with hydrochloride, sulphuric, and phosphoric acids, 2-(*N*-carbazolyl)thiiran is converted into oligomers; the interaction with adipic, sebacic, or phthalic acid results in the formation of oligoesters, which are promising as film forming materials for the non-silver recording of information.[117]

VII. THERMOLYSIS AND FRAGMENTATION OF CYCLIC SULPHIDES

A profound change in the carbon skeleton of thiacycloalkanes can occur during their thermolysis and also under the conditions of mass spectrometry (fragmentation under electron impact; the influence of the heating of the specimen cannot be ruled out either).

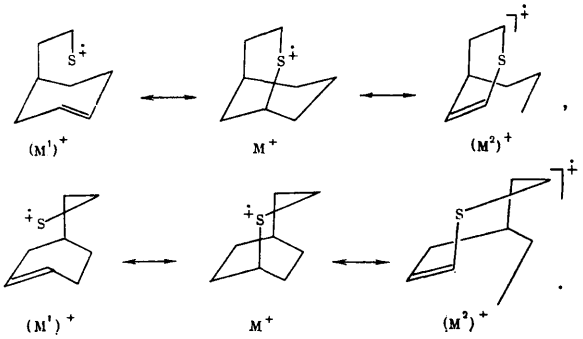
On pyrolysis, thiiran is converted into ethylenethiol and thiophen.[118] The thermolysis of the spirothiiran (XXV) leads to the formation of an olefin as a result of a complex (hitherto not ultimately elucidated) chain of reactions—the reaction order is other than first:[119]



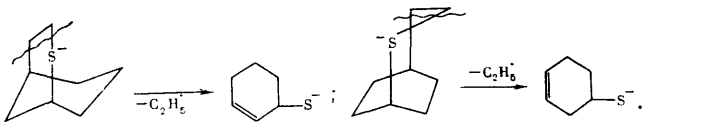
(XXV)

Mass-spectrometric study of alkyl-substituted thiolans and thianes showed[120] that the stability of the molecular ions of β-alkylthiolans is greater than for their α-isomers and that the main process in the decomposition of α-alkylthiolans is the ejection of alkyl radicals as a whole from the molecular ions. In the case of β-alkylthiolans, the main decomposition pathway involves the elimination of only part of the alkyl substituent with retention of one CH_2 group in the charged thiolanium fragment. In α- and β-thianes, the alkyl substituent is eliminated predominantly as a whole, while γ-alkylthianes behave similarly to β-alkylthiolans. The same has been observed for 4-alkyl-2-methylthianes,[121] for which, in addition, the CH_3 group is more readily split-off from the *trans*-isomers, i.e. the latter are less stable in relation to electron impact than the *cis*-isomers. In the *cis*- and *trans*-isomers of 2(4′-alkoxycarbonylbutyl-3-hydroxy-4-ureidothiolans, the splitting-off of the substituents in 3- and 4-positions under electron impact also takes place with different degrees of ease, which makes it possible to identify the geometrical structure.[122]

A combination of positive and negative ion mass spectrometry has been used to establish the structures of bridged thiabicyclooctanes and thiabicyclononanes, including methyl-substituted compounds.[12] The characteristic features of the fragmentation of the positive ions made it possible to establish the number of members in the carbon bridge. In order to account for the characteristic features of the decomposition process, it has been suggested that the positive ions M^+ exist in the transition state $(M^1)^+$,$(M^2)^+$:



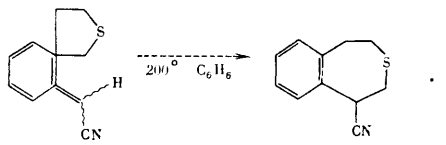
The decomposition of molecular negative ions involves the rupture of the C—C bonds (at the junction) and C—S bonds with localisation of the negative charge on the sulphur atom:



The characteristic feature of the decomposition of negative ions made it possible to infer unambiguously the presence of substituents at the α-carbon atom (relative to the sulphur atom).

The fragmentation of 1,3-dithiolan under electron impact has been examined[124] and the heat of formation of the free radical CHS, amounting to 63 kcal mol^{-1}, has been obtained from the appearance potentials of the $[C_2H_5S]^+$ ion.

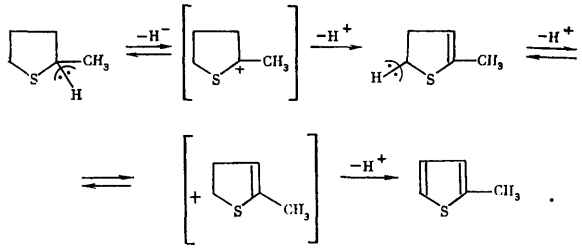
When the spiran (XIX) is heated in benzene (in a sealed tube), thermal isomerisation takes place with formation of a seven-membered ring:[75]



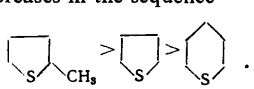
(XIX) 82%

VIII. DEHYDROGENATION AND DESULPHURISATION OF CYCLIC SULPHIDES

Thiolan, 2-methylthiolan, and 2-methylthiaindan are dehydrogenated to the corresponding thiophene derivatives in the presence of acid catalysts—$ZnCl_2/Al_2O_3$ and aluminosilicate;[82,125] the process takes place on aprotic catalyst centres and includes stages in which hydride ions are abstracted and cationic intermediates are formed:

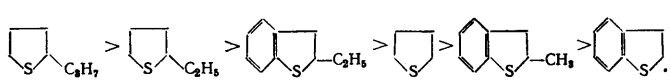


2-Methylthiolan is dehydrogenated more readily than the unsubstituted compound, owing to the greater hydride mobility of the hydrogen atom. It decreases in the sequence[126]



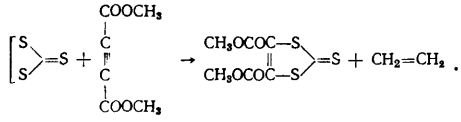
Using cyclic sulphides as hydride ion donors in the ionic reduction of carbonium ions, it is possible to obtain their dehydrogenation products: 2-methylthiophen from thiane (the reaction is accompanied by isomerisation)[127] and 2-methylthiaindene from 2-methylthiaindan in 87% yield (according to gas—liquid chromatographic data).[128]

The rate constants for the dehydrogenation of cyclic sulphides in the presence of activated charcoals at 400 °C decrease in the sequence[129]

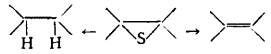


It is appropriate to mention that, according to the EPR spectra of the free radicals formed as a result of the abstraction of hydrogen, the protons in the α-position relative to the sulphur atom in thiolan, thiane, and 4-t-butylthiane are not equivalent.[130]

An unsaturated heterocycle can be obtained from a saturated hetearocycle not only on dehydrogenation but also in an exchange reaction:[131]

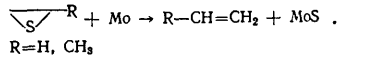


The hydrodesulphurisation of thiirans leads to alkanes; sometimes the reaction stops at the formation of olefins:

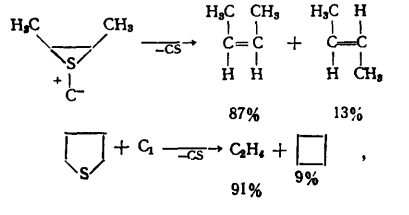


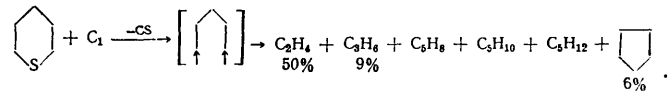
Various hydrodesulphurisation methods have been investigated[132] for the alkylthiirans: dodecylthiiran, 2-methyl-2-nonylthiiran, 2,3-dioctylthiiran, and 3-decyl-2,2-dimethylthiiran. In the presence of Raney nickel of lithium, monosubstituted 2,3-disubstituted thiirans react with ethylamine at a low temperature, giving rise to alkanes. The desulphurisation of tri- and tetra-substituted thiirans stops at the formation of alkenes. On treatment with zinc in acetic acid or with tributyltin tetrahydroborate, only olefins are formed, the reaction being regioselective but not fully stereoselective. The reduction with P_2I_4 in dimethylformamide (DMF) is highly stereoselective and leads to olefins having the same configuration as the initial thiiran. However, the first two methods can also be used to synthesise olefins if the reaction is carried out with heating. The yields are high in all the methods.

When cyclic sulphides are treated with metallic molybdenum, the degree of desulphurisation diminishes with decrease in ring strain.[133] The reaction of thiiran and 2-methylthiiran afforded the corresponding alkenes in 132 and 119% yields relative to the evaporated molybdenum:

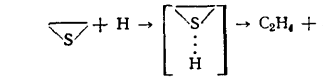


Propene and a small amount of cyclopropane are formed from thietan. It has been suggested that either a biradical is formed as a result of the simultaneous rupture of both C–S bonds or the reaction proceeds with participation of a π-allyl intermediate. The addition of tetraethylthiiran disulphide increases the yield of propene to 77%. The reaction of thiolan results in the formation mainly of hydrogen and a complex mixture of C_1-C_4 products, including 15% of butanethiol. When a cyclic sulphide interacts with carbon vapour (produced from carbon electrodes in a voltaic arc), desulphurisation takes place.[134] The process proceeds via an intermediate ylide, formed when the electrophilic carbon atom and the free electron pair of the suphur atom interact. A CS polymer is formed as a result of the decomposition of the ylide:

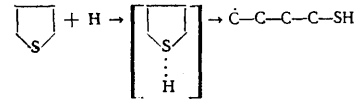




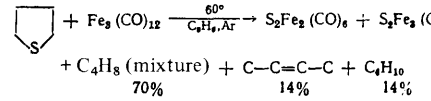
When thiiran is reduced with hydrogen under pressure,[135] ethylene is formed, the sulphur atom being eliminated in the form of a univalent radical:



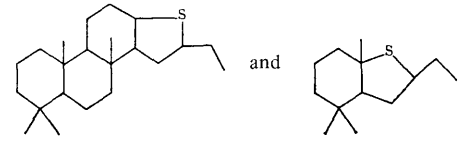
In the reaction involving thiolan, the formation of a mercaptobutyl radical is most probable and in this case the C–S bond is broken:[135]



In the desulphurisation of thiolan by treatment with triiron dodecacarbonyl, the reaction proceeds via a stage involving metal carbonyl sulphide clusters:[136]



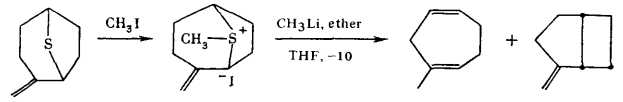
The hydrodesulphurisation of polymethylthiolans and polymethylthianes on the AP-56 industrial platinum catalyst at 350 °C takes place without the decomposition of the carbon skeleton and can be used to investigate petroleum sulphides present in the petrol fractions.[137] Despite the fact that the hydrodesulphurisation over Raney nickel can induce rearrangements and condensation reactions,[1] this reaction has been used to establish the structure in the synthesis of thiabicycloalkanes.[138] The structure of the bicyclic and tetracyclic terpenoid sulphides[139] of the type



found in Athabasca bitumen (a petroleum deposit in Virginia, USA) has also been established with its aid.

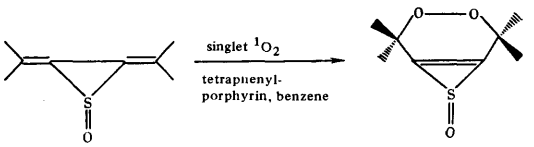
In the synthesis of gramicidin, the desulphurisation of 1,3-dithianes takes place on treatment with lead dioxide and boron trifluoride in methanol[37] (see above).

Sulphur is split-off on treatment of methylsulphonium salts [or their precursors?], for example, 2-methylene-8-thiabicyclo[3.2.1]-octane, with methyl-lithium;[140] for the removal of the sulphur atom, it is essential that at least one of the carbon atoms at the junction should be of the benzyl or allyl type:



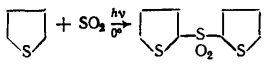
IX. PHOTOCHEMICAL REACTIONS OF THE SULPHIDES

There have been few studies on the photochemical reactions of saturated cyclic sulphurides. The photochemical oxidation of thiiranoradialene sulphoxide (XXVI) leads to thiirene sulphoxide (XXVII) joined to an *endo*-peroxide ring:[141]



(XXVI) (XXVII), 72%

Thiolan combines with sulphur dioxide on irradiation with UV light:[142]



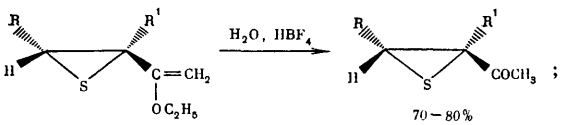
The methylenation of thietans, thiolans, and thianes with the aid of diazomethane on irradiation with UV light leads to alkylthiacycloalkanes;[143] the reaction has been used to identify cyclic sulphides by gas–liquid chromatography.

The decomposition of polycyclic "semi-aromatic" sulphides by light results in the formation of cyclophanes.[144]

X. INTRODUCTION OF FUNCTIONAL GROUPS WITHOUT CHANGE IN THE CARBON SKELETON

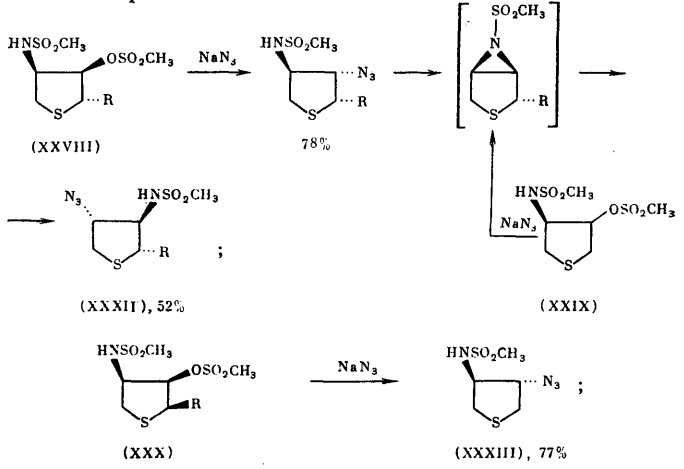
The stereochemical aspect of the study is of special interest in reactions involving the introduction of a functional group.

When ethoxyvinylthiirans undergo acid hydrolysis to acetylthiirans, the configuration is retained:[145]



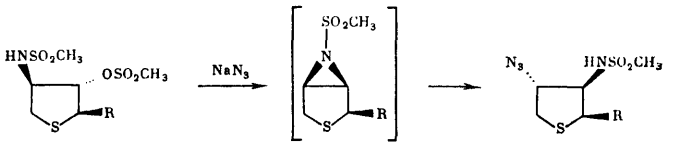
R, R' = H, CH_3.

The reaction of four stereoisomers of 2,3,4-trisubstituted thiolans (XXVIII)–(XXXI) with sodium azide[146] leads to the formation of only the *trans*-3,4-disubstituted compounds (XXXII)–(XXXIV). Consequently, the reaction of the *cis*-3,4-disubstituted thiirans takes place with inversion of the configuration at C(3), while the reaction of the *trans*-3,4-disubstituted compounds proceeds in an unusual manner—without change in configuration. The intermediate formation of the aziridine ring has been suggested[146] and in the case of compounds (XXVIII), (XXIX), and (XXXI) the reaction is accompanied by the migration of the substituents from the 3-position to the 4-position:



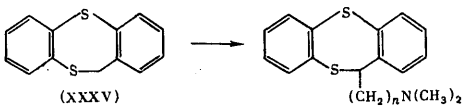
(XXVIII) (XXXII), 52% (XXIX)

(XXX) (XXXIII), 77%



(XXXI) R = $(CH_2)_4COOCH_3$ (XXXIV), 77%

The reaction of 11*H*-dibenzo[*b*,*e*]-1,4-dithiepin (XXXV) with fairly strong bases leads to the abstraction of the proton in the 11-position and the formation of the corresponding carbanion or an organometallic compound.[147] The reaction of the organolithium compound obtained in this way with 2-dimethylaminoethyl chloride or with 2-dimethylaminopropyl chloride affords compounds (XXXVI) or (XXXVII) (isolated in the form of acid oxalates), which exhibit an antireserpine activity:



(XXXV)

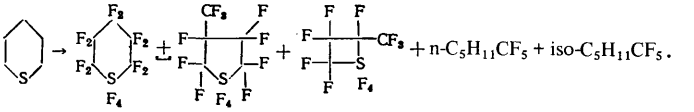
(XXXVI) $n=2$

(XXXVII) $n=3$

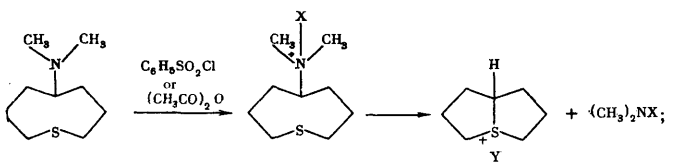
The cyanoethylation of methyl-4-thianones proceeds in different ways depending on the position of the substituent.[148] 2-Methyl-4-thianone gives rise to only 5-(2-cyanoethyl)-2-methyl-4-thianone, 2,2-dimethyl-4-thianone affords only 5,5-di(2-cyanoethyl-2,2-dimethyl-4-thianone, while 3-methyl-4-thianone gives rise to both 3-(2-cyanoethyl)-3-methyl-4-thianone and 3,5-di(2-cyanoethyl)-3-methyl-4-thianone. The authors[148] explain this by the different influences of the substituent on the conformation of the intermediate carbanions.

On treatment with *N*-chlorosuccinimide in benzene (at 20–25 °C), thiolan, thiane, and thiepan produce the corresponding α-chlorothiacycloalkanes.[149]

The electrochemical fluorination of thiolan, 2-methylthiolan, and thiane in anhydrous HF at 5–6 °C [150] involves complete fluorination, for example:



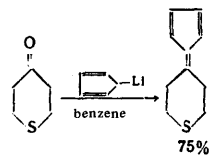
The unusual "functional group elimination" reaction occurring in the interaction of 5-(dimethylamino)-1-thiacyclo-octane with benzenesulphonyl chloride[151] leads to 1-thioniabicyclo[3.3.0]octane benzenesulphonate (compounds of this type are called Eastman's salts) and *NN*-dimethylbenzenesulphonamide in nearly quantitative yields. Acetic anhydride behaves analogously:



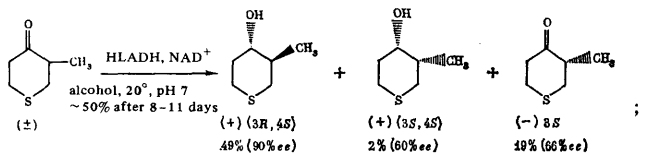
X = $C_6H_5SO_2$ or CH_3CO;

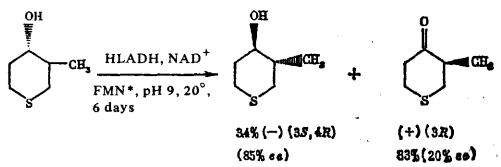
Y = $C_6H_5SO_2O^-$ or CH_3COO^-.

The reactions of the keto-group in thiacycloalkanes are used for synthetic purposes; for example, lithiocyclopentadiene reacts with 4-thianone:[152]



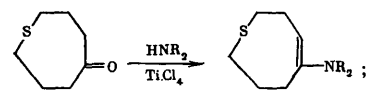
The enzymatic reduction of the keto-group in 4-thianones by horse liver alcohol dehydrogenase (HLADH) in the presence of a co-enzyme—a nicotinamide derivative (NAD^+)—proceeds with high stereoselectivity and enantiomeric selectivity.[153] The oxidation of *trans*-4-thianols with participation of HLADH is also promising for the synthesis of enantiomers which have not reacted (the *cis*-isomers are oxidised very slowly):[143]





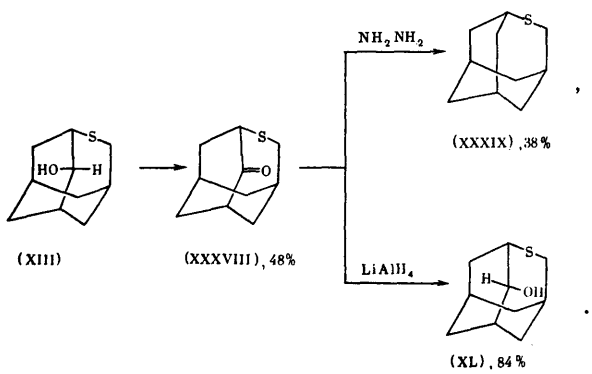
*FMN = flavin mononucleotide (recyclising agent).

5-Thiocanone reacts with secondary amines to produce enamines—derivatives of tetrahydrothiocin:[154]



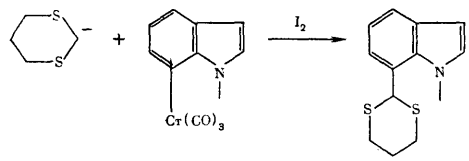
$R_2 = (CH_3)_2, -(CH_2)_4-, -(CH_2)_2-O-(CH_2)_2-$.

The reduction of 2-methyl-1-thiadecalones and 2-methyl-1-thiahydrindanones with hydrazine hydrate leads to a mixture of stereoisomeric 2-methyl-1-thiadecalins or 2-methyl-1-thiahydrindans; the stereoisomers are separated chromatographically.[155] 4-Thiahomoadamantan-2-one (XXXVIII) [obtained by oxidising compound (XIII)] is reduced[39] to 4-thiahomoadamantane (XXXIX) in the same way; the reduction of compound (XXXVIII) with lithium tetrahydroaluminate leads to a stereoisomer of 2-hydroxy-4-thiahomoadamantane (XL):



Treatment of compound (XIII) with thionyl chloride produces[39] the corresponding chloride in 98% yield; it is reduced with lithium tetrahydroaluminate to compound (XXXIX) in 82% yield.

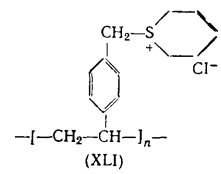
The nucleophilic attack by 2-lithio-1,3-dithiane is directed to the 7-position in π-indolechromium tricarbonyl and a 7-substituted indole is formed in a high yield;[156] the chromium π-complexes are decomposed with iodine:



XI. THE SYNTHESIS AND REACTIONS OF CYCLIC SULPHONIUM SALTS

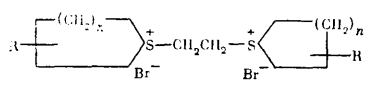
The introduction of functional groups into cyclic sulphides by converting them into sulphonium compounds is important. They are extremely promising for practical use and also open up pathways to the synthesis of a wide variety of polyfunctional compounds, especially compounds based on thioniacycloalkanes.

Chlorobenzylthiolanium and chlorobenzylthianium halides are formed when cyclic sulphides interact with chlorobenzyl halides in nitromethane (the yields of the sulphonium salts are 43–72%).[157] The vinylbenzylthianium and vinylbenzyl(3-pentyl)thiolanium halides are obtained analogously to serve as monomers for the preparation of polymers of type (XLI) by radical polymerisation; aqueous solutions of the polymers are used as flocculants:[158]



(XLI)

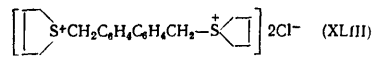
Ethylenebis-sulphonium salts of type (XLII) have been patented[159] as fungicides and agents active against phytopathogenic microbes; the salts are obtained from ethylene dihalide and a cyclic sulphide in DMF at 75 °C:



$n = 0.1$; R = Cl, Br, alkyl, alkoxyl, carboxyl

(XLII)

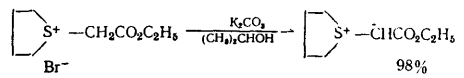
The bis-sulphonium salt (XLIII)



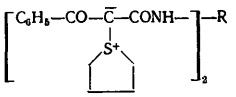
$2Cl^-$ (XLIII)

was obtained[160] by heating thiolan and 4,4′-di(chloromethyl)biphenyl in concentrated hydrochloric acid at 65 °C (yield 98%). Salts of this type, including those obtained from thiane and thiepan,[160] serve as intermediates in the synthesis of dyes.

Stable ylides, for example:[161]



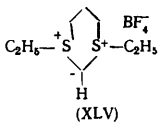
can be obtained by treating with bases thiolanium[161] or dithiolanium[162] salts having electron-accepting substituents. Ylides of types (XLIV) are used as cross-linking agents for carboxyl-containing polymers:[163]



(XLIV)

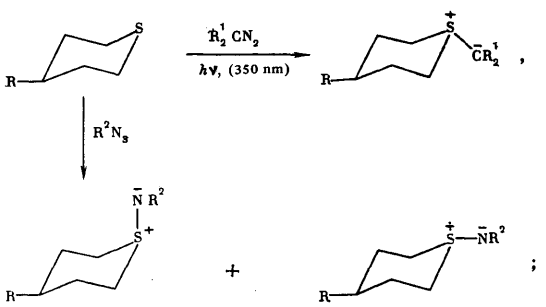
R=$C_6H_4OC_6H_4$, from C_2 to C_{20}.

Bis-sulphonium salts—alkyl-substituted 1,3-dithiolanium and 1,3-dithianium picrates and fluoroborates—are powerful CH acids:[164] 1,3-diethyl-1,3-dithianium bis(tetrafluoroborate) is deprotonated and gives rise to the stable ylide salt (XLV):



(XLV)

Only one sulphonium ylide is formed on interaction of 4-t-butylthiane with carbenes as a result of equatorial addition; on interaction with nitrenes, a 1 : 1 mixture of diastereoisomeric iminosulphuranes is formed in each case:[165]



R = t-C_4H_9, R^1 = $COCH_3$, $COOCH_3$, R^2 = *p*-CH_3-$C_6H_4SO_2$, COO_2H_5.

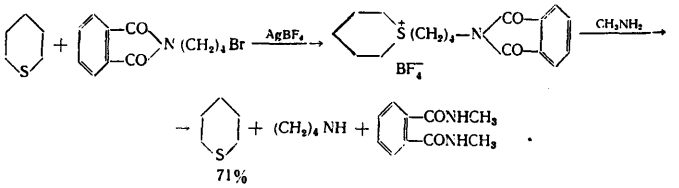
Eastman's salts—fluorides of 1-thioniabicyclo[4.4.0]decane and 6-methoxycarbonyl-1-thioniabicyclo[4.4.0]decane—have been obtained as *cis*- and *trans*-stereoisomers (isolated in the purest form) and from them ylides were synthesised:[166] the ylide from the *cis*-isomer is more stable.

Conformational analysis of the salts of methyl-substituted *cis*-1-thioniabicyclo[4.3.0]nonane derivatives has been carried out.[167]

The conformational energy of the equilibrium transition between the axial and equatorial forms of 1-methylthianium hexafluorophosphates and perchlorates, obtained by methylating thiane, 2-, 3-, and 4-methylthianes, and the *cis*- and *trans*-stereoisomers of 2,6-, 3,5-, 2,5-, and 2,4-dimethylthianes, 3,4-, 3,3-, and 4,4-dimethylthianes, 3,3,5- and 2,2,4-trimethylthianes, and 4-t-butylthiane, has been measured.[168] Its value is low for these salts (0.0 – 0.3 kcal mol^{-1}). 1-Phenyl- and benzyl-thianium and the diastereoisomeric 4-t-butyl- and 1-benzyl-2,6-dimethyl-thianium fluoroborates, 4-t-butyl-1-ethylthianium perchlorates, and 1-methyl-*cis*- and 1-methyl-*trans*-thiadecalinium hexafluorophosphates and perchlorates have been obtained by alkylating the corresponding sulphides.[168]

Thianes are deuteriated using sulphonium salts;[169] the methiodides are obtained and the acid α-hydrogen atoms are subjected to deuterium exchange (base catalysis in solution in D_2O), the sulphonium salt is reisolated, and dry-distilled to give the deuteriated thiane.

A method for protecting the sulphide sulphur against the action of metal catalysts, electrophiles, and oxidants by converting the sulphides into the 4-aminobutyl- or *p*-methoxybenzyl-sulphonium salts, which are cleaved with regeneration of the sulphides, has been proposed recently:[170]



A method for the preparation of the perchlorates of 4-hydroxyarylthioniacycloalkanes by condensing thiacycloalkanes with phenols in the presence of perchloric acid, phosphoryl chloride, and hydrogen peroxide or by condensing thiacycloalkane oxides under the same conditions but without hydrogen peroxide has been put forward.[171] In the 4-hydroxy-phenylthiolanium and 4-hydroxy-1-naphthylthiolnium perchlorates obtained in this way, there is a hydrogen bond between the hydroxyls of the cation and the oxygen of the anion.[172,173] Furthermore, in 4-hydroxyphenylthianium perchlorate there is a bifurcated hydrogen bond formed by the hydroxyl of another cation and two oxygen atoms of two other anions.[174]

The perchlorates of *p*-hydroxy- and *p*-methoxy-phenylthioniacycloalkanes have been obtained from the petroleum sulphoxides and phenol and anisole.[175] The condensation of the petroleum sulphoxides with phenol then proceeds selectively—only thiamonocycloalkane oxides interact under these conditions.

4-Hydroxy-2(3)-methyl-, 2,4-dihydroxy-, 2,3,4-trihydroxy-, and 2,5-dihydroxy-phenylthiolanium chlorides have been obtained by the reaction of substituted phenols with thiolan and chlorine;[6] the yields (57 – 75%) vary in parallel with the activity of the phenols.

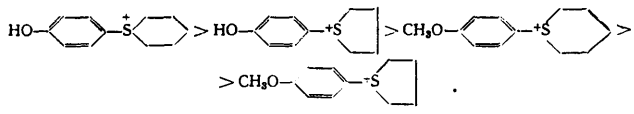
Sulphonium salts have been obtained by the interaction of thiolan with alkenes or quinones in a strong acid.[176,177] The latter method has been modified[178] and has led to a single-stage procedure for the synthesis of a wide variety of salts of 2,5-dihydroxyphenylthioniacycloalkanes in good yields (as a rule 60 – 100%). The OH group in 2,5-dihydroxyphenylthianium perchlorate, located in the 5-position in the cation, is hydrogen-bonded to the oxygen atom of the anion.[179] In the hydrate of 2,5-dihydroxyphenylthianium chloride,[178] there are three types of hydrogen bonds: between the OH group in the 2-position in the cation and the chloride anion, between the OH group in the 5-position in the cation and the oxygen atom of water, and also between a water molecule and two chloride anions.[180]

The petroleum sulphides obtained from the middle fractions of petroleum have been converted by condensation with *p*-benzoquinone and hydrochloric acid into the chlorides of 2,5-dihydroxyphenylthioniacycloalkanes (yield up to 75%).[181] Sulphonium salts—water-soluble dyes for polyester fibres—have been obtained[182] by condensing thiacycloalkanes with anthraquinones by Bosshard's method.[177]

The C – S bond dissociation reactions on treatment of arylthiolanium and arylthianium salts with nucleophiles have been investigated.[183-185] The ease of dissociation of the C – S bond varies in parallel with the degree of nucleophilicity of the reagent:[185]

$$CH_3O^- \geqslant Cl^- > Br^- > I^- \geqslant (NO_2)_2C_6H_2O^- .$$

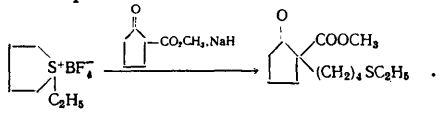
The relative stabilities of the heterocycle in the cations of sulphonium perchlorates decrease in the sequence[185]



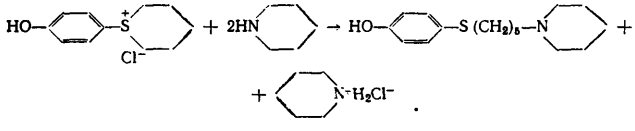
The interaction of salts of *p*-methoxyphenylthioniacycloalkanes with an aqueous or methanol solution of potassium hydroxide gives rise to ω-hydroxy-, ω-methoxy-, or ω-chloro-substituted butyl or pentyl *p*-methoxyphenyl sulphides in preparative yields (60–86%).[185]

On treatment with potassium t-butoxide in DMSO, phenylthiolanium perchlorate decomposes into phenyl vinyl sulphide and ethylene, while phenylthianium perchlorate affords 100% of the β-elimination product $C_6H_5S(CH_2)_3CH=CH_2$.[183] When these salts are treated with sodium ethoxide in alcohol, mixtures of β-elimination and α-substitution products are formed; in the case of the thianium salt, the latter predominates.[183]

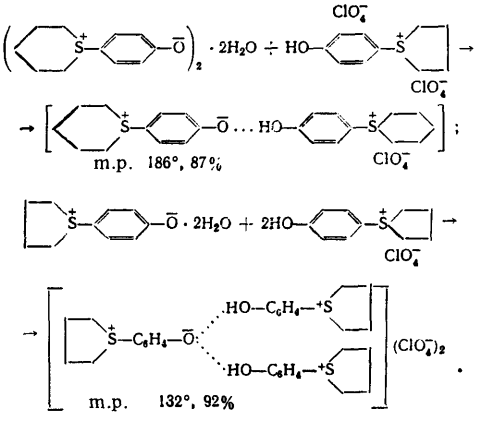
Cyclic sulphonium salts have been used for the *C*-alkylation of β-ketoesters,[186] for example:



When salts of arylthioniacycloalkanes interact with amines, the C–S bond is broken and the main amine adds on; this reaction constitutes a simple single-stage method of synthesis of ω-aminoalkyl aryl sulphides and their salts, for example:[187,188]



On treatment with bases, *p*-hydroxyphenyl-1-thiolanium and *p*-hydroxyphenyl-1-thianium salts form hydrated zwitter-ions, which readily lose water on heating and polymerise.[171,185,189–193] The zwitter-ions are also stabilised by the perchlorates of *p*-hydroxyphenylthioniacycloalkanes; stable crystalline polysulphonium salts with complex cations, formed with participation of hydrogen bonds, are then obtained:[189,190]



The oligomers produces from *p*-(1-thiolania)phenoxide with the $-[S(CH_2)_4OC_6H_6]-$ fragment have an end group with an unopened thiolanium ring; on treatment with amines, the end group is opened, affording an aminosulphide residue.[190]

Hydroxyarylthioniacycloalkane zwitter-ions are apparently polymerised via a cationic mechanism. The polymers can be used to obtain water-resistant thermoplastic resins, coatings, films, and impregnating agents.[192–195] The hydrated *p*-(1-thiolania)phenoxide and *p*-(1-thiolania)-*o*-cresolate zwitter-ions are used[196,197] as catalysts of the polycyclotrimerisation of aryl isocyanates.

The addition of *p*-t-butylthiolanium bicarbonate or bisulphate to carboxylated polymers increases the water resistance of the films obtained from them.[198]

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