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The Reactivity of Epithio-compounds†

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The available information about the reactions of epithio-compounds with nucleophilic and electrophilic agents, about the homolytic reactions of alkene sulphides, and about reactions leading to the elimination of sulphur with formation of alkenes is examined, the mechanisms of the opening of thiiran rings are discussed, and the comparative characteristics of the reactivities of O- and S-heteroanalogues of cyclopropane compounds are given.
The bibliography includes 276 references.

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I. INTRODUCTION

The increasing interest in the chemistry of sulphur-containing organic compounds is not fortuitous and is due primarily to the urgent necessity for the utilisation of large amounts of sulphur and its simple compounds, the reserves of which are continuously increasing as a result of the increasing output of the metal extracting industry. In terms of this aspect, the chemistry of thiirans has unlimited possibilities. It is sufficient to mention that the methods of synthesising epithio-compounds developed in recent years are based on the use of sulphur chlorides, carbon disulphide, carbon oxide sulphide, metal sulphides, and other simple sulphur compounds [1].

In contrast to oxirans, the chemistry of which is closely related to the large-scale manufacture of a wide variety of substances and materials, thiirans have not as yet found extensive applications. The prospects for the practical utilisation of epithio-compounds became apparent only in the last decade. The polymerisation reactions of thiirans, which have become an independent field of study, are specially important from this point of view [2-4].

The most notable advances in the synthesis of high-molecular-weight compounds (HMC) based on thiirans have been achieved after the discovery of the high initiating capacity in these processes of organic and inorganic derivatives of zinc-subgroup metals. Using catalysts of this type, methods have been developed for the stereospecific polymerisation of racemic thiirans [5-8] and procedures for the formation of elastomeric homo- and co-polymers [9-19], thermoplastic fibre-forming high-molecular-weight compounds [20], and latexes resembling rubber latexes [21]. Polymers synthesised by this method are frequently vulcanised by sulphur [22] and can be readily worked by casting or pressing [23,24]; the articles obtained are resistant to corrosive media, solvents, and light, and possess useful mechanical properties. Elastomeric poly(alkylene sulphides) are satisfactorily covulcanised with rubbers [25,26]. The covulcanisates obtained exhibit low swellability in organic solvents and an enhanced resistance to the action of light.

Various methods for anionic and cationic polymerisation of thiirans [27-31] and for their copolymerisation with other monomers [32-35], whereby it is possible to obtain high-molecular-compounds with properties valuable in practice, have been extensively studied. The possibility of imparting water-repellent properties and of increasing the light resistance of materials made of synthetic and natural polymers by grafting poly(alkylene sulphides) on to them has also been demonstrated. The above, by no means complete, list of applications of the polymerisation capacity of thiirans shows that their practical utilisation in the immediate future is feasible.

The possibility of direct applications of thiirans has been studied much less. Among the compounds examined, there are substances with a high nematocidal activity [36] and with insecticidal [37], bactericidal [38-40], and herbicidal [41] properties. However, their use in practice is limited because of their extremely unpleasant smell. For the same reason, the use of epithio-compounds as components of pesticidal preparations is unlikely, despite their high stabilising activity [42]. The unpleasant smell makes it possible to use certain thiirans to impart an odour to gases and poisonous liquids [43].

The employment of epithio-compounds as intermediates in the synthesis of anticorrosion and antiwear additives to lubricating oils and greases, surfactants, flotation reagents, extractants, sorbents for hydrometallurgy, and pesticidal preparations is more promising. The advances achieved in research in the above fields are in many respects determined by the level of knowledge of the reactivities of the compounds.

The chemistry of epithio-compounds is at present being established. During the last ten years, studies have been made on the reactions of thiirans with a wide variety of electrophilic and nucleophilic compounds. The first qualitative and semiquantitative determinations have been made of the reactivities of thiirans. The extensive application of physicochemical methods to demonstrate the structures of the reaction products made it possible to reassess the characteristics of the reactions involving the opening of thiiran rings. For these reasons, the latest reviews on the chemistry of thiirans available to the Soviet reader [44,45] no longer reflect the present state of the problem. In the present paper an attempt is made to give a systematic account and a critical assessment of the available information about the reactivities of epithioalkanes.

† Sulphur-containing heteroanalogues of cyclopropane derivatives are also called epithioalkanes, alkylene sulphides, and thiirans [1].

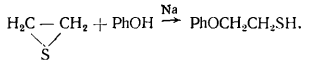
II. NUCLEOPHILIC CLEAVAGE REACTIONS

Alcohols, phenols, phosphites, thiols, organometallic compounds, primary and secondary amines, certain C–H acids, and metal hydrides have been involved in the nucleophilic opening of the three-membered ring of epithio-compounds. The characteristics of the above reactions have been by no means completely elucidated and in analysing the results one can only speak of the most general relations between the properties of the starting materials, the nature of the products, and the conditions governing their formation.

a. Reactions with Hydroxy-Compounds

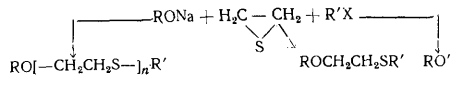
The attempts to introduce water and ethanol into reactions with 2-methylthiiran in the absence of catalysts led to the formation of a complex mixture of oligomeric products [46]. Ring opening occurred only under severe conditions (100°C). Thiiran and 2-methylthiiran react vigorously with water and alcohols in the presence of various alkaline agents [47–54], forming polymeric products. Thiiran itself polymerises particularly readily under these conditions (at room temperature). The polymerisation of 2-methylthiiran in alcoholic solutions of bases requires moderate heating. Monomeric products are not formed in reactions of thiirans with alcohols in the presence of bases and with alkali metal alkoxides.

Sodium phenoxide is said [55–57] to condense with thiiran to form 2-phenoxyethanethiol:

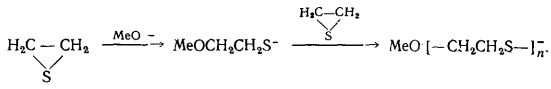


However, it has been shown recently [58] that polymerisation reactions are the main processes in this case too and monomeric products are formed in extremely small amounts.

Certain hypotheses concerning the nature of the nucleophilic reactions involving the opening of thiiran rings by hydroxy-compounds may be based on data obtained in studies of competing reactions in sodium alkoxide (phenoxide)–thiiran–electrophilic agent systems [59]. The opening of the thiiran ring by sodium methoxide and phenoxide in non-polar media proceeds at a satisfactory rate only at 40–50°C and is accompanied by polymerisation reactions. In the presence of electrophilic reagents, polymerisation reactions are suppressed. Depending on the properties of the electrophilic agent, low-molecular-weight oligomeric substances or products of the alkylation of 2-methoxy-(phenoxy)ethanethiol are formed under these conditions:

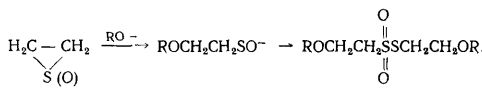


In the presence of strong electrophilic agents such as allylic alkyl halides, the reactions in the above system lead to monomeric products, and diethers of ethylene monothioglycol are formed in yields up to 50%. These results led to the hypothesis that, in media of low polarity, the electrophilic properties of thiiran and allylic alkyl halides are comparable. A study [59] has shown that the polymerisation reactions of thiirans with hydroxy-compounds in the presence of alkaline catalysts are due to the formation of thiolate anions, which are more reactive than alkoxide anions:

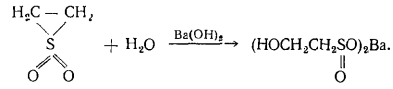


The ability of hydroxy-compounds to cleave thiiran rings comparatively readily has been used to graft poly(ethylene sulphide) and poly(propylene sulphide) to cotton, cellulose, paper, and similar materials in order to make them light resistant, water repellent, etc. [60–66].

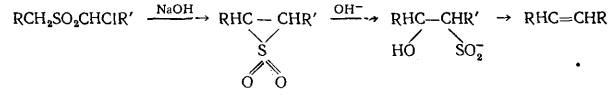
In contrast to thiirans, episulphoxides and episulphones are cleaved by hydroxy-compounds to monomeric products. On heating with water and alcohols, thiiran 1-oxide interacts according to the equation [67]



In the presence of barium hydroxide, the thiiran 1,1-dioxide ring undergoes hydrolytic cleavage under mild conditions [68]:

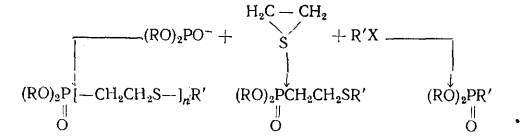


In the presence of sodium and potassium hydroxides a wide variety of alkylene episulphones, which are intermediates in the Ramberg–Baeckland rearrangement [1], react similarly:

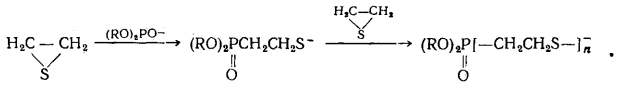


b. Reactions with Phosphites

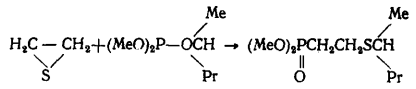
The acidity of dialkyl phosphites is higher almost by two orders of magnitude than that of alcohols. Despite this, the reactions of sodium dialkyl phosphites with thiiran lead to polymeric products only [69]. Polymerisation takes place also when a mixture of dialkyl phosphite and thiiran is treated with sodium alkoxides. In the presence of alkyl halides, the polymerisation reactions are suppressed. In a system of competing reactions between dialkyl phosphites, thiiran, and alkyl halides, the direction of the process is determined by the relative reactivities of the electrophilic agents:



In the presence of allylic alkyl halides, the reactions proceed only with formation of monomeric products. Thus, as in the reactions with hydroxy-compounds, the polymerisation of thiiran on interaction with dialkyl phosphites in the presence of bases is a consequence of the more pronounced nucleophilic properties of the resulting thiolate anions compared with dialkyl phosphite anions:

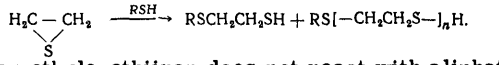


Trialkyl phosphites eliminate sulphur from epithio-compounds under comparatively mild conditions (see below). However, according to patent data [70], phosphites with secondary alkyl groups are involved in thiiran ring opening reactions:



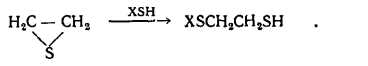
c. 2-Mercaptoalkylation of Thiols

The cleavage of the thiiran ring by thiols takes place even in the absence of catalysts. The reaction conditions are determined by the nature of the nucleophile and of the epithio-compound. According to a patent [71], aliphatic thiols interact with thiiran at 100–200°C, forming mixtures of 2-alkylthioethanethiols (up to 50%) with products of oligomerisation reactions:



2,3-Tetramethylenethiiran does not react with aliphatic thiols under these conditions [46]. According to a later report [72], thiiran condenses with thiols in the presence of a two-fold excess of the latter even at 50–70°C.

2-Mercaptoalkylation is facilitated with increase of the acidity of the thiol. Hydrogen sulphide in methanol condenses with thiiran at 45–60°C, forming ethylene dithioglycol and oligomeric products [73]. Thiophenol [72], dialkyl phosphorodithioic, phosphonothioic, and phosphonodithioic acids react under similar conditions with formation of monomeric reaction products [74–77]:

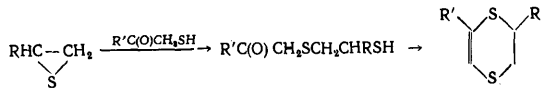


[X=Ph, $(RO)_2P(S)$, R $(R'O)_2P(S)$].

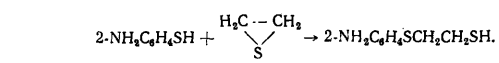
Thus unambiguous non-catalysed reactions occur only between thiirans and highly nucleophilic thiols. The relatively mild conditions of the above reactions make it possible to graft thiiran to wool fibres and human and animal hair [78,79]. In the latter case the reactions involve cysteinyl residues of protein molecules.

The condensation of thiirans with thiols is promoted by bases. 2-Methyl-, 2,3-tetramethylene-, and 2-hexylthiirans react with sodium and potassium hydrogen sulphides under mild conditions [46,80,81]. Like 2-chloromethyloxiran, 2-chloromethylthiiran forms polymeric products in this reaction [82]. The epithio-compound proved to be less reactive than its oxygen analogue. On moderate heating in the presence of sodium methoxide or ethoxide, aliphatic thiols condense with thiiran, 2,2-dimethylthiiran, and 2,3-tetramethylenethiiran [46,73,83–85]. The yield of monomercaptoalkylation products for stoichiometric proportions of the reactants does not exceed 40–50%, but may be raised to 75% by using a twofold excess of the thiol [83]. Similar results were obtained also in reactions of 2-methylthiiran [86,87], 2-mercaptomethylthiiran, and its acetyl analogue [87]. The amount of catalyst does not have a marked influence on the yield of reaction products.

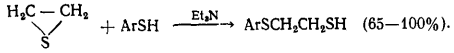
In the presence of alkali metal alkoxides, primary, secondary, and tertiary aliphatic thiols were made to react with thiirans. The yield of condensation products was found to decrease with increasing steric effects at the mercapto-group [46]. 2-Alkoxyalkanethiols react with thiirans just as readily as other primary thiols [83,85]. On reaction with thiirans, α-mercaptoketones form 2-mercaptoalkylation products, which cyclise under the reaction conditions to 2,3-dehydro-1,4-dithiane derivatives [88]:



Reactions involving 2-mercaptoalkylation of thiols catalysed by organic bases have been investigated. *o*-Aminothiophenol reacts smoothly with thiiran at 20°C [89]:

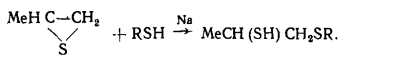


In the presence of triethylamine, thiophenol and its halogeno-, methyl-, and methoxy-substituted homologues condense with thiiran at 40–50°C [90]:

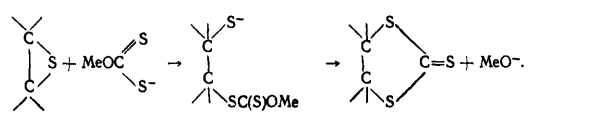


For equimolar proportions of the reactants, monomeric products are formed quantitatively when sterically unhindered thiophenols are used [91]. Quantitative 2-mercaptoethylation of aliphatic thiols and *o*-substituted thiophenols proceeds only in the presence of an excess (100–200%) of the initial thiol. The condensation of thiiran with thioacetic acid under these conditions is accompanied by polymerisation reactions.

The addition of thiophenols to thiiran in non-polar media catalysed by triethylamine proceeds with somewhat greater difficulty than the addition to oxiran [91]. Thiophenol and *p*-thiocresol are quantitatively titrated by oxiran at 20°C, while titration by thiiran requires heating above 40°C. The mode of opening of the thiiran ring by thiolate anions has been investigated [84,87,92] and it has been shown that 2,2-dimethylthiiran is cleaved mainly in accordance with Krasuskii's rule at the carbon atom with the largest number of hydrogen atoms [84]. However, products with the "anomalous" structure (primary thiols) are formed in small amounts (up to 4%). 2-Methylthiiran also reacts with thiols in accordance with Krasuskii's rule [87]. This conclusion was confirmed in a later study [92] where the structure of the condensation product was demonstrated by gas–liquid chromatography (GLC) and NMR:



Unusual reactions between thiiran and salts of thio- and dithio-carbonic acids have been discovered. Potassium methyl xanthate converts 2,3-tetramethylenethiiran into 1,2-cyclohexylene trithiocarbonate [80,93]. The reaction proceeds via a ring-opening stage according to the mechanism



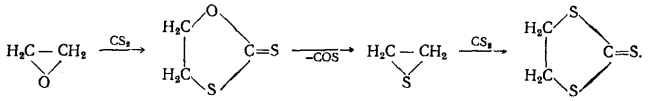
In polar media the cleavage of thiiran and oxiran rings by xanthates proceeds with equal ease. For this reason, the reactions of oxirans and thiirans with carbon disulphide and alkalis in methanol give rise to the same products—trithiocarbonates [80,93–97]. With increase of the size of the alkyl group in the xanthate, the yield of the condensation product falls because of side reactions. The reaction of ethyl xanthate with steroid epoxides already gives rise to small amounts of unsaturated compounds together with dithiocarbonates, while in the reaction with butyl xanthate the unsaturated compounds are the only products [97].

The formation of alkenes is probably associated with steric effects in the opening of the thiiran ring. In the reaction with methyl xanthate even thioglycidic acids, which readily eliminate sulphur, are smoothly converted into trithiocarbonates [98].

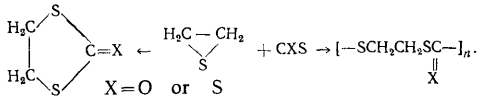
The formation of trithiocarbonates is not the only pathway in the reactions of thiirans with xanthates. High-molecular-weight compounds containing dithiocarbonic acid groups in the polymer chain react with thiiran like the usual thiols. Thus, on treatment of viscose fibres with thiirans, the xanthate groups in the polymer matrix are not split off [99]. The nucleophilic opening of the thiirans by thiols is widely used in the synthesis of polymers. By grafting poly(alkylene sulphides) to alkaline viscose, water repellent viscose fibres are obtained [99]. Elastomeric high-molecular-weight compounds have been obtained by the copolymerisation of 2-methylthiiran with 1,3-dimercaptopropane in the presence of tertiary amines [100]. Certain thiols (sodium sulphide and hydrogen sulphide, hydrogen sulphide, and 1,2-dimercaptoethane) are effective catalysts in the polymerisation of lower epithio-compounds in polar media [101]. Hydrogen sulphide and aliphatic thiols are used as effective cocatalysts of organic and inorganic zinc-subgroup metal derivatives in the polymerisation and copolymerisation of various thiirans [102-105]. Zinc xanthates [106] and iron, cobalt, and other metal mercaptides [107] have also been used as polymerisation catalysts.

d. Condensation of Thiirans with Thiono-Compounds

The possibility of the nucleophilic condensation of thiiran with thiono-compounds was suggested for the first time by Durden et al. [108] in order to explain the formation of ethylene trithiocarbonate in the reaction of oxiran with carbon disulphide catalysed by triethylamine:



Razuvaev and coworkers confirmed this hypothesis experimentally having shown that in the presence of triethylamine as the catalyst thiiran condenses with carbon disulphide [109,110] and carbonyl sulphide [111,112], forming monomeric cycloaddition products or regular low-molecular-weight polymers:

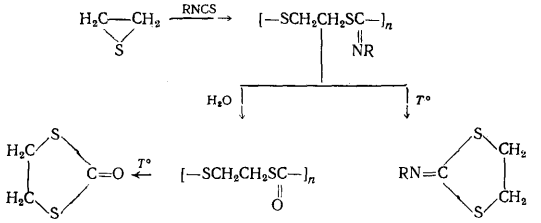


The reaction proceeds even at 20°C and at 95–100°C reaches completion in several hours. In the above reactions carbon disulphide is much more reactive than carbonyl oxide sulphide. Apart from oxiran, 3-methyloxiran and 2,3-tetramethyleneoxiran condense with carbon disulphide and carbonyl sulphide. 2-Chloromethylthiiran does not enter into these reactions probably because of the inactivation of the catalyst in the reaction mass.

The mechanism of the above reactions has not been investigated. Presumably the species initiating the process is the thiolate anion formed when the thiono-compound reacts with triethylamine. The product of its condensation with a thiiran molecule undergoes an intramolecular rearrangement or reacts with a second molecule of the thiono-compounds, propagating the polymer chain.

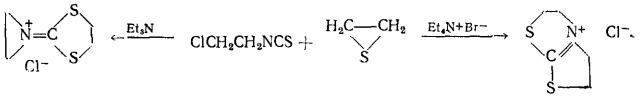
The nucleophilic addition of carbon disulphide and carbonyl sulphide to thiirans proceeds under somewhat more severe conditions than in the reactions with oxirans. As a result, the reactions of thiirans with carbonyl sulphide and carbon disulphide are used under suitable conditions to obtain epithio-compounds and alkylene monothiocarbonates and dithiocarbonates [113-122].

The thiono-compounds used in reactions with thiirans included alkyl and aryl isothiocyanates. The condensation of thiiran and 2-methylthiiran with methyl, ethyl, n-butyl, phenyl, *p*-tolyl, and α-naphthyl isothiocyanates proceeds under mild conditions in the presence of triethylamine as the catalyst. The reaction products are low-molecular-weight polymers, which are decomposed by bases and acids [123,124]:



Polymers with higher molecular weights are formed when the reactions are catalysed by butyl-lithium and sodionaphthalene [125-130]. The rate of copolymerisation of thiirans is reduced in this case with increase of the molecular weight of the isothiocyanate and when the electron-accepting properties of the substituent at the isothiocyanato-group are enhanced. The process proceeds via a stepwise mechanism with participation of "live" polymer molecules. The degree of reaction increases with increase of the basicity of the solvent, exceeding 90% in hexamethylphosphoramide. It is believed that the thiolate anion formed when the catalyst reacts with the isothiocyanate initiates the copolymerisation.

In contrast to unsubstituted alkyl isothiocyanates, 2-chloroethyl isothiocyanate reacts with thiiran to form monomeric products: 1-(1,3-dithian-2-yl)aziridinium chloride in the presence of triethylamine as the catalyst and 2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolinium chloride in the presence of tetraethylammonium bromide [131]:

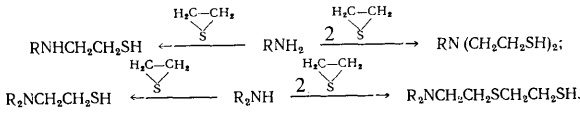


e. 2-Mercaptoalkylation of Amines

Nucleophilic reactions involving the opening of thiiran rings by nitrogen-containing compounds have been most thoroughly investigated among processes of this type. Despite this, the published studies are confined mainly to the description of the reactions of thiirans with primary and secondary amines. Ammonia, hydroxylamine, hydrazine, and acid amides and imides have not so far been 2-mercaptoalkylated.

The report of the synthesis of monomeric products of the condensation of thiirans with primary and secondary aliphatic, aromatic-aliphatic, and aromatic amines first appeared in the patent literature [132]. Thiiran and 2-methylthiiran react with amines in a closed vessel at

100–200°C. It was assumed that, depending on the reactant ratio, mono- or di-mercaptoalkylation products are formed:

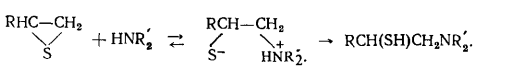


Under the conditions described in the above patent[132], thiiran was condensed with various secondary amines[133,134]. Gilmann and Woods[135] described the reaction of thiiran with lithium diethylamide and showed that the yield of product is in this case even lower than in Ref. 132. The structure of primary thiols was attributed to products of the condensation of 2-methylthiiran with amines[132], i.e. the "anomalous" opening of the thiiran ring by these substances was postulated. Hansen[136,137], who investigated the reaction of dimethylamine with thiiran and 2-methylthiiran in ether, later reached a similar conclusion.

The reactions of thiiran, 2-methylthiiran, 2,2-dimethylthiiran, and 2,3-tetramethylenethiiran with primary and secondary amines were described extensively for the first time by Snyder et al. [138], who showed that the rate of reaction of primary and secondary amines with thiirans at 100°C, using stoichiometric reactant ratios, depends significantly on steric effects. The reaction products were obtained in a high yield only from sterically unhindered amines. Amines with the iso-structure are mercaptoethylated with greater difficulty than n-alkylamines. Diphenyl- and dicyclohexyl-amines are not mercaptoethylated at 100°C. Among thiirans, the unsubstituted thiiran is the most reactive. With increase of the bulk of the substituents in the thiiran ring, the reactivity of the latter falls. Thiirans can be arranged in the following sequence in terms of decreasing capacity for cleavage by amines: thiiran > 2-methylthiiran > 2,2-dimethylthiiran > 2,3-tetramethylenethiiran.

According to Snyder et al. [138], the addition of secondary amines to 2,2-dimethylthiiran leads to the formation of tertiary mercaptans. This disproves the hypothesis of the "anomalous" opening of thiiran rings by amines and shows that the nucleophilic agent attacks the ring carbon atom with the greatest number of hydrogen atoms, in accordance with Krasuskii's rule. The "normal" cleavage of the thiiran ring by amines was subsequently demonstrated in reactions of secondary amines with 2-methylthiiran and 2,2-dimethylthiiran[139], alkoxy- and aryloxy-derivatives of 2-methylthiiran[140,141], 2-phenylthiiran[142], aminomethylthiirans[143], and 2-vinylthiiran[144].

The principal characteristics of the reactions of thiirans with amines, obtained by Snyder et al., in qualitative and semiquantitative studies, were confirmed by the kinetic data[145]. The study of the influence of the basicity of amines and steric factors on the rate of cleavage of thiiran rings in dioxan at 60°C suggested a typical S_N2 mechanism for these reactions. The first step is believed to be slow attack by the nucleophilic agent on the relatively unhindered ring carbon atom, after which there is rapid migration of a proton from the nitrogen atom to the sulphur atom:



However, Oddon and Wylde's ideas[145] concerning the formation of an intermediate dipolar adduct are doubtful. Analysis of data for the influence of the structure of the amine on the optimal conditions in the formation of monomeric condensation products suggests synchronous transfer of a proton to the sulphur atom and of the nucleophilic species to the carbon atom. Otherwise the reaction is accompanied by polymerisation processes.

The influence of solvents on 2-mercaptoalkylation reactions of amines was discussed wisely for the first time in a report by Braz[54]. It was shown that thiiran reacts with secondary amines even without heating. In order to exclude the polymerisation of thiiran, it is desirable to carry out the reactions in an excess of the amine employed or in non-polar solvents in the presence of an excess of the amine. At 50–60°C the lower amines react rapidly with thiiran. These results[54] were confirmed by other studies and have been widely used by many investigators[146–149]. It proved possible to condense thiiran with aziridine in non-polar solvents, the two compounds copolymerising readily in the absence of a solvent[149].

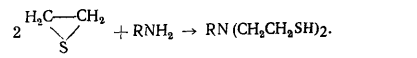
Other investigators made somewhat different recommendations concerning the choice of solvents. Thus it is recommended that thiirans be condensed with highly polar amines under homogeneous conditions using their solutions in a mixture of benzene and anhydrous alcohol[148,150]. The 2-mercaptoalkylation of *N*-methylaniline by 2,3-tetramethylenethiiran proceeds smoothly in aqueous alcohol, but does not occur in the absence of a solvent[46]. 2-Phenylthiiran undergoes sulphur-elimination reactions with piperidine and morpholine in the absence of solvents[151]. Normal addition products are formed in the mixture of benzene and alcohol and the degradation of the thiiran is not observed.

The above and other similar data[140,143,147] suggest that the optimal conditions for the 2-mercaptoalkylation reactions depend greatly on the electrophilic properties of the thiiran and on the basicity of the amine. The polarity of the medium facilitates the nucleophilic opening of the thiiran ring by amines, which may be used only in reactions with amines of low basicity. Highly basic amines can be made to react with relatively unreactive thiirans in polar solvents. The lower representatives of the class of thiirans polymerise extremely easily under these conditions. This conclusion is confirmed by the results of Reynolds and coworkers[152,153] obtained in a study of the mercaptoethylation of amines by ethylene monothiocarbonate and other similar compounds, which react via the stage involving the formation of thiiran. In the general case the formation of monomeric products of the condensation of amines with thiirans requires reaction conditions (temperature, solvent, and reactant ratio) which exclude the possibility of nucleophilic sulphur elimination and tend to reduce the stability of the sp^3-hybrid state of the nitrogen atom.

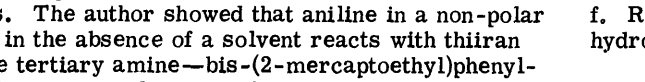
The reactions of thiirans with primary aliphatic and aromatic amines can proceed with formation of mono- and di-2-mercaptoalkylation products. Thus it has been shown[54–57,85,132,138,145–150,154–165] that, under homogeneous conditions in non-polar media and media of low polarity, substituted and unsubstituted alkylamines condense with thiirans on heating, forming mainly mono-(2-mercaptoalkyl)amines. 2-Chloromethylthiiran reacts with primary amines to form polymers[143].

Aromatic amines condense with thiirans under more severe conditions than aliphatic amines. In order to complete the reaction, heating to 100–110°C is usually necessary. The products of the condensation of an amine molecule and two thiiran molecules, which are formed to some extent in the reactions, are secondary amines according

to some data[54,142]. The structure of tertiary amines was attributed to similar substances in other investigations[132,138]:



Bulavin's report[160] deals with the structure of these substances. The author showed that aniline in a non-polar solvent or in the absence of a solvent reacts with thiiran to form the tertiary amine—bis-(2-mercaptoethyl)phenylamine. The same product was obtained by condensing thiiran with *N*-(2-mercaptoethyl)aniline. Secondary amines are formed only when the reaction is catalysed by sodium ethoxide, i.e. under the conditions for the condensation of thiols with thiirans:



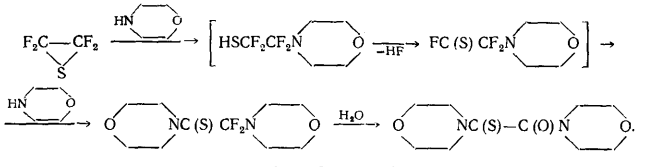
Aminoacid esters react with thiiran similarly to aniline. Thus in non-polar media thiiran can be used, like oxirans, for the exhaustive 2-mercaptoalkylation of primary amines. Under these conditions, best results are obtained in two-stage rather than single-stage synthesis[132,160].

The catalytic effects in 2-mercaptoalkylation reactions of amines have been little studied. The promoting influence of phenols in the condensation of thiiran with amines is noted in a patent[132]. However, it was later shown[138] that phenol and aluminium chloride do not catalyse these reactions.

According to patent data[166], the condensation of thiiran with primary amines is facilitated in the presence of aluminosilicates.

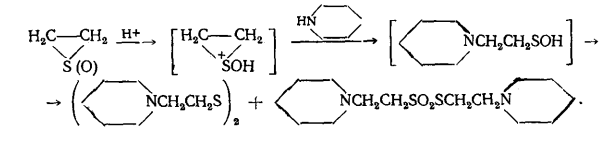
Apart from primary and secondary amines, cyanamide, guanylurea, biguanide[167-169], and monophosphorylated phenylenediamines[165] have been introduced into the reaction with thiiran. The structures of the products formed were not elucidated.

Unusual reactions occur between tetrafluorothiiran and morpholine[170]. The product of the primary cleavage of the C–S bond readily undergoes dehydrofluorination with formation of difluoro(morpholino)thioacetyl fluoride. The latter reacts with an excess of morpholine to form a morpholide, which is converted in the presence of water into the dimorpholide of thio-oxalic acid:



The reactions proceed under mild conditions, which shows that tetrafluorothiiran has marked electrophilic properties.

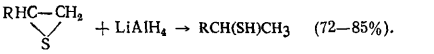
The nucleophilic opening of the thiiran 1-oxide ring by piperidine takes place readily in the presence of an acid catalyst[67]. The reaction results in the formation of di-(2-piperidinoethyl) disulphide and the 2-piperidinoethyl ester of *NN*-cyclopentamethylenethiolotaurine:



The comparatively high rates of cleavage of thiiran rings by amines are used in polymerisation processes. Ammonia, alkylenediamines, and alkylenepolyamines are effective cocatalysts of zinc-subgroup metal compounds for the preparation of polymers (copolymers) in bulk[12,21,171] and also of latexes of vulcanisable rubbers based on thiirans[21].

f. Reactions of Thiiran with Metal Hydrides and Tetrahydroborates

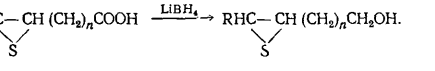
Mousseron and coworkers were the first to use lithium tetrahydroaluminate for the reduction of tetramethylthiiran and 2,3-tetramethylenethiiran[172,173]. The reaction resulted in the formation of the corresponding thiols in yields up to 85%. Later Bordwell et al.[174] used this reaction to demonstrate the mode of opening of the thiiran ring by the nucleophilic AlH_4^- species. The reduction of 2-methylthiiran, 2-butylthiiran, and 2,3-tetramethylenethiiran leads to secondary thiols, which indicates the rupture of the C–S bond involving the sterically unhindered carbon atom. The same mode of cleavage obtains in the reduction of 2-hexylthiiran[175] and 2-alkoxymethylthiirans[176] by lithium tetrahydroaluminate:



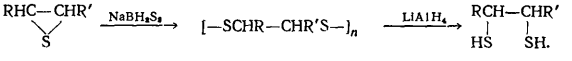
The unambiguous occurrence of the "normal" opening of the thiiran ring in reduction by lithium tetrahydroaluminate has been demonstrated by GLC[92]. The reduction process is accompanied by the inversion of the molecular configuration, as shown by data obtained in a study of the reactions of 2,3-dimethylthiiran isomers with lithium tetradeuteroaluminate[177]. Epithio-derivatives of carbohydrates are reduced similarly to the usual aliphatic epithio-derivatives[178].

A side process in the reactions discussed above is polymerisation of thiirans. In many cases this is the only process. It has been shown that, in the presence of lithium tetrahydroaluminate, 2-alkoxymethylthiirans are reduced while 2-phenoxymethylthiiran polymerises[176]. The polymerisation of 2-hexylthiiran by lithium tetrahydroaluminate proceeds readily and quantitatively in tetrahydrofuran, although in ethyl ether mainly the reduction of the thiiran takes place[175]. Polymerisation reactions in such cases are due to the pronounced polarisation of the nucleophilic agent in the reaction complex or to the specific solvation of the cation, which stabilises the thiolate anions of the final products.

In contrast to lithium tetrahydroaluminate, tetrahydroborates do not reduce the thiiran ring under mild conditions. Thiiranylcarboxylic acids form the corresponding thiiranyl alcohols in these reactions[179]:

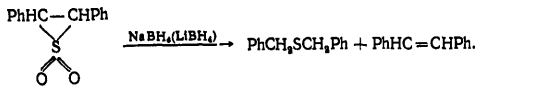


Sodium trithionodihydroborate behaves as a source of elemental sulphur in its reactions with thiirans[180]. The reaction results in the formation of polymers with disulphide linkages, the reduction of which yields 1,2-dimercaptoalkanes:



An interesting example of the reductive cleavage of the C–C bond in the thiiran ring has been described[181]. When 2,3-diphenylthiiran 1,1-dioxide reacts with sodium and

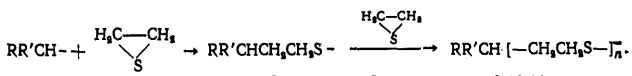
lithium tetrahydroborates, dibenzyl disulphide is formed together with small amounts of a product of side reactions—stilbene:



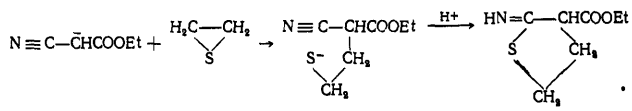
Lithium tetrahydroaluminate and sodium and lithium hydrides do not cleave the C–C bond.

g. The Opening of the Thiiran Ring by Carbanions

Despite the high basicity of carbanions, their interaction with thiirans leads to polymerisation [182]. The latter is probably due to the greater susceptibility of the thiiran ring to cleavage by thiolate anions than by carbanions:

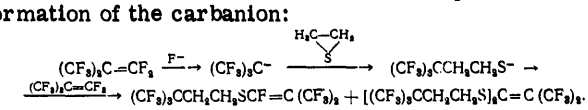


Monomeric products of the condensation of thiirans with substances generating carbanions are formed only when effective acceptors of thiolate anions are present in the reaction sphere. Examples of such reactions are the condensation of thiiran, 2-methylthiiran, and 2,2-dimethylthiiran [182] as well as 2-phenylthiiran [181] with cyanoacetic ester via the mechanism



The cyano-group of the initial compound serves as the acceptor of thiolate anion in these reactions, which leads to the formation of iminotetrahydrothiophen derivatives as cyclisation products. The above reactions are accompanied by the polymerisation of thiirans. The yield of monomeric products is higher the lower the reactivity of the thiiran competing with the cyano-group in processes involving the capture of thiolate anions.

An interesting example of the opening of thiiran rings by carbanions has been described [183]. The reaction of octafluoroisobutene with thiiran in the presence of potassium or caesium fluoride is accompanied by the nucleophilic opening of the thiiran ring and nucleophilic substitution of a fluorine atom in the perfluoro-olefin by the thiolate anion formed. The first reaction step involves the formation of the carbanion:



The yield of monomeric condensation products in the above reaction is higher than in the reaction of thiiran with cyanoacetic ester, which can be accounted for by the more effective capture of thiolate anions by perfluoroisobutene.

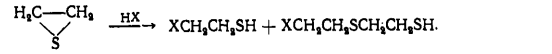
III. ELECTROPHILIC CLEAVAGE REACTIONS

A wide variety of electrophilic agents have been introduced into electrophilic reactions involving the cleavage of thiirans: hydrogen halides and their aqueous solutions, other inorganic and organic acids, halogens, carboxylic acid halides and anhydrides, sulphur, phosphorus, and arsenic halides, isothiocyanatoarsines, alkyl halides, and compounds with multiple bonds (nitriles, ketens, carbonyl and thiocarbonyl compounds, and perfluoroalkenes).

Together with these, thiirans condense with nucleophilic agents (alcohols, thiols, tertiary amines) in the presence of initiators of electrophilic processes.

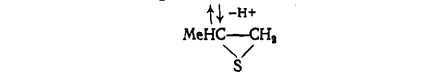
a. Reactions with Acids

Delepin and coworkers [47,49] showed that the reactions of thiiran with dilute hydrogen halides lead to the formation of polymeric products. Only in the presence of concentrated hydrochloric acid with cooling is thiiran converted into 2-chloroethanethiol [47] and in the presence of hydrobromic acid into 2-bromoethanethiol [49]. Together with monomeric substances, oligomers are formed in these reactions:

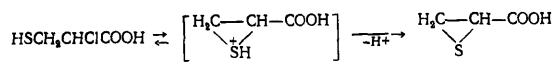


2,3-Tetramethylenethiiran and 2-chloromethylthiiran react with concentrated hydrochloric acid on cooling similarly to thiiran itself, polymerising in boiling acid [46].

The reactions of substituted alkylthiirans with aqueous hydrochloric acid solutions may be regarded as reversible. It has been shown [92] that 2-chloropropanethiol isomerises in the presence of water with formation of a mixture of substances containing about 60% of 2-methylthiiran:



α-Chloro-β-mercaptoalkanecarboxylic acids undergo similar reactions with 10% HCl. [184] In this case equilibrium is strongly displaced towards the formation of the thiiran:



The opening of the ring in these compounds also occurs only in concentrated hydrochloric acid solutions.

Anhydrous hydrogen halides in ether or methylene chloride cleave thiirans under mild conditions with formation of monomeric products only [73,92,142,185–189].

The mode of cleavage of the ring in asymmetric thiirans by hydrogen halides was investigated by chemical methods in early studies. According to some workers [185–188], the reactions of 2-methylthiiran and 2-chloromethylthiiran with hydrogen halides lead to primary thiols, i.e. the thiiran ring is cleaved "anomalously" at the ring carbon atom with the smallest number of hydrogen atoms.

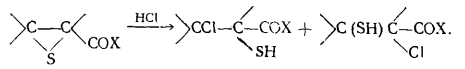
Only Stewart and Cordts [190] demonstrated the occurrence of "normal" ring opening in 2-methylthiiran by hydrogen chloride. However in a later report [142] the primary thiol structure was also attributed to the product of the reaction of 2-phenylthiiran with hydrogen halides.

Schwarts [92] made a careful study of the mode of cleavage of the rings in 2-methyl-, 2,2-dimethyl, and 2-chloromethyl-thiirans by anhydrous hydrogen halide solutions in ether and methylene chloride by GLC and NMR. He showed that the reactions proceed in different ways, with formation of a mixture of products of the "normal" and "anomalous" ring opening. Reactions in accordance with Krasuskii's rule predominate. The content of products with the "normal" structure in the resulting mixture is 76% for 2-methylthiiran, 66% for 2,2-dimethylthiiran, and 96% for 2-chloromethylthiiran. In the presence of water

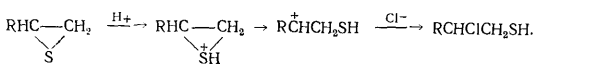
or hydrochloric acid, the primary thiols formed isomerise. The content of products with the "anomalous" structure in the equilibrium mixture reaches 90–98%:

$$\underset{(76\%)}{MeCH(SH)CH_2Cl} + \underset{(24\%)}{MeCHClCH_2SH} \overset{H^+}{\rightleftarrows} \underset{(10\%)}{MeCH(SH)CH_2Cl} + \underset{(90\%)}{MeCHClCH_2SH}.$$

This property of 2-halogenoalkanethiols explains to some extent the contradictory results of early investigations and of Schwarts's study of the mode of cleavage of the thiiran ring by hydrogen halides. Different types of cleavage of the thiiran ring in $\alpha\beta$-epithioglycidic acids and their derivatives by concentrated hydrochloric acid have been observed[184]:

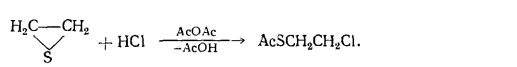


The first ideas concerning the mechanism of the reactions of thiirans with hydrogen halides were described by Davies and Savige[185,186]. The authors suggest that the reaction proceeds via the formation of an episulphonium cation, which is cleaved to the corresponding carbonium ion:



A similar reaction mechanism was proposed by Oddon and Wylde[188] on the basis of the authors' demonstration that the reactions of anhydrous hydrogen chloride and hydrogen bromide with thiiran are of second order.

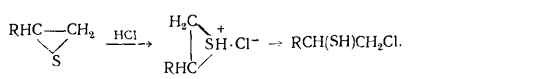
The possibility that the reactions proceed by a carbonium mechanism was confirmed in an experimental test[191]. It was shown that tetrahydrofuran, which tends to undergo reactions of this type, forms a mixture of ω-halogenobutyl acetate and 1,4-bisdiacetoxybutane in the reaction with hydrogen halides in the presence of acetic anhydride. 1,4-Bisdiacetoxybutane may be the main product when hydrogen halide is slowly introduced into a solution of tetrahydrofuran in acetic anhydride. Even under these conditions, thiiran reacts with hydrogen halides to form only 2-halogenoethyl thioloacetates:



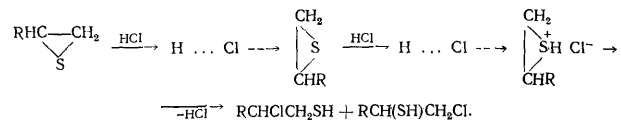
It was therefore concluded that the formation of monomeric products of the condensation of thiirans with hydrogen halides is hardly likely to be associated with the formation of carbonium ions.

Presumably only the reactions of thiirans with dilute solutions of hydrogen halides proceed via the carbonium mechanism, which is promoted by the effective solvation of the chloride ion by water molecules. In such reactions thiiran polymerises, because the carbonium ion involving the primary carbon atom is extremely electrophilic. Substituted thiirans form carbonium ions with the charge at the secondary or tertiary carbon atom. Their reduced reactivity is the reason for the stability of substituted thiirans in dilute acids noted above.

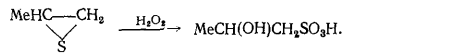
The formation of monomeric products in the reactions of thiirans with concentrated solutions or anhydrous hydrogen halides is a consequence of the formation and opening of the thiiranium halide ring in a close ion pair, which should lead to the formation of "normal" cleavage products:



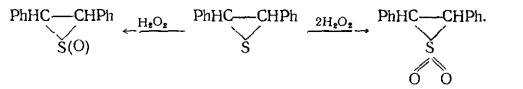
The low basicity of the sulphur atom in thiirans suggests the possibility that the reaction proceeds via a trimolecular mechanism involving the preliminary formation of π complexes:



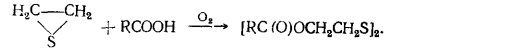
The reactions of thiirans with other inorganic acids have been little investigated. Sulphuric acid is an active initiator of the polymerisation of thiiran[47–49], 2-methylthiiran[48], 2-chloromethylthiiran[192,193], tetramethylthiiran[194], and 2,3-tetramethylenethiiran[195]. Nitric acid oxidises thiiran to sulphonic acids[46,47]. Oxidative cleavage also occurs when 2-methylthiiran reacts with hydrogen peroxide[190]:



Thiiran is converted under these conditions into poly(ethylene sulphones)[68,196] and arylthiirans react without ring opening[197,198]:



Carboxylic acids show a smaller tendency to cleave thiiran compounds. Thiiran polymerises slowly in acetic acid and 2-methylthiiran and butylene sulphide remain unchanged in acetic acid solutions in the absence of heat[47,48]. 2,3-Tetramethylenethiiran condenses with acetic acid on heating, forming a mixture of monomeric and oligomeric products[146,199]. Under severe conditions, higher carboxylic acids condense with thiiran[200]. In the presence of oxygen, the 2-mercaptoethyl ethers formed initially are oxidised to disulphides:



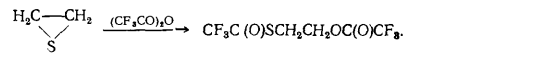
In contrast to unsubstituted carboxylic acids, trifluoroacetic acid undergoes an exothermic reaction with thiiran, initiating its polymerisation under any conditions and for any order of mixing of the reactants[201]. Thiiran reacts smoothly with perbenzoic acid, forming polymers of thiiran 1,1-dioxide[68]. Substituted thiirans are oxidised by peracids to thiiran oxides and dioxides[197,198].

b. Reactions with Carboxylic Acid Anhydrides

The anhydrides of unsubstituted carboxylic acids condense with thiiran[192,200,202,203], 2-methylthiiran[92,185], 2,2-dimethylthiiran[186], and 2,3-tetramethylenethiiran[109] under severe conditions in the presence of pyridine as the catalyst. The reaction products are diesters of 2-mercaptoalkanols. Only epithio-derivatives of steroids fail to react with acetic anhydride even in the presence of pyridine[204,205].

According to some data[185,186], the cleavage of the thiiran ring by acetic anhydride takes place in accordance with Krasuskii's rule and is a second-order process. An S_N2 reaction mechanism was therefore postulated. However, subsequently it was shown that the opening of the ring of 2-methylthiiran by acetic anhydride takes place in different ways. The proportions of the products with the "normal" and "anomalous" structures (86 and 14%) in

these reactions are almost the same as in the analogous reactions with hydrogen halides. It was also shown that the reactions of acid anhydrides with thiiran are promoted not only by bases but also by their hydrochlorides and the ease of reaction is determined primarily by the reactivity of the anhydride. Trifluoroacetic anhydride undergoes an exothermic reaction with thiiran even in non-polar media without catalysts[201]:

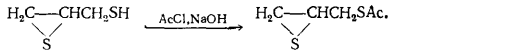


Thus the above reactions can be regarded as the usual processes involving electrophilic cleavage of thiirans.

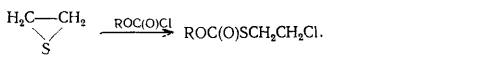
c. Reactions with Acyl Halides

Acetyl, chloroacetyl, and aroyl chlorides as well as the bromides and iodides of aliphatic and aromatic carboxylic acids have been made to react with a wide variety of thiirans. According to Ivin's data[206], acid chlorides react only on heating. Acid bromides and particularly iodides undergo exothermic reactions with thiiran and 2-methylthiiran. With increase of the molecular weight of the acid halide, its capacity for condensation with thiirans diminishes. Aroyl chlorides react with greater difficulty than acetyl chloride[46]. 3,5-Dinitrobenzoyl chloride and benzoyl fluoride initiate the polymerisation of thiiran and their reactions with the latter compounds do not lead to monomeric products.

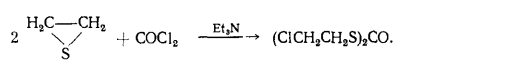
A wide variety of thiirans, including unsubstituted thiiran[136,203,206-208], 2-methylthiiran[46,92,185,206,209], 2-chloromethylthiiran[46,73,92,186], 2,2-dimethylthiiran[92], 2-phenylthiiran[142], and 2,3-tetramethylenethiiran[46,199] condense smoothly with acyl halides. 2-Mercaptomethylthiiran reacts smoothly with acetyl chloride in the presence of bases to form 2-acetylthiomethylthiiran[210,211]:



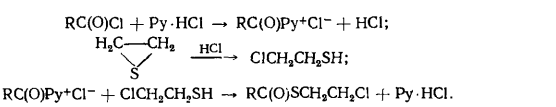
On heating, chlorocarbonic esters react with thiirans similarly to acyl chlorides[212]:



Phosgene undergoes exothermic condensation with thiiran and 2-methylthiiran via only one C–Cl bond. The attempts to achieve exhaustive substitution by 2-chloroethylthio-groups on heating were unsuccessful. Only in the presence of triethylamine as catalyst does the phosgene molecule condense with two thiiran molecules[213]:



Tertiary amines in the presence of traces of moisture or tertiary amine hydrohalides are effective catalysts of the reactions of thiiran with relatively unreactive acyl chlorides[208]. In the presence of pyridine hydrochloride or pyridine and moisture at 40–60°C thiiran condenses quantitatively with aryloxyacetyl chlorides. In the absence of catalysts, thiiran polymerises. The following mechanism may be postulated for the above reaction:

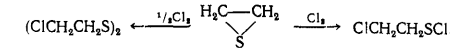


The opening of the 2-methylthiiran and 2-chloromethylthiiran rings by acetyl chloride and acetyl iodide and of the 2-methylthiiran ring by phosgene proceeds "anomalously" at the secondary ring carbon atom according to a number of investigations[185,206,212]. However, it has been shown by GLC and NMR [92] that mixtures of substances are formed in the reactions of 2-methyl-, 2-chloromethyl, and 2,2-dimethyl-thiirans with acetyl chloride and bromide and also with aroyl chlorides. The products of the "normal" cleavage of thiiran rings are mainly formed (54–85%). Only in the reaction of 2,2-dimethylthiiran with acetyl chloride do the "anomalous" pathways, accompanied by the formation of isobutenyl thioloacetate, predominate.

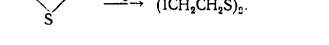
It is striking that in the 2-methylthiiran–*p*-aroyl chloride series a significant influence of the ring substituent on the proportions of the "normal" and "anomalous" products was not demonstrated[92]. The insignificant influence of the electrophilic properties of the acyl chloride on the mode of thiiran ring opening indicates a complex mechanism of the above reactions. Depending on the nature of the reactants employed and the reaction conditions, the electrophilic opening of the thiiran ring by acyl halides occurs to some extent via the carbonium mechanism or via the formation of an acyl sulphonium ion and the cleavage of the ring of the latter in the state of a contact ion pair. In many cases the process is decisively influenced by the presence of traces of moisture in the reaction sphere and by the involvement of the hydrogen halide in the ring opening step.

d. Reactions with Halogens

The earlier attempts to halogenate thiirans under severe conditions were unsuccessful. The exothermic reaction of thiiran with bromine yielded a viscous product of unidentified composition. 1,2-Dichlorocyclohexane and polymeric products were obtained by the chlorination of 2,3-tetramethylenethiiran under similar conditions[46,47]. The extensive study of the above reactions began only after the investigations by Stewart[192,214], who achieved the chlorination and bromination of 2-methylthiiran under mild conditions. It is now known that thiiran[215], 2-methylthiiran[92,192,214,215], 2-chloromethylthiiran[92,143], 2-phenylthiiran[142], and 2,2-dimethylthiiran[92,142] are smoothly chlorinated in solution in halogenoalkanes. In the absence of traces of moisture from the reaction, the halogenation reactions are not accompanied by the polymerisation of the thiirans and are usually completed after the introduction of the halogen into the reaction sphere. Depending on the reactant ratio, di-(2-halogenoalkyl) sulphide or 2-halogenoalkylsulphenyl halides are formed:

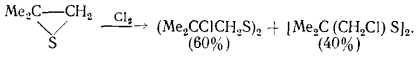


Like chlorine, sulphuryl chloride readily enters into the reaction[215]. The iodination of thiiran, 2-methylthiiran, and 2,3-dimethylthiiran is completed at the stage involving the formation of di-(2-iodoalkyl) sulphides:

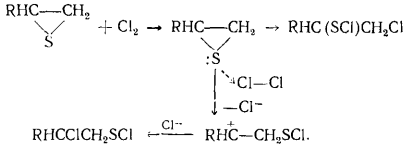


In order to demonstrate the mode of ring opening, the products of the halogenation of 2-methylthiiran were converted into derivatives of 2-substituted alkanesulphonic acids the properties of which were compared with those of substances of known structure[192,214]. The "normal" opening of the thiiran ring was demonstrated in this way. The

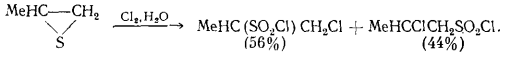
mode of 2-methylthiiran ring opening was also established by condensing with alkenes the 2-halogenoalkanesulphenyl halides formed in the reaction and by identifying the resulting sulphides in the form of their derivatives[215]; the "anomalous" opening of the 2-methylthiiran ring was thus demonstrated. Schwarts[92] showed by GLC and NMR that the above reaction takes place in several ways. The main products in the resulting mixture have the "normal" structure (55–85%), but in 2,2-dimethylthiiran the C–S bond is cleaved preferentially at the tertiary carbon atom:



It is of interest that under the usual conditions tetrafluorothiiran does not interact with chlorine and bromine[170]. The reaction apparently requires comparatively marked nucleophilic properties of the ring heteroatom, which creates conditions favouring the heterolytic addition of a halogen molecule to the thiiran:

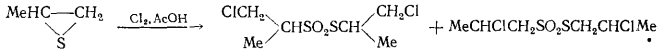


The chlorination and bromination of 2-methylthiiran in the presence of water and other hydroxy-compounds leads to the formation of products of the oxidative cleavage of the ring[92,192,214]. It has been shown[92] that the exhaustive oxidation of 2-methylthiiran by chlorine in water results in a mixture of substances where "normal" ring opening predominates:

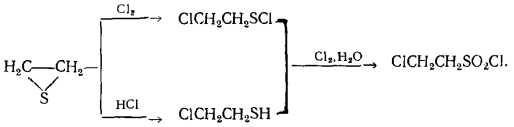


The proportions of the "normal" and "anomalous" products are the same as in chlorination under anhydrous conditions. This suggests that the oxidative processes take place after the opening of the thiiran ring, which occurs in aqueous media via the same mechanism as under anhydrous conditions.

Exhaustive oxidative ring cleavage also occurs in the chlorination of 2-phenylthiiran[142] and 2-chloromethylthiiran[143] in aqueous acetic acid. In anhydrous acetic acid it is also possible to obtain a product of the partial oxidation of 2-methylthiiran by chlorine[192]. In this case a mixture of isomeric 2-chloroalkanethiyl esters of 2-chloroalkanesulphonic acids is probably formed:

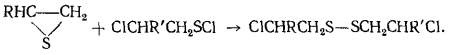


The chlorination of thiiran in the presence of water is always accompanied by the polymerisation of the former[217]. The reason for this is the unusually high capacity of thiiran for polymerisation via a cationotropic mechanism. The conditions for such reactions are created at the very beginning of the process on formation of a dilute HCl solution. The chlorination of thiiran in the presence of concentrated hydrochloric acid makes it possible to eliminate polymerisation reactions and to obtain 2-chloroethanesulphonyl chloride in a high yield. The unambiguous course of the reactions is in this case due to the involvement of hydrogen chloride in the ring opening processes:

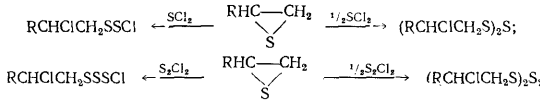


e. Reactions with Non-Metal Halides

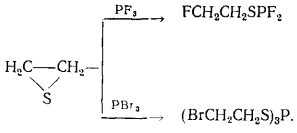
Sulphur halides react smoothly with thiirans in non-polar media[218,219]. Thus sulphenyl chlorides condense, on cooling their solutions in carbon tetrachloride, with thiiran, 2-methylthiiran, and 2,2-dimethylthiiran, forming the corresponding disulphides. According to Epshtein et al.[218], "anomalous" ring opening takes place in these reactions:



Sulphur chlorides react with thiirans under similar conditions[219]. Depending on the reactant ratio, di- and tri-sulphenyl chlorides or tri- and tetra-sulphides are formed in the reactions of sulphur monochloride and dichloride with thiiran and 2-methylthiiran. The structures corresponding to the "anomalous" ring cleavage were also attributed to these products:

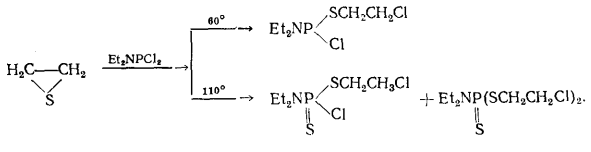


The reactions of phosphorus halides with thiiran proceed less smoothly. According to patent data[220–222], phosphorus trifluoride and tribromide condense with thiirans, forming 2-halogenoalkanethiol esters:

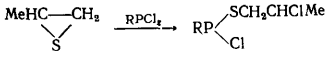


Phosphorus chloride dibromide and dichloride bromide as well as phosphoryl bromide react similarly.

Phosphorus trichloride condenses with thiiran and 2-methylthiiran only in the presence of zinc chloride. Depending on the reactant ratio, mono- and di-addition products are formed[223,224]. Exhaustive substitution by 2-chloroalkylthio-groups is accompanied by the polymerisation of thiirans. In the absence of catalysts, ***NN***-diethylphosphoramidous dichloride reacts with thiirans on moderate heating (60–70°C), forming small amounts of monoaddition products. On heating above 100°C, a mixture of phosphorodithioate and phosphorotrithioate was obtained:

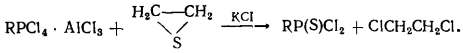


Alkyldichlorophosphines condense unambiguously with thiiran and 2-methylthiiran via one P–Cl bond[225,226]. It is assumed that the opening of the 2-methylthiiran ring takes place at the secondary carbon atom:



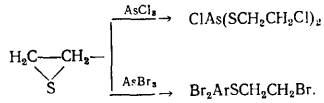
Condensation reactions between thiirans and phosphorous(III) chloride apparently takes place in steps. This may be a consequence of inductomeric and weaker mesomeric effects of the 2-chloroalkanethiol groups. The presence of substituents with a strong +*M* effect (amino-groups) at the phosphorus atom virtually rules out the possibility of condensation.

Among other phosphorus compounds, complexes of alkyltetrachlorophosphoranes and aluminium trichloride have been made to react with thiiran[227,228]. The reaction is accompanied by the elimination of sulphur from thiiran:

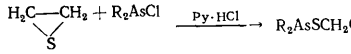


Phosphorus pentafluoride initiates the polymerisation of thiirans and does not form monomeric products on reacting with them[229,230].

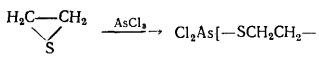
In dilute carbon tetrachloride solutions arsenic halides condense with thiiran, forming monomeric products in low yields[231]:



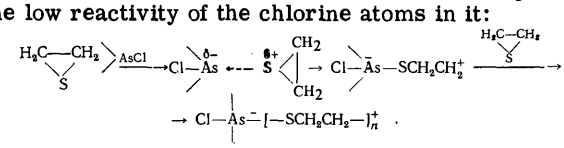
Under these conditions, arsenic trifluoride initiates the polymerisation of thiiran. Dialkylchloroarsines and alkyldichloroarsines condense with thiiran even in concentrated solutions and in the presence of pyridine or its hydrochloride as catalysts are converted quantitatively into 2-chloroethylthioarsinites[232]:



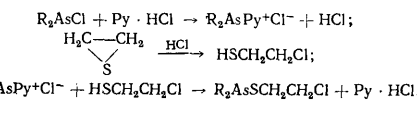
The reactions of thiiran with arsenic trichloride in concentrated solutions lead to oligomeric products even in the presence of catalysts:



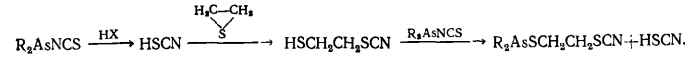
The ability of arsenic chlorides to initiate the polymerisation of thiiran increases in the series of compounds characterised by decreasing electron density at the arsenic atom ($R_2AsCl < RArAsCl < Ar_2AsCl < RAsCl_2 < ArAsCl_2$). This suggests that polymerisation reactions are caused primarily by the strength of the $3p_\pi$–$4d_\pi$ bonding between the sulphur and arsenic atoms in the reaction complex and by the low reactivity of the chlorine atoms in it:



The catalytic effect of pyridine hydrochloride is due to the appearance in the reaction sphere of highly reactive hydrogen chloride and the activation of nucleophilic substitution at the arsenic atom:



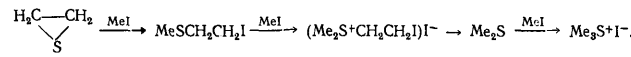
Dialkylisothiocyanatoarsines react with thiiran similarly to chloroarsines[223,234]. The reactions proceed only in the presence of substances promoting the formation of thiocyanic acid in the reaction sphere, which is the reason for the anomalous conversion of isothiocyanatoarsines into 2-thiocyanatoethyl thioarsinites:



In contrast to sulphur, phosphorus, and arsenic halides, halogenosilanes, and isothiocyanatosilanes do not interact with thiiran even in the presence of catalysts[235].

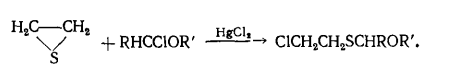
f. Reactions with Alkyl Halides

According to Merill and Perkins[194], the reaction of tetramethylthiiran with methyl iodide is more difficult than the corresponding reaction of acyclic sulphides. Regardless of the nature of the thiiran employed, the reaction leads to the formation of trimethylsulphonium iodide[46,236–238] and not *S*-alkylthiiranium iodide. The available data suggest that the primary reaction products are unstable. The opening of their rings leads to polymerisation reactions and to partial formation of linear sulphides. The latter are readily iodomethylated, which leads to degradative transformations:



2-Phenylthiiran is alkylated by dimethyl sulphate at room temperature[239]. However, in this case the thiiranium salt or its monomeric cleavage product were not isolated either. Only 2,5-diphenyldithiane was isolated in a low yield.

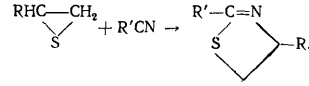
The usual products of the electrophilic opening of the rings of thiiran and 2-methylthiiran were obtained only when the latter reacted with alkyl α-chloroalkyl ethers in the presence of mercury(II) chloride[240]:



The reactions proceed under mild conditions. The "anomalous" cleavage of the 2-methylthiiran ring by alkyl α-chloroalkyl ethers is postulated.

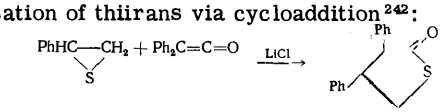
g. Cycloaddition Reactions of Thiirans

Several examples of such reactions are known. In the presence of strong inorganic acids the nitriles of aliphatic acids and thiirans react to form thiazolines[241]:



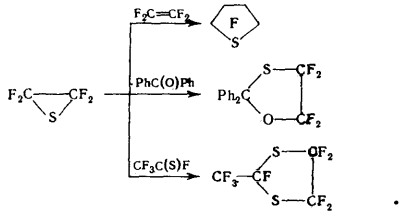
The condensation reactions are stereospecific, which shows that the cycloaddition proceeds via a stage involving the formation of a π complex of the thiiran molecule and the iminocarbonium ion. The thiirans polymerise simultaneously with condensation, in consequence of their cationotropic reactions.

The reaction of diphenylketen with 2-phenylthiiran in the presence of lithium chloride is the next example of the condensation of thiirans via cycloaddition[242]:

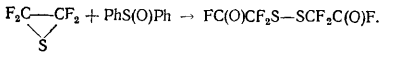


Thiiran and its aliphatic derivatives polymerise under these conditions.

A high capacity for cycloaddition reactions is characteristic of tetrafluorothiiran[170]. This compound condenses with tetrafluoroethylene to form octafluorotetrahydrothiophen, with benzophenone to form 2,2-diphenyloxathiolan, and with thioacetyl fluoride to form 1,3-dithiolan:



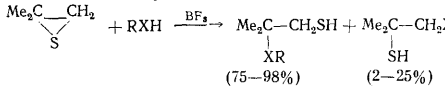
Only diphenyl sulphoxide enters into exchange reactions with tetrafluorothiiran:



h. Electrophilic Condensation Reactions with Nucleophilic Agents

The condensation reactions of thiirans with alcohols and thiols in the presence of boron trifluoride or boron trifluoride-ether have been investigated[142,183-185] and it has been shown that 2,2-dimethyl- and 2-phenyl-thiirans give rise to monomeric products in 20–40% yield on reaction with primary alcohols and thiols. Steric effects at the nucleophilic centre lead to a sharp decrease of the yield of monomeric products. 2-Methyl- and 2,3-tetramethylene-thiirans polymerise in these reactions.

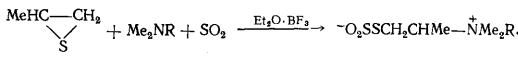
According to conductimetric titration data, the products of the condensation of 2,2-dimethylthiiran and alcohols and thiols consist of a mixture of substances in which the "anomalous" isomers predominate:



Similar results were obtained also in the reaction of ethanol with 2-phenylthiiran catalysed by sulphuric acid[243].

The condensations of thiiran with lauryl alcohol and nonylphenols were investigated recently in the presence of catalysts for electrophilic reactions[58]. It was established that HCl, $SnCl_4$, and BF_3 promote the formation of 2-mercaptoethylation products. However, the yield of monomeric substances is low and polymeric products are mainly formed.

An example of the condensation of tertiary amines with 2-methylthiiran in the presence of boron trifluoride-ether and sulphur dioxide has been described[244]:

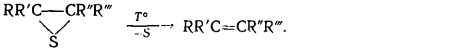


IV. ELIMINATION OF SULPHUR

The capacity to split off sulphur is one of the characteristic properties of thiiran. Sulphur is usually eliminated on pyrolysis and on moderate heating in the presence of metals, metal oxides, and bases.

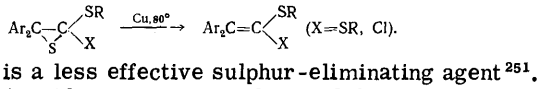
a. Pyrolytic Elimination of Sulphur

The thermal stability of thiirans depends significantly on their structure. The presence of electronegative substituents at the ring carbon atoms sharply increases the tendency of the thiiran to split off the sulphur atom. On heating, sulphur is readily eliminated from tetraaryl-thiirans[243-245], 2,2-diaryl-3,3-diethylthiirans[246], tetrachlorothiirans, and symmetrical diaryldichlorothiirans[247]:



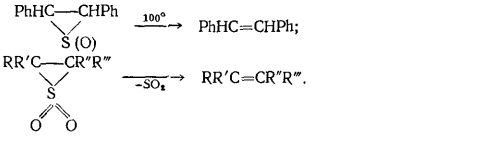
Monosubstituted thiirans, including 2-phenylthiiran[151], 2,3-tetramethylenethiiran[195], and 2-hexylthiiran[175] split off sulphur with somewhat more difficulty.

The elimination of sulphur takes place particularly readily (and quantitatively) in the presence of copper bronze[248-250]. The mild conditions in this sulphur elimination reaction make it possible to obtain even relatively unstable keten mercaptals and their derivatives[248,249]:



Zinc oxide is a less effective sulphur-eliminating agent[251].

Thiiran 1-oxides are converted into olefins on heating in toluene[252]. The 1,1-dioxides are cleaved even more readily on heating[253-256]:



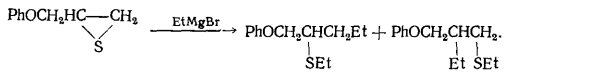
Thiirene 1,1-dioxides, which are more stable than thiiran dioxides, also tend to split off sulphur dioxide[257].

Investigations have shown that the pyrolytic elimination of sulphur from thiirans takes place via a homolytic mechanism. The deformation of the heterobonds as a result of the involvement of the ring electrons in π-conjugated systems greatly facilitates the process. The ease of the homolysis of heterobonds in the thiiran ring is attributed to the weak bonding and antibonding nature of the C–S σ bonds.

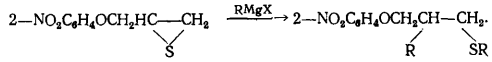
b. Elimination of Sulphur in Nucleophilic Thiiran Ring Opening Reactions

The elimination of sulphur from thiirans is promoted by bases. $\alpha\beta$-Epithioglycidic acids and their derivatives[93,184] and 2,3-diphenylthiiran[93] split off sulphur in the presence of bases even at room temperature. Secondary amines eliminate sulphur from 2-phenylthiiran in non-polar media[151].

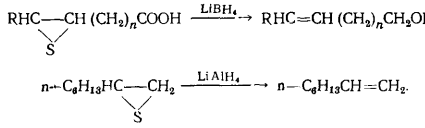
When 2,3-tetramethylenethiiran and substituted 2-methylthiirans are treated with Grignard reagents and other organometallic compounds in non-polar media, sulphur is eliminated from the thiirans[174,238]. It has been shown for the reactions of *cis*- and *trans*-butene sulphides with butyllithium that this process is stereospecific[258]. In many instances Grignard reagents behave also as alkylating agents in relation to thiirans. According to Takeda[141], phenoxymethylthiiran reacts with ethylmagnesium bromide to form a mixture of "normal" and "anomalous" products:



Higher alkyl magnesium bromides react with phenoxymethylthiiran to form only "normal" products of thiiran ring cleavage and with *o*-nitrophenoxymethylthiiran to form only the "anomalous" products:



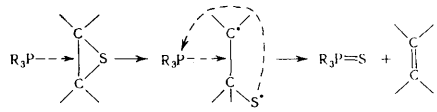
When thiiranylalkanecarboxylic acids are reduced by lithium tetrahydroborate [179] and 2-hexylthiiran is reduced by lithium tetrahydroaluminate [175], alkenes are also formed:



The latter reaction occurs only in non-polar media. In tetrahydrofuran 2-hexylthiiran polymerises. Sulphur is also eliminated in the reactions of epithio-derivatives of steroids with higher alkyl xanthates [97]. Conditions favouring nucleophilic sulphur elimination reactions and the similarity of the effects of structural factors on the pyrolytic and nucleophilic sulphur elimination processes indicate their homolytic mechanisms. Ring opening in nucleophilic sulphur elimination reaction proceeds most probably at the stage involving the formation of transition complexes comprising the thiiran and the nucleophilic agent under conditions preventing charge transfer.

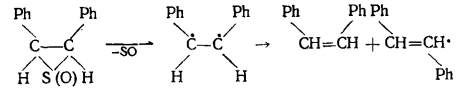
c. Elimination of Sulphur by Phosphites and Phosphines

Trialkyl phosphites and phosphines behave as nucleophilic agents in such reactions. Their inability to dissociate, low polarity and polarisability, and their high capacity for the homolytic formation of the thiophosphoryl linkage determine an unambiguous course of the process. The results obtained in a number of studies [46,176,238,258-266] show that the ease of sulphur elimination depends primarily on the basicity of the nucleophilic agent. Thus sulphur is eliminated by triethyl phosphite only on heating (100–110°C), while tributyl- or triphenyl-phosphine eliminates sulphur even at 20°C. The rate of reaction depends little on the polarity of the solvent and is of first order with respect to each reactant. The process is sterospecific to the extent of 99–100%. All these factors are consistent with a homolytic mechanism of the sulphur elimination process:

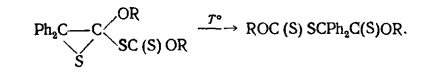


V. FREE-RADICAL REACTIONS

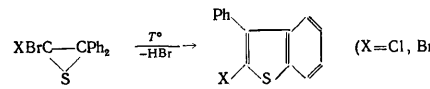
Free-radical reactions are to a large extent characteristic of thiirans with electronegative substituents at the ring carbon atoms. The commonest reactions of this type are the pyrolytic syntheses of alkenes from thiirans. The free-radical mechanism of the pyrolytic reactions of the thiiran ring have been demonstrated [252]. Thermal degradation of *trans*-2-phenylthiiran 1-oxide takes place stereospecifically with quantitative formation of *trans*-stilbene. Pyrolysis of the *cis*-isomer is accompanied by racemisation. This indicates the intermediate formation of a biradical, tending to isomerise with formation of the energetically more favourable conformer:



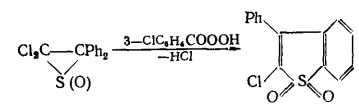
The free-radical mechanism of the pyrolytic transformations of thiirans is the cause of their unusual reactions. For example, the pyrolysis of *S*-(2-alkoxy-3,3-diaryl-2-thiiranyl) xanthates leads to mercaptoacetic acid derivatives instead of olefins [266]:



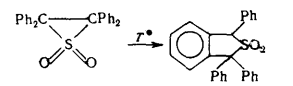
The pyrolysis of 2,2-diaryl-3,3-dichlorothiirans is accompanied by the formation of olefins. However, their bromoderivatives rearrange to derivatives of benzo[*b*]thiophen with elimination of HBr [247]:



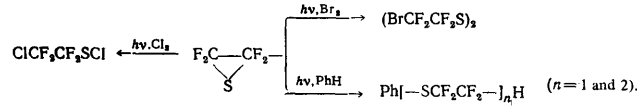
The thiiran–thiophen rearrangement takes place also in oxidative reactions of certain thiirans [202]:



In the above examples the C–S bond undergoes homolytic cleavage. An example of pyrolytic ring opening at the C–C bond is also known. Thus tetraphenylthiiran 1,1-dioxide isomerises to a dihydroisothianaphthene derivative on heating [267]:



Polyfluorothiirans undergo free-radical reactions particularly readily [170,268,269]. On irradiation with ultraviolet light, they are readily chlorinated and brominated and condense with benzene:



Tetrafluoro- and chlorotrifluoro-thiirans polymerise on irradiation or in the presence of di(trifluoromethyl) disulphide and form copolymers with ethylene and propene.

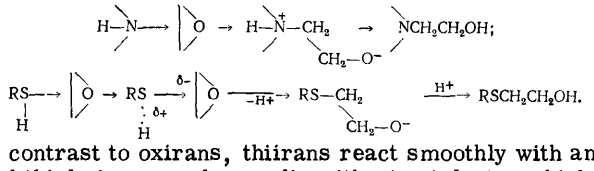
Thiiran and its simplest homologues show a smaller tendency to undergo free-radical reactions. On being irradiated, these substances polymerise [270,271], but the quantum yield of the reactions is comparatively low. Radical reactions are facilitated in the presence of substances capable of forming charge-transfer complexes [272]. This suggests that the increased stability of thiiran and its alkyl-substituted homologues under the conditions of homolytic reactions is a consequence of the oscillatory properties of the heterobond in their rings, associated with the low probability that the $n \rightarrow \sigma^*$ transitions of the lone electron pairs of the sulphur atoms to the antibonding orbitals of the C–S σ bond will become allowed. A similar

phenomenon has been noted in a study of poly(alkylene sulphides), the free-radical reactions of which involve the dissociation of C–C bonds and not C–S bonds [273].

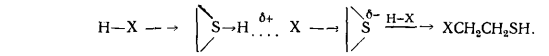
VI. CONCLUSION

The present state of the chemistry of thiirans is to a large extent determined by the development of the comparative chemistry of three-membered heterocycles. Comparison of the properties of thiirans and their oxygen analogues, the heteroatoms of which have the same number of valence electrons in different energy states, is of greatest interest.

There are no unambiguous hypotheses concerning the relation between the reactivities of oxirans and thiirans. However, it is frequently stated that the rates of cleavage of thiiran rings are somewhat lower than those of oxiran rings. Our comparison of the data presented in this review with surveys of the chemistry of liquid-phase reactions of oxirans [44,274] failed to confirm such ideas and showed that an unambiguous answer to this question, unrelated to the reaction conditions, is impossible. This may be illustrated by the following example. The reactions of oxirans with amines are known to occur in polar aprotic solvents, and take place particularly readily in water and alcohols, i.e. under conditions favouring the transition of the nitrogen atom to the sp^3-hybrid state. There is a similar phenomenon also in uncatalysed reactions of oxirans with thiols, the occurrence of which is associated with the presence of hydroxy-compounds in the reaction sphere. In non-polar media, thiols condense with oxirans only in the presence of basic catalysts [275]. Thus one of the characteristics of the nucleophilic oxiran ring cleavage reactions is the necessity to activate the formation of ionic transition complexes, without which the process does not occur under the usual conditions:



In contrast to oxirans, thiirans react smoothly with amines and thiols in non-polar media without catalysts, which suggests that the thiiran ring has more pronounced electrophilic properties than the oxiran ring. The optimal conditions for the formation of monomeric condensation products in these reactions are associated with the creation of conditions for a virtually synchronous formation of a covalent bond between the nucleophilic atom and the ring carbon atom and proton transfer to the sulphur atom. The hydride transfer is mediated by the molecules of the nucleophilic agent, as a result of which the excess of the latter increases the yield of monomeric reaction products:



Consequently, in non-activated nucleophilic ring opening reactions thiirans are distinguished by lower energy barriers to the processes and higher reactivities than oxirans. This is quite natural, bearing in mind the weak bonding and antibonding nature of the C–S σ bond.

The ratio of the rates of the nucleophilic opening of oxiran and thiiran rings changes in polar media. Oxirans react somewhat more readily with amines in dioxan and with thiols in non-polar media in the presence of basic catalysts. In alcohols the opening of the oxiran ring by thiolate anions also takes place quantitatively even below 0°C. In this case thiirans interact on moderate heating. The reversal of the relative reactivities in the above reactions is due to the much smaller sensitivity of thiirans to solvolysis [276] and the impossibility of activating the thiiran ring by the formation of hydrogen bonds. The above facts are intrinsically extremely interesting, since they indicate a definite role of polarisation effects in oxiran and thiiran ring opening reactions.

The energetics of the transition states probably determine the ratio of the reactivities of oxirans and thiirans in electrophilic ring opening processes. This is manifested most clearly in the reactions of the above compounds with phosphorus and arsenic halides. The high rates of reaction of oxirans with phosphorus halides and of thiirans with arsenic halides are attributed to the possibility of the $(n - 1)p_\pi - nd_\pi$ interaction between the reacting molecules in the transition complex. A deviation from the above rule is accompanied by a sharp decrease of reactivity. This example demonstrates the impossibility of an unambiguous estimation of the relative reactivities of thiirans and oxirans also in their electrophilic cleavage reactions.

It is noteworthy that, from the standpoint of the chemistry of three-membered saturated heterocycles, the reactivity of thiirans is of special interest. Their low sensitivity to solvolysis, the high lability of the heterobond, and the high polarisability of the heteroatom in thiirans make it possible to discover even fine details of the effects of substituents and of the influence of the structure of the reactants on the reactivity and its nature. Only in the chemistry of thiirans are there so many instances of reactions with the same reactant where all types of transformations of the heterocycle are possible depending on the conditions: elimination of the heteroatom, condensation with formation of monomeric substances, and polymerisation. A detailed elucidation of the nature of this phenomenon is of undoubted interest from the standpoint of the chemistry of three-membered heterocyclic compounds.

The data presented in this review indicate the scope of the synthesis of sulphur-containing substances on the basis of thiirans which has been by no means completely elucidated. However, the known reactions of thiirans already make it possible to obtain by simple technological procedures a wide variety of products of interest for the synthesis of physiologically active and technically valuable compounds. The introduction of these chemically reactive compounds into agricultural practice, into hydrometallurgical processes, and other branches of the National Economy would make it possible to limit the use of stable substances which accumulate in the biosphere and contaminate it.

REFERENCES

1. A.V. Fokin and A.F. Kolomiets, Uspekhi Khim., 44, 306 (1975) [Russ. Chem. Rev., No. 2 (1975)].
2. L.A. Korotneva and E.P. Belonovskaya, Uspekhi Khim., 41, 150 (1972) [Russ. Chem. Rev., No. 1 (1972)].
3. "Encyclopaedia of Polymer Science and Technology", Interscience, New York, 1969, Vol. 10.
4. "Ring Opening Polymerisation", Dekker, New York–London, 1969.
5. H.G. Buehrer, Chimia (Switz.,) 26, 501 (1972).
6. M. Sepulchre, N. Spassky, and P. Sigwalt, Macromol., 5, 92 (1972).

7. P. Dumas, N. Spassky, and P. Sigwalt, Macromol. Chem., 156, 55, 65 (1972).
8. US P. 3 649 561 (1972); Chem. Abs., 77, 6960 (1972).
9. US P. 3 337 513 (1963); Chem. Abs., 67, 82 541 (1967).
10. US P. 3 624 052 (1962); Chem. Abs., 76, 86 888 (1972).
11. Neth. Appl., 6 400 797 (1963); Chem. Abs., 68, 2846 (1965).
12. Belgian P. 645 691 (1964); Chem. Abs., 63, 8518 (1965).
13. Belgian P. 648 436 (1964); Chem. Abs., 63, 13 498 (1965).
14. BRD P. 1 194 147 (1965); Chem. Abs., 63, 5876 (1965).
15. Neth. Appl., 6 405 917 (1965); Chem. Abs., 64, 14 395 (1966).
16. US P. 3 624 055 (1972); Chem. Abs., 76, 114 499 (1972).
17. US P. 3 222 325 (1965); Chem. Abs., 64, 8455 (1966).
18. US P. 3 222 326 (1965); Chem. Abs., 64, 8457 (1966).
19. B. P. 1 036 091 (1966); Chem. Abs., 65, 13 924 (1966).
20. Neth. Appl., 6 608 767 (1966); Chem. Abs., 66, 105 827 (1967).
21. French P. 1 470 917 (1967); Chem. Abs., 67, 83 029 (1967).
22. S. Adamesk and B. B. Y. Wood, Rubber Age, New York, 96, 581 (1965).
23. B. P. 1 092 604 (1965); Chem. Abs., 68, 22 358 (1968).
24. US. P. 3 668 060 (1972); Chem. Abs., 77, 89 979 (1972).
25. US. P. 2 962 457 (1960); Chem. Abs., 55, 6009 (1961).
26. French P. 1 430 154 (1966); Chem. Abs., 65, 12 390 (1966).
27. P. Wigwalt, in "Kinetics and Mechanics of Polyreactions", IUPAC, International Symposium on Macromolecular Chemistry, Plenary Main Lecture, New York, 1969, p. 251.
28. I. P. Solomatina, E. P. Tyurina, A. D. Aliev, and B. A. Krentsel', Fiziol. Opt. Akt. Polim. V-va, 10 (1971).
29. J. M. Panajotov and I. V. Berlinova, Macromol. Chem., 154, 139 (1972).
30. Japanese P. 17 733 (1962); Chem. Abs., 65, 10 687 (1966).
31. P. Hemery, S. Boileay, and P. Sigwalt, Europ. Polymer. J., 1581 (1971).
32. A. Gourdenne, Macromol. Chem., 158, 261, 271 (1972).
33. Japanese P. 7 208 641 (1972); Chem. Abs., 77, 63 094 (1972).
34. French P. 2 056 487 (1971); Chem. Abs., 76, 73 504 (1972).
35. US P. 3 648 986 (1969); Chem. Abs., 77, 6105 (1972).
36. Japanese P. 9997 (1962); Chem. Abs., 60, 3440 (1964).
37. BRD P. 1 082 915 (1960); Chem. Abs., 55, 25 983 (1961).
38. S. Kaye, Amer. J. High Polym., 50, 289 (1949).
39. US P. 2 225 573 (1940); Chem. Abs., 35, 2269 (1941).
40. B. P. 810 389 (1959); Chem. Abs., 54, 2360 (1960).
41. US P. 3 634 457 (1967); Chem. Abs., 77, 34 211 (1972).
42. BRD P. 2 145 390 (1970); Chem. Abs., 77, 84 508 (1972).
43. B. P. 1 008 154 (1965); Chem. Abs., 64, 503 (1966).
44. A. Weissberger, "The Chemistry of Heterocyclic Compounds", Interscience Publ., New York and London, 1964, Vol. 19.
45. M. Sander, Chem. Rev., 66, 297 (1966).
46. C. C. J. Culvenor, W. Davies, and N. S. Heath, J. Chem. Soc., 262 (1949).
47. M. Delepine, Bull. Soc. chim. France, 27, 740 (1920).
48. M. Delepine and P. Jaffcut, Bull. Soc. chim. France, 29, 136 (1921).
49. M. Delepine and S. J. Eschenbrenner, Bull. Soc. chim. France, 33, 703 (1923).
50. M. Ohta, A. Kondo, and R. Ohi, J. Chem. Soc. Japan, 75, 985 (1954); Chem. Abs., 51, 14 668 (1957).
51. S. Boileau and P. Sigwalt, Compt. rend., 252, 882 (1961).
52. C. S. Marvel and E. D. Weil, J. Amer. Chem. Soc., 76, 61 (1945).
53. D. D. Reynolds, D. L. Fields, and D. L. Johnson, J. Org. Chem., 26, 5116 (1961).
54. G. I. Braz, Zhur. Obshch. Khim., 21, 688 (1951).
55. R. Oda, J. Japan. Chem., 5, 589, 644, 705 (1951); Chem. Abs., 49, 166 (1955).
56. R. Oda, Mem. Fac. Eng. Kyoto Univ., 14, 195 (1952); Chem. Abs., 48, 1935 (1954).
57. K. Furukava, M. Nemura, and R. Oda, J. Chem. Soc. Japan, Ind. Chem. Sect., 55, 671 (1952); Chem. Abs., 49, 1626 (1955).
58. K. Negoro and M. Nagao, Bull. Fac. Eng. Hiroshima Univ., 19, 65 (1971); Chem. Abs., 76, 59 116 (1972).
59. A. V. Fokin, A. F. Kolomiets, and L. S. Rudinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2841 (1974).
60. G. Champetier and F. Lucas, Compt. rend., 252, 2782 (1961).
61. US P. 3 370 787 (1963); Chem. Abs., 67, 74 669 (1967).
62. Belgian P. 646 285 (1964); Chem. Abs., 63, 11 798 (1965).
63. P. Cremonesi, Ric. Doc. Tessile, 3, 25 (1966).
64. P. Cremonesi, Ric. Doc. Tessile, 3, 162 (1966).
65. A. Zavada, A. D. Virnik, and K. R. Khomyakov, Khim. Prirodn. Soed., 2, 437 (1966).
66. D. Tilakodzhaev, M. M. Tulyaganov, and T. G. Gafurov, USSR P. No. 308 130 (1968); Chem. Abs., 76, 47 334 (1972).
67. G. H. Hartzell and J. N. Paige, J. Amer. Chem. Soc., 88, 2616 (1966).
68. G. Hesse, E. Reichoed, and S. Majumdar, Chem. Ber., 90, 2106 (1957).
69. A. V. Fokin, A. F. Kolomiets, and T. I. Fedyushina, Izv. Akad. Nauk SSSR, Ser. Khim. (in the Press).
70. US P. 2 793 225 (1957); Chem. Abs., 51, 16 515 (1957).
71. German P. 696 774 (1940); Chem. Abs., 35, 5909 (1941).
72. M. A. Korshunov, R. G. Kuzovleva, and I. V. Furaeva, Prom. Sintezy Kauchuka, 7, 7 (1970).
73. E. M. Meade and F. N. Woodward, J. Chem. Soc., 1894 (1948).
74. T. A. Mastryukova, V. N. Odnoralova, and M. I. Kababachnik, Zhur. Obshch. Khim., 28, 1563 (1958).
75. US P. 3 211 649 (1965); Chem. Abs., 64, 510 (1966).
76. US P. 3 213 020 (1965); Chem. Abs., 64, 509 (1966).
77. US P. 3 213 023 (1965); Chem. Abs., 64, 509 (1966).
78. T. Barr and J. B. Speakman, J. Soc. Dyers Colourists, 60, 238 (1944).
79. S. Blackburn and H. Phillips, J. Soc. Dyers Colourists, 61, 203 (1945).

80. C. C. J. Culvenor, W. Davies, and K. H. Pausacker, J. Chem. Soc. 1050 (1946).
81. C. G. Moore and M. Porter, J. Chem. Soc., 2062 (1958).
82. K. Negoro, T. Watanabe, and J. Morishita, Bull. Fac. Eng. Hiroshima Univ., 19, 71 (1971); Chem. Abs., 77, 113 444 (1972).
83. H. R. Snyder, J. M. Stewart, and J. B. Ziegler, J. Amer. Chem. Soc., 69, 2675 (1947).
84. US P. 2 490 984 (1949); Chem. Abs., 44, 2550 (1950).
85. US P. 2 497 422 (1950); Chem. Abs., 44, 4025 (1950).
86. W. Reppe, Annalen, 601, 127 (1956).
87. E. P. Adams, F. P. Doyle, D. L. Hatt, D. O. Holland, W. H. Hunter, K. R. L. Mansford, J. H. C. Nayler, and A. Queen, J. Chem. Soc., 2649 (1960).
88. F. Asinger and A. Saus, Annalen, 753, 151 (1971).
89. US P. 3 111 541 (1963).
90. L. A. Kalutskii, A. F. Kolomiets, N. K. Bliznyuk, and S. L. Varshavskii, USSR P. No. 191 543 (1966); Byul. Izobret., No. 4, 25 (1967).
91. A. V. Fokin, A. F. Kolomiets, L. S. Rudnitskaya, and V. I. Shevchenko, Izv. Akad. Nauk SSSR, Ser. Khim., 660 (1975).
92. N. V. Schwarts, J. Org. Chem., 33, 2895 (1968).
93. C. C. J. Culvenor, W. Davies, and N. S. Heath, J. Chem. Soc., 278 (1949).
94. C. C. J. Culvenor and W. Davies, Austral. J. Sci. Res. Ser. A, 1, 236 (1948).
95. A. M. Creigton and L. N. Owen, J. Chem. Soc., 1024 (1960).
96. S. M. Idbal and L. N. Owen, J. Chem. Soc., 1030 (1960).
97. J. F. McGhie, W. A. Ross, and F. J. Jolietti, Chem. Ind. (London), 460 (1964).
98. M. G. Lin'kova, A. M. Orlov, O. V. Kil'disheva, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1148 (1968).
99. Japanese P. 23 253 (1962); Chem. Abs., 60, 3158 (1964).
100. BRD P. 2 114 124 (1971); Chem. Abs., 76, 60 701 (1972).
101. French P. 1 435 307 (1966); Chem. Abs., 65, 17 085 (1966).
102. B. P. 1 034 346 (1966); Chem. Abs., 65, 13 898 (1966).
103. B. P. 1 040 935 (1966); Chem. Abs., 65, 20 245 (1966).
104. Neth. Appl. 6 608 767 (1966); Chem. Abs., 66, 105 827 (1967).
105. B. P. 1 092 604 (1967); Chem. Abs., 68, 22 358 (1968).
106. US P. 3 649 561 (1972); Chem. Abs., 77, 6960 (1972).
107. Japanese P. 17 733 (1962); Chem. Abs., 65, 10 687 (1966).
108. J. Durden, H. Stansbury, and W. Catlette, J. Amer. Chem. Soc., 82, 3082 (1960).
109. V. S. Etlis, L. N. Grobov, and G. A. Razuvaev, Dokl. Akad. Nauk SSSR, 140, 623 (1961).
110. G. A. Razuvaev, V. S. Etlis, and L. N. Grobov, Zhur. Obshch. Khim., 33, 1366 (1963).
111. G. A. Razuvaev, V. S. Etlis, and L. N. Grobov, Zhur. Obshch. Khim., 32, 994 (1962).
112. V. S. Etlis, L. N. Grobov, and G. A. Razuvaev, Zhur. Obshch. Khim., 32, 2940 (1962).
113. US P. 3 687 976 (1972); Chem. Abs., 77, 152 831 (1972).
114. Neth. Appl. 6 506 490 (1965); Chem. Abs., 64, 15 843 (1966).
115. B. P. 1 092 610 (1967); Chem. Abs., 68, 21 823 (1968).
116. B. P. 1 135 800 (1965); Chem. Abs., 70, 47 278 (1969).
117. French P. 1 515 077 (1965); Chem. Abs., 70, 96 782 (1969).
118. French P. 1 505 715 (1965); Chem. Abs., 70, 19 908 (1969).
119. US P. 3 409 635 (1963); Chem. Abs., 70, 20 047 (1969).
120. J. Durden, H. Stansbury, and W. Catlette, J. Org. Chem., 26, 836 (1961).
121. US P. 3 213 108 (1965); Chem. Abs., 64, 3483 (1966).
122. French P. 1 390 207 (1965); Chem. Abs., 63, 1768 (1965).
123. V. S. Etlis, A. P. Sineokov, and G. A. Razuvaev, Khim. Geterotsikl. Soed., 223 (1967).
124. V. S. Etlis, A. P. Sineokov, and G. A. Razuvaev, USSR P. No. 176 397 (1965); Byul. Izobret., No. 22, 27 (1965).
125. A. P. Sineokov and V. S. Kutyreva, Khim. Geterotsikl. Soed., 1651 (1971).
126. Zh. D. Chernova, G. P. Belonovskaya, B. A. Dolgoplosk, and L. S. Andrianova, USSR P. No. 204 585 (1965); Byul. Izobret., No. 1 (1967).
127. Zh. D. Chernova, G. P. Belonovskaya, and B. A. Dolgoplosk, Dokl. Akad. Nauk SSSR, 178, 376 (1968).
128. Zh. D. Chernova, G. P. Belonovskaya, and B. A. Dolgoplosk, Vysokomol. Soed., 11B, 144 (1969).
129. G. P. Belonovskaya, L. A. Korotneva, Zh. D. Chernova, and Yu. P. Kuznetsova, in "Sintez, Struktura i Svoistva Polimerov" (The Synthesis, Structure, and Properties of Polymers), Izd. Nauka, Leningrad, 1970, p. 71.
130. Zh. D. Chernova, A. I. Kol'tsov, G. P. Belonovskaya, L. S. Andrianova, and B. A. Dolgoplosk, Vysokomol. Soed., 14B, 521 (1972).
131. Zh. D. Chernova, G. P. Belonovskaya, L. S. Andrianova, and B. A. Dolgoplosk, Vysokomol. Soed., 14B, 543 (1972).
132. German P. 631 026 (1936); Chem. Abs., 31, 6008 (1936).
133. N. F. Albertson and R. O. Clinton, J. Amer. Chem. Soc., 67, 1222 (1945).
134. R. O. Clinton, V. J. Salvador, and S. C. Laskowski, J. Amer. Chem. Soc., 70, 950 (1948).
135. H. Gilmann and L. A. Woods, J. Amer. Chem. Soc., 67, 1843 (1945).
136. B. Hansen, Acta Chem. Scand., 11, 537 (1957).
137. B. Hansen, Acta Chem. Scand., 13, 151 (1959).
138. H. R. Snyder, J. Stewart, and J. Ziegler, J. Amer. Chem. Soc., 69, 2672 (1947).
139. S. D. Turk, R. P. Louthan, and R. L. Cobb, J. Org. Chem., 29, 974 (1964).
140. R. L. Jacobs and R. D. Schuetz, J. Org. Chem., 26, 3472 (1961).
141. H. Takeda, J. Pharm. Soc. Japan, 92, 1117 (1972); Chem. Abs., 77, 164 335 (1972).
142. J. M. Stewart, J. Org. Chem., 28, 596 (1963).
143. J. M. Stewart, J. Org. Chem., 29, 1655 (1964).
144. B. P. 823 482 (1959); Chem. Abs., 54, 9956 (1960).
145. A. Oddon and J. Wylde, Bull. Soc. chim. France, 1603 (1967).
146. N. S. Isaacs, Canad. J. Chem., 44, 395 (1966).
147. F. Yu. Rachinskii, N. M. Slavachevskaya, and D. V. Ioffe, Zhur. Obshch. Khim., 28, 2998 (1958).
148. R. J. Wineman, M. H. Gollis, and J. C. James, J. Org. Chem., 27, 4222 (1962).
149. French P. 1 504 888 (1966); Chem. Abs., 70, 19 909 (1969).
150. US P. 3 231 617 (1966); Chem. Abs., 64, 9594 (1966).

151. C. O. Guss and D. L. Chamberlain, J. Amer. Chem. Soc., 74, 1342 (1952).
152. D. D. Reynolds, M. K. Massard, and D. L. Fields, J. Org. Chem., 26, 5109 (1961).
153. D. D. Reynolds, D. L. Fields, and D. L. Johnson, J. Org. Chem., 26, 5111 (1961).
154. Yu. K. Yur'ev and L. S. German, Izv. Moskov. Gos. Univ., Ser. Fiz.-Khim., 197 (1956).
155. Yu. K. Yur'ev and S. V. Dyatlovitskaya, Zhur. Obshch. Khim., 27, 1787 (1957).
156. Yu. K. Yur'ev, S. V. Dyatlovitskaya, and L. G. Bulavin, Zhur. Obshch. Khim., 27, 3271 (1957).
157. K. Yu. Novitskii, Yu. K. Yur'ev, and A. F. Oleinik, Zhur. Obshch. Khim., 33, 65 (1963).
158. L. G. Bulavin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2103 (1961).
159. L. G. Bulavin, Zhur. Org. Khim., 7, 2086 (1971).
160. L. G. Bulavin, Zhur. Org. Khim., 7, 2604 (1971).
161. E. D. Bergmann and A. Kaluszyner, Rec. Trav. chim., 78, 289 (1959).
162. H. M. Woodburn and B. G. Pautler, J. Org. Chem., 19, 863 (1954).
163. J. R. Schmolka and P. E. Spoerri, J. Amer. Chem. Soc., 79, 4716 (1957).
164. J. W. Haefele and R. W. Brode, Amer. Parfum. and Aromatics, 75, 39 (1960).
165. E. V. Kuznetsov and A. I. Sitnikova, USSR P. No. 148 406 (1962); Ref. Zhur. Khim., 3N272 (1963).
166. US P. 3 369 019 (1963); Chem. Abs., 69, 43 938 (1968).
167. US P. 2 323 409 (1943); Chem. Abs., 38, 212 (1944).
168. US P. 2 442 957 (1948); Chem. Abs., 42, 7328 (1948).
169. US P. 2 453 333 (1948); Chem. Abs., 43, 1799 (1949).
170. W. R. Brasen, H. N. Cripps, C. G. Bottomley, M. W. Farlow, and C. G. Krespan, J. Org. Chem., 30, 4188 (1965).
171. French P. 1 459 812 (1964); Chem. Abs., 67, 22 726 (1967).
172. M. Mousseron and M. Canet, Bull. Soc. chim. France, 18, 792 (1951).
173. M. Mousseron, R. Jacguier, and M. Mousseron-Canet, Bull. Soc. chim. France, 19, 1042 (1952).
174. F. G. Bordwell, H. M. Andersen, and B. M. Pitt, J. Amer. Chem. Soc., 76, 1082 (1954).
175. C. G. Moore and M. Porter, J. Chem. Soc., 2062 (1958).
176. R. L. Jacobs and R. D. Schuetz, J. Org. Chem., 26, 3472 (1961).
177. G. K. Helmkamp and N. Schnautz, Tetrahedron, 2, 304 (1958).
178. A. M. Creighton and L. N. Owen, J. Chem. Soc., 1024 (1960).
179. J. F. McGhie, B. A. Ross, F. J. Juliett, B. C. Girmwood, G. Usher, and W. M. Waldrom, Chem. Ind. (London), 1980 (1962).
180. J. M. Lalaucette and M. Laliberte, Tetrahedron Letters, 1401 (1973).
181. S. Matsumura, T. Nagai, and N. Tokura, Tetrahedron Letters, 3929 (1966).
182. H. R. Snyder and W. Alexander, J. Amer. Chem. Soc., 70, 217 (1948).
183. N. I. Delyagina, E. Ya. Petrova, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 376 (1972).
184. M. G. Lin'kova, Doctoral Thesis, Institute of Organic Derivatives of the Elements, USSR Academy of Sciences, Moscow, 1972.
185. W. Davies and W. E. Savige, J. Chem. Soc., 317 (1950).
186. W. Davies and W. E. Savige, J. Chem. Soc., 774 (1951).
187. G. Yu. Epshtein, I. A. Usov, and S. Z. Ivin, Zhur. Obshch. Khim., 33, 3638 (1963).
188. A. Oddon and J. Wylde, Bull. Soc. chim. France, 1607 (1967).
189. E. Kamejana and N. Nakajiama, Bull. Chem. Soc. Japan, 45, 1244 (1972).
190. J. M. Stewart and H. P. Cordts, J. Amer. Chem. Soc., 74, 5880 (1952).
191. A. V. Fokin, A. F. Kolomiets, and T. I. Fedyushina, Izv. Akad. Nauk SSSR, Ser. Khim., 670 (1975).
192. K. Furukawa and R. Oao, Bull. Inst. Chem. Res., Kyoto Univ., 30, 50 (1952); Chem. Abs., 47, 3661 (1953).
193. K. Furukawa, M. Nomura, and R. Odo, J. Chem. Soc. Japan, 56, 189 (1953).
194. A. Y. Merril and P. P. Perkins, J. Amer. Chem. Soc., 51, 3508 (1929).
195. M. Mousseron, M. Bousquet, and O. Marett, Bull. Soc. chim. France, 84 (1948).
196. G. Hesse, E. Reichold, and S. Majumdar, Chem. Ber., 90, 2106 (1957).
197. D. S. Dittmer and C. C. Levy, J. Org. Chem., 30, 636 (1965).
198. B. B. Jarvis, S. D. Dutkey, and H. L. Ammon, J. Amer. Chem. Soc., 94, 2136 (1972).
199. E. E. van Tamelen, J. Amer. Chem. Soc., 73, 3444 (1951).
200. I. M. Slobodin, S. S. Al'tman, and K. D. Tammik, Proizv. Smaz. Mater., 5, 58 (1959).
201. A. V. Fokin, A. F. Kolomiets, and T. I. Fedyushina, Izv. Akad. Nauk SSSR, Ser. Khim., 2126 (1975).
202. L. Thijs, J. Strating, and B. Zwanenburg, Rec. Trav. chim., 91, 1345 (1972).
203. US P. 2 212 141 (1940); Chem. Abs., 35, 463 (1941).
204. K. Takeda, T. Komeno, and J. Kawanami, Chem. Farm. Bull. (Tokyo), 8, 621 (1960); Chem. Abs., 55, 12 451 (1960).
205. T. Komeno, Chem. Farm. Bull. (Tokyo), 8, 672 (1960); Chem. Abs., 55, 17 685 (1960).
206. S. Z. Ivin, Zhur. Obshch. Khim., 28, 177 (1958).
207. S. Z. Ivin, Zhur. Obshch. Khim., 22, 267 (1952).
208. N. K. Bliznyuk, A. F. Kolomiets, R. V. Strel'tsov, and S. L. Varshavskii, USSR P. No. 249 370 (1966); Ref. Zhur. Khim., 16N741 (1970).
209. K. A. Petrov and G. A. Sokol'skii, Zhur. Obshch. Khim., 27, 2711 (1957).
210. E. P. Adams, K. N. Ayad, and F. P. Doyle, J. Chem. Soc., 2665 (1960).
211. B. P. 819 688 (1960); Chem. Abs., 54, 8849 (1960).
212. G. Yu. Epshtein, I. A. Usov, and S. Z. Ivin, Zhur. Obshch. Khim., 34, 1954 (1964).
213. H. Ringsdorf and C. G. Overberger, Macromol. Chem., 1418 (1961).
214. J. M. Stewart, US P. 2 774 794 (1956); Chem. Abs., 51, 7400 (1957).
215. G. Yu. Epshtein, I. A. Usov, and S. Z. Ivin, Zhur. Obshch. Khim., 34, 1948 (1964).
216. G. K. Helmkamp and D. J. Pettitt, J. Org. Chem., 27, 1942 (1962).
217. A. V. Fokin, A. F. Kolomiets, N. K. Bliznyuk, and R. N. Golubeva, Izv. Akad. Nauk SSSR, Ser. Khim., 2124 (1975).
218. G. Yu. Epshtein, I. A. Usov, and S. Z. Ivin, Zhur. Obshch. Khim., 34, 2347 (1964).
219. G. Yu. Epshtein, I. A. Usov, and S. Z. Ivin, Zhur. Obshch. Khim., 34, 1951 (1964).
220. US P. 2 862 949 (1958).

221. US P. 2 866 809 (1958); Chem. Abs., 53, 19 879 (1959).
222. US P. 2 866 808 (1958); Chem. Abs., 53, 12 176 (1959).
223. O. N. Nuretdinova, Izv. Akad. Nauk SSSR, Ser. Khim., 1255 (1966).
224. O. N. Nuretdinova and L. Z. Nikonova, Izv. Akad. Nauk SSSR, Ser. Khim., 1125 (1965).
225. O. N. Nuretdinova, Azv. Akad. Nauk SSSR, Ser. Khim., 1901 (1965).
226. S. Z. Ivin and I. D. Shelakova, Zhur. Obshch. Khim., 35, 1220 (1965).
227. L. E. Dmitrieva, S. Z. Ivin, and K. V. Karavanov, Symposium, "Khimiya Organicheskikh Soedinenii Fosfora" (The Chemistry of Organophosphorus Compounds), Izd. Akad. Nauk SSSR, Leningrad, 1967, p. 1557.
228. K. V. Karavanov, S. Z. Ivin, and V. V. Lutsenko, Zhur. Obshch. Khim., 35, 737 (1965).
229. J. K. Stille and J. A. Empen, Amer. Chem. Soc. Polymer Prepr., 6, 619 (1965).
230. J. K. Stille and J. A. Empen, J. Polymer. Sci., 5, A-1, 273 (1967).
231. G. Yu. Epshtein and S. Z. Ivin, Zhur. Obshch. Khim., 34, 2355 (1964).
232. A. F. Kolomiets, G. S. Levskaya, and N.K. Bliznyuk, USSR P. No. 196 823 (1966); Byul. Izobret., No. 12, 21 (1967).
233. A. F. Kolomiets, G. S. Levskaya, and N.K. Bliznyuk, USSR P. No. 192 809 (1966); Byul. Izobret., No. 6, 24 (1967).
234. A. V. Fokin, A. F. Kolomiets, and G. S. Levskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 406 (1975).
235. A. V. Fokin, A. F. Kolomiets, Yu. N. Studnev, and A. I. Rapkin, Izv. Akad. Nauk SSSR, Ser. Khim., 2348 (1974).
236. G. K. Helmkamp and D. J. Pettitt, J. Org. Chem., 25, 1754 (1960).
237. G. K. Helmkamp and D. J. Pettitt, J. Org. Chem., 29, 3258 (1964).
238. R. D. Schuetz and R. L. Jacobs, J. Org. Chem., 26, 3467 (1961).
239. A. Noshay and C. C. Price, J. Polymer. Sci., 54, 533 (1961).
240. B. A. Arbuzov and O. N. Nuretdinova, Izv. Akad. Nauk SSSR, Ser. Khim., 927 (1963).
241. G. K. Helmkamp, D. J. Pettitt, J. R. Lowell, W. R. Mabey, and R. G. Wolcott, J. Amer. Chem. Soc., 88, 1030 (1966).
242. O. Yoshiki, M. Toru, Y. Kiyoshi, and A. Toshio, Tetrahedron Letters, 259 (1969).
243. H. Staudinger and J. Siegwalt, Helv. Chim. Acta, 3, 833 (1920).
244. A. Schönberg, Ber., 58, 1793 (1925).
245. A. Schönberg, A. Fateen, and A. Sammour, J. Amer. Chem. Soc., 79, 6020 (1957).
246. G. P. Hagen and R. M. Burgison, J. Amer. Pharm. Assoc., 39, 7 (1950).
247. D. Seyferth, W. Tronich, and K. S. Marmor, J. Org. Chem., 37, 1537 (1972).
248. A. Schönberg and L. V. Vargha, Annalen, 483, 176 (1930).
249. A. Schönberg and L. V. Vargha, Ber., 64, 1390 (1931).
250. D. J. Pettitt and G. K. Helmkamp, J. Org. Chem., 28, 2932 (1963); 29, 2702 (1964).
251. S. Kambara, K. Okita, and S. Tayima, High Polymers, 5, 376 (1948).
252. K. Kondo, M. Matsumoto, and A. Negishi, Tetrahedron Letters, 2131 (1972).
253. G. Opitz and K. Fischer, Angew. Chem., 77, 41 (1965).
254. L. V. Vargha and E. Kovacs, Ber., 75, 794 (1942).
255. L. A. Carpino and R. N. Rynbrandt, J. Amer. Chem. Soc., 88, 5682 (1960).
256. L. A. Paquette and L. S. Wittenbrook, Chem. Comm., 471 (1966).
257. L. A. Carpino and L. Y. McAdams, J. Amer. Chem. Soc., 87, 5804 (1965).
258. N. P. Neureiter and F. G. Bordwell, J. Amer. Chem. Soc., 81, 578 (1959).
259. R. D. Schuetz and R. L. Jacobs, J. Org. Chem., 23, 1799 (1958).
260. R. E. Davies, J. Org. Chem., 23, 1768 (1958).
261. M. J. Boskin and D. B. Denney, Chem. Ind. (London), 330 (1959).
262. M. J. Boskin, Diss. Abs., 20, 4273 (1960).
263. D. B. Denney and M. J. Boskin, J. Amer. Chem. Soc., 82, 4736 (1960).
264. J. E. Christensen and L. Goodmann, J. Amer. Chem. Soc., 83, 3827 (1961).
265. US P. 2 950 337 (1960); Chem. Abs., 55, 1440 (1961).
266. A. Schönberg, W. Knoefel, E. Frese, and K. Praefeke, Chem. Ber., 103, 949 (1970).
267. H. Klosterziel and H. J. Backer, Rec. Trav. chim., 71, 1235 (1952).
268. B. P. 949 374 (1962); Chem. Abs., 60, 5460 (1963).
269. US P. 3 136 744 (1964); Chem. Abs., 61, 4312 (1964).
270. E. C. Sabatino, Diss. Abs., 24, 4408 (1964).
271. K. Ueno, H. Tsukamoto, K. Hayashi, and S. Okamura, J. Polymer Sci., B5, 395 (1967).
272. S. Suga and T. Hakajama, Nippon Kagaku Kaishi, 4779 (1972).
273. V. A. Zakrevskaya and E. E. Tomashevskii, Vysokomol. Soed., 8, 1295 (1966).
274. M. S. Malinovskii, "Okisi Olefinov i Ikh Proizvodnye" (Epoxyalkanes and their Derivatives), Gos. Nauchno-Tekhn. Izd. Khim. Lit., Moscow, 1961.
275. L. A. Kalutskii, N. K. Bliznyuk, and A. F. Kolomiets, USSR P. No. 215 965 (1967); Byul. Izobret., No. 14, 26 (1968).
276. R. Ketcham and V. P. Shah, J. Chem. Eng. Data, 11, 106 (1966).