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U. D. C. 547.311 : 547.422.22-31

REACTIONS OF EPOXYALKANES TAKING PLACE WITH EXPANSION OF THE OXIRAN RING

L. N. Grobov, A. P. Sineokov, and V. S. Etlis

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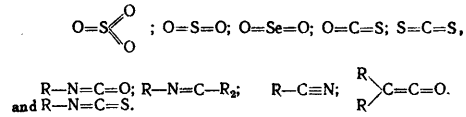
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1. INTRODUCTION

Epoxyalkanes are known to be very reactive; their many reactions have been adequately studied and described in the literature [1-4]. Most of the reactions of epoxyalkanes are accompanied by opening of the epoxide ring. Reactions accompanied by enlargement of the ring have been much less studied. The best known among these reactions are the dimerisation of the oxides and the reaction of the oxides with aldehydes and ketones, leading to the production of dioxolans.

The reactions of the oxides with carbon dioxide, leading to cyclic esters of carbonic acid, have also been studied. This process has been carried out on an industrial scale. The alkylene carbonates obtained find application in organic synthesis, as a solvent and for the production of polymers. The methods of making alkylene carbonates, their properties, and applications have been reviewed [5,6].

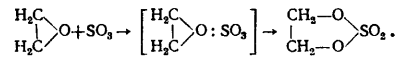
Cyclic products have now been obtained by the reaction of oxides with certain other compounds containing multiple bonds. Such compounds are:



2. REACTIONS WITH SO_3, SO_2, AND SeO_2

The epoxyalkanes react with the anhydrides of some inorganic acids to form cyclic esters.

Thus ethylene sulphate was obtained by the reaction of sulphur trioxide with ethylene oxide in dioxan. It is suggested that initially a coordination compound of sulphur trioxide with ethylene oxide is formed, which then rearranges into the ester [7]:



1,4-Oxathian can be used instead of dioxan [8]. Cyclic alkylene sulphates with 2–6 carbon atoms are obtained by the reaction of corresponding epoxyalkanes with sulphur trioxide in the gas phase at 140°. Sometimes the reagents are diluted with inert gas. 0.1–7.5 moles sulphur trioxide per mole oxide are taken. The cyclic alkylene sulphates formed are removed from the reaction mixture by sublimation [9].

The addition of sulphur dioxide to epoxyalkanes has been studied in greater detail. When sulphur dioxide is passed into ethylene oxide at below 0°, a molecular compound of composition $C_2H_4OSO_2$ is formed [10]. It is used for sterilising soil, as its boiling point is about 20 deg above that of its components.

To obtain ethylene sulphite the reaction is carried out at a higher temperature, either without a catalyst or in the presence of various catalysts. When a catalyst is not used, the ethylene oxide and sulphur dioxide are mixed in the liquid phase and heated under pressure to 140°. The patent states that the reaction is almost complete [11].

Pyridine, amines, amides, phosphines [12], and also quaternary ammonium bases [13,14] have been proposed for use as catalysts in this process.

The polymers of ethylene sulphite formed in the presence of catalysts depolymerise on heating at 140–150°.[13,15] Propylene sulphite can also be obtained by the thermal decomposition of the polysulphite but poly(cyclohex-1,2-ylene sulphite) does not give a monomeric product but forms cyclohexanediol and cyclopentanecarbaldehyde.

The decomposition of polysulphites can also take place under the action of atmospheric oxygen, peroxides, and hydroperoxides, and also under the action of ultraviolet light even at room temperature. By initiating depolymerisation in this way, cyclohex-1,2-ylene sulphite was also obtained from the corresponding polysulphite[16].

The method can be used for making cyclic sulphites which are otherwise unobtainable. For example, 3-hydroxypropylene sulphite, previously unobtainable by other methods, was made by direct reaction of glycidol [2,3-epoxypropan-1-ol (Ed. of Translation)] with sulphur dioxide[14].

To increase the yield of ethylene sulphite, it is recommended that the reaction of ethylene oxide with sulphur dioxide should be carried out in ethylene sulphite or in a mixture of ethylene sulphite and its polymer[17].

Activated carbon, aluminium oxide, zinc chloride, copper(II) chloride, chromium(III) chloride, manganese(II) sulphate, and phosphates at 120–150° can also be used as catalysts for the reaction of ethylene oxide with sulphur dioxide. When active carbon is used (140–160°), dioxan is formed as well as ethylene sulphite (in 1 : 1 ratio)[18].

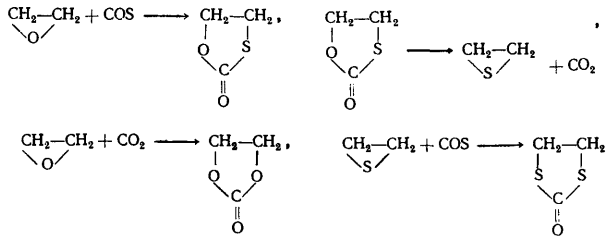
Dioxan is also formed in the thermal decomposition of poly(ethylene sulphite) obtained in the presence of salts of quaternary ammonium bases. Acetaldehyde and water are produced at the same time[14].

Another proposal for making cyclic sulphites is to pass gaseous epoxyalkanes with sulphur dioxide (molar ratio 1 : 2) under pressure over a catalyst at 200°. The pressure is chosen so that the reaction product is volatilised from the catalyst together with the unreacted reagents. The catalyst can be activated carbon, treated with alkali or silver nitrate and then alkali. Sulphur-resistant catalysts are also used, for example, nickel and/or tungsten sulphides. The cyclic ester is condensed from the effluent gas. Another possibility is to condense the ester product together with the unreacted substances and then separate the mixture by distillation[19]. von Woerden gives other methods of preparing cyclic sulphites and their properties[20].

In the presence of tetraethylammonium bromide, selenium dioxide also adds on to some epoxyalkanes to form cyclic esters of selenous acid[21]. The product of the reaction between selenium dioxide and 1,2-epoxycyclohexane could not be isolated pure. With trimethylene oxide a linear polymeric ester of selenous acid is apparently formed.

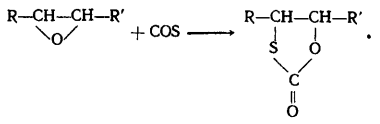
3. REACTIONS WITH CARBONYL SULPHIDE AND CARBON DISULPHIDE

The reactions of the sulphur analogues of carbon dioxide, carbonyl sulphide, and carbon disulphide with epoxyalkanes and the properties of products have been much less studied. At 150° under pressure in the presence of trimethylamine, ethylene oxide and carbonyl sulphide form a copolymer of ethylene *OS*-thiocarbonate and ethylene sulphide[22]; in the presence of tetraethylammonium bromide two products are formed: ethylene carbonate and ethylene *SS*-dithiocarbonate[23,24]. To explain their formation the following scheme has been suggested:



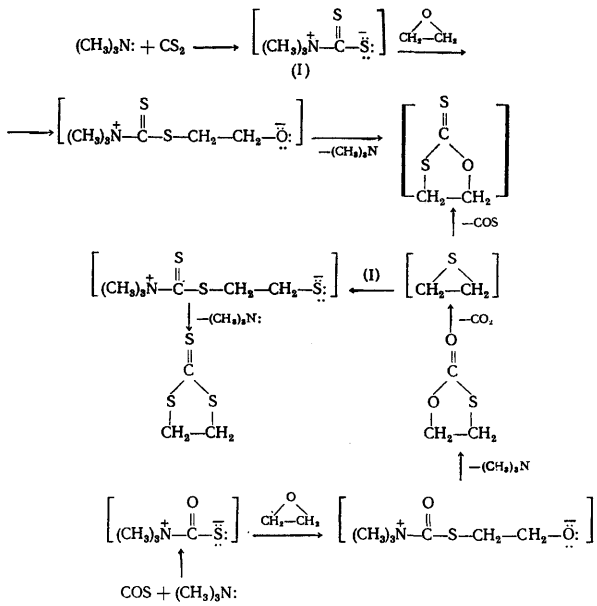
It has been shown that ethylene *OS*-monothiocarbonate in the presence of ethylene oxide and crystalline tetraethylammonium bromide actually decomposes into ethylene sulphide and carbon dioxide at 40–50°.[25]

In the reactions of propylene oxide, 3-chloro-1,2-epoxypropane[23,24], 1-chloro-2,3-epoxybutane, and 1,2-dichloro-3,4-epoxybutane with carbonyl sulphide only one product is formed, by the scheme:



Cyclohex-1,2-ylene oxide and symmetrical oxides such as 2,3-epoxybutane and 1,4-dichloro-2,3-epoxybutane do not react with carbonyl sulphide[26].

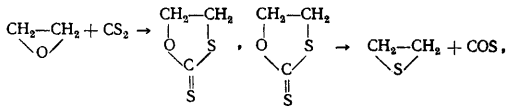
Carbon disulphide also reacts with epoxyalkanes with ring enlargement. In this way Durden and coworkers[27,28] obtained several alkylene trithiocarbonates. The reaction was carried out in the liquid phase under pressure of nitrogen with excess of the epoxyalkane. The maximal yield of ethylene trithiocarbonate was obtained at a carbon disulphide : ethylene oxide molar ratio of 1 : 2.5 and the presence of 0.5 mole % trimethylamine. Carbon dioxide and carbonyl sulphide are formed as side-products, the amount of carbon dioxide formed increasing with decrease in the carbon disulphide : alkene oxide ratio:

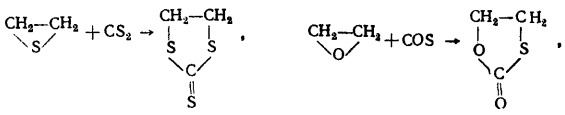


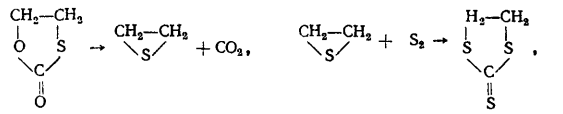
Ethylene sulphide, the intermediate formation of which is postulated in this mechanism, was not isolated from the reaction products.

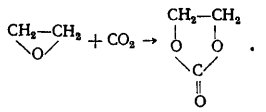
By the same method the authors obtained propylene trithiocarbonate, cyclohex-1,2-ylene trithiocarbonate, phenylethylene trithiocarbonate, and 4-cyanocyclohex-1,2-ylene trithiocarbonate.

The reaction proceeds differently when an equimolar ratio of the reactants is used. Ethylene oxide and carbon disulphide then form a mixture of ethylene trithiocarbonate and ethylene carbonate in the molar ratio 2:1.[29] Their formation can be represented by the scheme:[30]



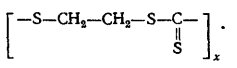




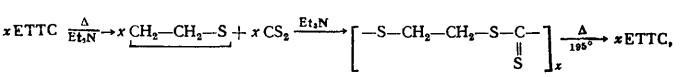


The absence of ethylene dithiocarbonate from the products, although it could be obtained by the reaction of the carbonyl sulphide formed in the process with the ethylene sulphide, suggests that the rate of reaction of the latter with carbon disulphide is much greater than the rate of reaction with carbonyl sulphide.

In connection with the proposed scheme of reaction, the authors made a detailed study of the reaction of ethylene sulphide with carbon disulphide. The reaction proceeded in the presence of triethylamine as catalyst. Temperature was found to greatly affect this reaction. Whereas ethylene trithiocarbonate is the sole product at 100°, at 25° it was accompanied by 37% of a copolymer of ethylene sulphide and carbon disulphide, of composition:



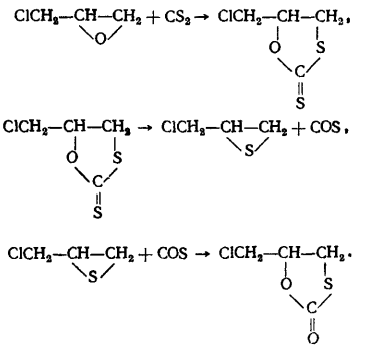
At 195–200° this copolymer decomposes, with formation of ethylene trithiocarbonate. All this can be represented by the scheme[29]:



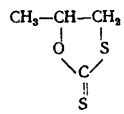
in which ETTC represents ethylene trithiocarbonate.

The decomposition of the ethylene dithiocarbonate obtained initially, which takes place in the presence of hydrogen peroxide and tetraethylammonium bromide, was also confirmed experimentally[31].

3-Chloropropylene *OS*-monothiocarbonate and 3-chloro-1,2-epithiopropane are formed in the reaction of 3-chloro-1,2-epoxypropane with carbon disulphide. Their formation can be represented by the following series of reactions:

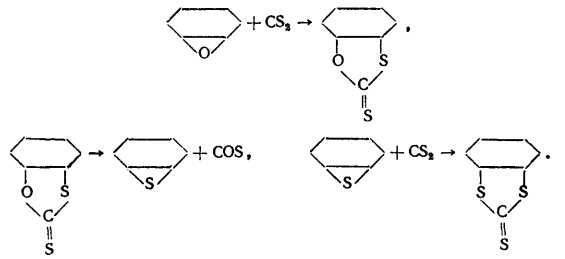


OS-Propylene dithiocarbonate



was obtained as the main product of the reaction of propene with carbonyl sulphide. A little ethylene sulphide was also isolated.

Cyclohex-1,2-ylene trithiocarbonate, a little *OS*-cyclohex-1,2-ylene dithiocarbonate, and carbonyl sulphide are formed in the reaction of 1,2-epoxycyclohexane with carbon disulphide:

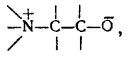


For the reactions of alkylene thiocarbonates see Refs. 32–52.

4. REACTIONS OF EPOXYALKANES WITH ISOCYANATES

Ethylene oxide, propylene oxide, 2-phenyloxiran, and 3-chloro-1,2-epoxypropane bring about the trimerisation of isocyanates. Thus tri(phenyl isocyanate) was obtained by the reaction of ethylene oxide with phenyl isocyanate at room temperature and at 100°.[53] The trimerisation of isocyanates is accelerated in the presence of tertiary amines[54–57].

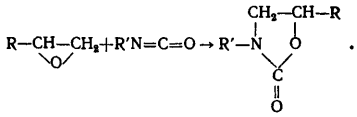
The catalytic action of oxides in the presence of bases is probably due to the formation of the bipolar ion



the existence of which has been shown experimentally[58].

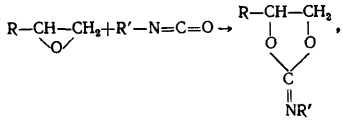
Substituted oxazolid-2-ones were obtained in high yield in the reaction of isocyanates with epoxyalkanes in the presence of tetraethylammonium bromide or potassium iodide

in dioxan, dimethylformamide, or acetonitrile at 150–200°:[54]

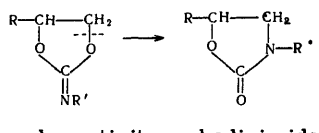


Oxazolid-2-ones were also obtained by the reaction of phenyl isocyanate and epoxides without a solvent at 180–200°.[59-61] Pyridine, tribenzylamine, zinc chloride, lithium chloride, iron(III) chloride, disodium phthalate, alkali, and lead naphthenate act as catalysts for the reaction. Carbonates or sulphites of 1,2-diols, and also cyclic carbonates of α-hydroxy-acids and their sulphite and nitrite analogues[59,61,62], can be used instead of epoxides in the reaction with isocyanates, when they decompose on heating to form the epoxyalkanes. Under the stated conditions, the 3,5-disubstituted oxazolid-2-ones are always formed, as the opening of the epoxide or carbonate ring takes place at the unsubstituted carbon atom[61]. 3-Phenyloxazolid-2-ones were isolated in high yield by the reaction of ethylene carbonate with isocyanate at 130–160° in the presence of *N*-methylmorpholine[63].

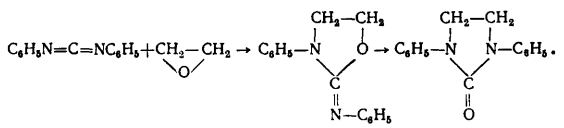
From the above, it follows that reactions between isocyanates and epoxides take place at the N=C bond of the isocyanate. However, Gulbins and Hamann[64,65] showed, by a detailed investigation of this reaction, that the first stage is the addition of the epoxyalkane at the C=O bond of the isocyanate with the intermediate formation of 2-phenylamino-1,3-dioxolane:



which under the conditions of the reaction rearranges into an oxazolid-2-one. This was demonstrated with the aid of a counter-synthesis. 2-Phenylamino-1,3-dioxolan was obtained from phenylimidocarbonyl dichloride and disodium glycollate, and on heating at 200° in the presence of lithium chloride it rearranged to an oxazolidone. A similar reaction takes place at 100° under the action of aluminium chloride[66]. The rearrangement takes place in such a way that the dioxolane ring is broken between the oxygen atom and the unsubstituted CH_2 group:

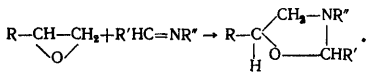


In their structure and reactivity carbodi-imides are reminiscent of isocyanates, therefore their reaction with epoxides or alkylene carbonates in the presence of lithium chloride or pyridine at 200° would be expected to yield substituted imino-oxazolidines. However, instead of these products cyclic ureas, derivatives of imidazolid-2-one, are isolated. As Gulbins and Hamann have shown[65], here initially an imino-oxazolidine is formed, which is converted into 1,3-diphenylimidazolid-2-one by breaking of the C–O bond:



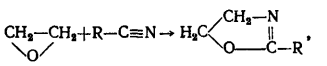
5. REACTIONS OF EPOXYALKANES WITH COMPOUNDS CONTAINING THE GROUPS >C=N–, –C≡N, OR >C=C=O

The reaction of epoxyalkanes with compounds containing >C=N– and –C≡N bonds were investigated by Oda and coworkers[67,68]. Ethylene oxide, propylene oxide, and 3-chloro-1,2-epoxypropane add on to Schiff bases in the presence of tin(IV) chloride (5–10 mole %), to form oxazolidines:



The reactions were carried out in carbon tetrachloride at 10–20°. *N*-t-Butylazomethine reacts with epoxyalkanes with a moderate yield in the absence of catalysts, which can be attributed to its high nucleophilic nature. The use of boron trifluoride as catalyst led to a fall in the yield.

The expected oxazolines



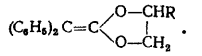
where R = CH_3, $(CH_3)_2CH$, $C_6H_5CH_2$, or CH_2=CH, were isolated from the reaction of epoxyalkanes with nitriles[68].

The reaction was carried out in concentrated sulphuric acid at 5–10°. The existence of side-reactions necessitated the use of a twofold excess of the epoxide, but the yield of the total product was very low (up to 21%). Two isomeric oxazolines were obtained from propylene oxide and acetonitrile. The preferential opening of the epoxide ring at the secondary carbon atom suggests an S_N1 mechanism, which includes the attack of the nitrile on the carbonium ion, and that leads to the opening of the ring of the protonated epoxide.

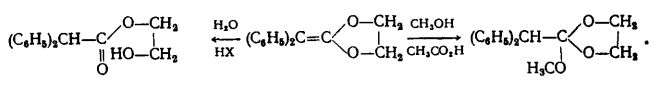
Diphenylacetonitrile reacts with ethylene and propylene oxides in the presence of sodium amide to form imidolactones[65].

In the presence of the >C=C=O system of bonds in ketenes the formation of reaction products with epoxides at both the C=C and the C=O bond can be expected.

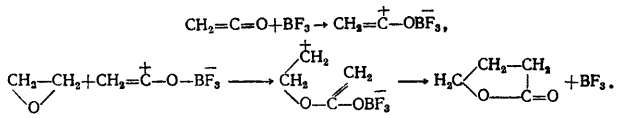
Diphenylketen forms cyclic acetals of diphenylketen on reaction with styrene oxide [phenyloxiran (Ed. of Translation)], γ-phenoxypropylene oxide, ethylene carbonate, and propylene carbonate at 180–200° in the presence of lithium chloride[65]:



The infrared spectra of the compounds obtained show a strong absorption band at 6.05 μm (1653 cm^{-1}) due to the C=C double bond; the absorption band of the carbonyl group was not observed. The structure of the acetals was confirmed by the formation of the ortho-ester of diphenylacetic acid on reaction of the acetal from diphenylketen and ethylene oxide with methanol in the presence of acetic acid, and also by the formation of 2-hydroxyethyl diphenylacetate on hydrolysis:



Hence it was shown that diphenylketen reacts with epoxides at the C=O bond. The rearrangement of the acetal into a γ-lactone was not observed. In contrast to this, Oda and coworkers[70] showed that aliphatic and aromatic α-oxides react with keten in the presence of boron trifluoride–diethyl ether at the C=C bond to form γ-lactones:

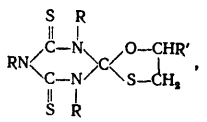


Lactones are obtained in ~ 10% yield on passing keten into an ethereal solution of an epoxide in the presence of 5 mole % boron trifluoride–diethyl ether at 5–50°. In this way, ethylene oxide, 1,2-epoxypropane, styrene oxide, and 3-chloro-1,2-epoxypropane gave respectively γ-butyrolactone, γ-valerolactone, γ-phenyl-γ-butyrolactone, and γ-chloromethyl-γ-butyrolactone.

6. REACTIONS OF EPOXYALKANES WITH ISOTHIOCYANATES

The reaction of epoxyalkanes with the nearest sulphur analogues of the isocyanates — the isothiocyanates — is quite unique.

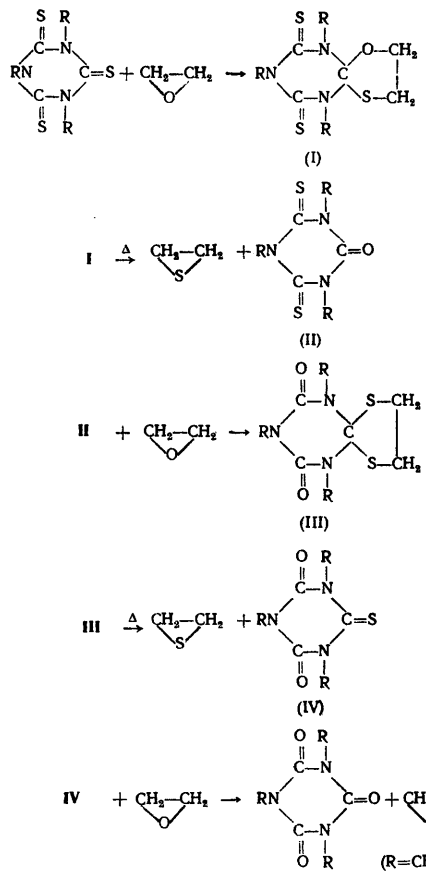
The simplest isothiocyanate, methyl isothiocyanate, reacts with ethylene oxide in the presence of tetraethylammonium bromide to form hexahydro-1,3,5-trimethyltriazine-2,6-dithione-4-spiro-2′-(1,3-oxathiolan):[71]



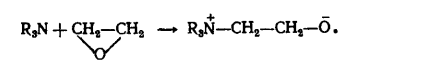
where R = CH_3 and R′ = H.

When this compound is heated to 200° in dioxan it decomposes with liberation of ethylene sulphide and trimethyl dithioisocyanurate; oxidation of it with nitric acid led to trimethyl isocyanurate. It was shown that the formation of a spiro-compound proceeds through the formation of the trimethyl ester of trithioisocyanuric acid, which then reacts at the C=S bond with the ethylene oxide[72]. Trimethyl trithioisocyanurate was obtained by trimerisation of methyl isothiocyanate in a solution of the oxides in the presence of catalytic amounts of triethylamine or pyridine, An analogous reaction also takes place in a solution of triethylamine in the presence of catalytic amounts of epoxyalkanes, that is, the latter in conjunction with tertiary amines bring about trimerisation of the methyl isothiocyanate. The reaction does not take place in the absence of the oxides.

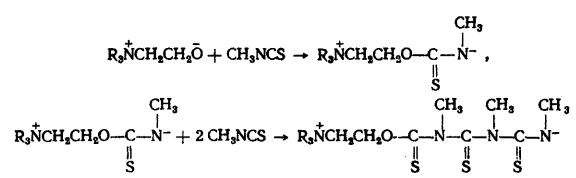
The liberated trimethyltrithioisocyanurate reacts with ethylene oxide, propylene oxide, and 3-chloro-1,2-epoxypropane in the presence of tetraethylammonium bromide to form the corresponding spiro-compounds, which when heated to 200° decompose into alkylene sulphide and trimethyl dithioisocyanurate[72]. On the reaction of propylene oxide with methyl isothiocyanate, the trimer of methyl isothiocyanate is obtained in addition to the spiro-compound; increasing the duration of the reaction leads to the production of only one spiro-compound[72]. This once again confirms that in the reactions with epoxyalkanes the methyl isothiocyanate is first trimerised and then the trimer reacts with the alkylene oxide at the C=S bond. The decomposition product of the spiro-compounds, trimethyl dithioisocyanurate, also reacts with ethylene oxide at the C=S bond to form a new spiro-compound which when heated to 200° liberates ethylene sulphide and trimethyl monothioisocyanurate. The latter reacts with ethylene oxide to give first a spiro-compound and then trimethyl isocyanurate. Hence, on starting from trimethyl trithioisocyanurate, trimethyl isocyanurate was obtained, that is, complete replacement of sulphur by oxygen took place under the action of ethylene oxide[72]:

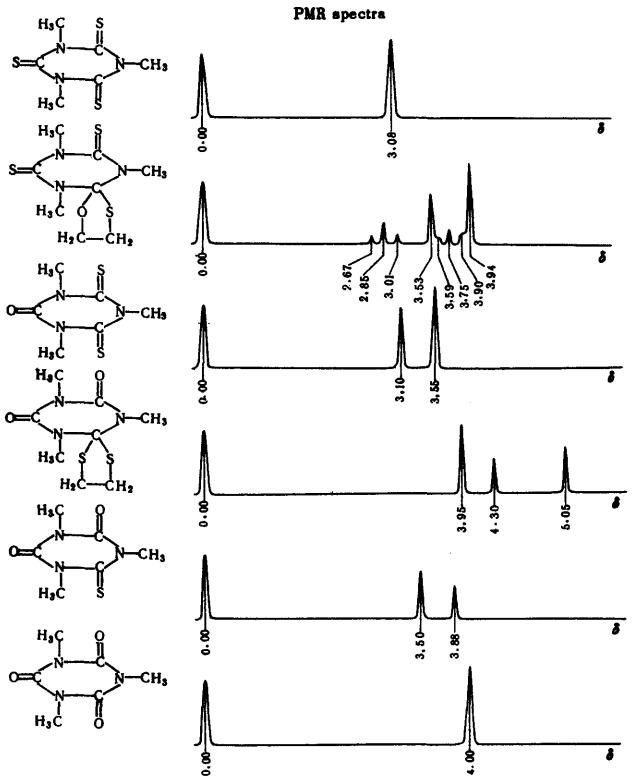


The structure of all the compounds obtained was confirmed by use of PMR spectroscopy (Figure).[73] It can be assumed that the mechanism of formation of trimethyl trithioisocyanurate and the spiro-compound is analogous to the reaction of the trimerisation of isocyanates. A bipolar ion acts as catalyst[58]:

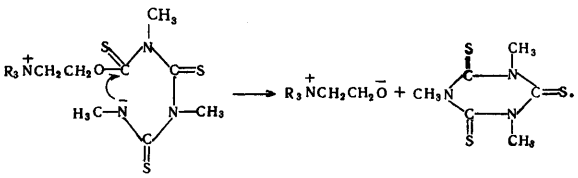


The ion formed adds on to the N=C bond of the isothiocyanate to form a nitrogen anion, which continues the chain growth up to the stage of the trimer:

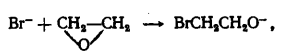




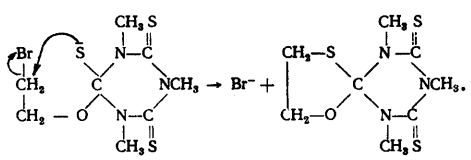
Then the ring closes with release of the original catalyst:



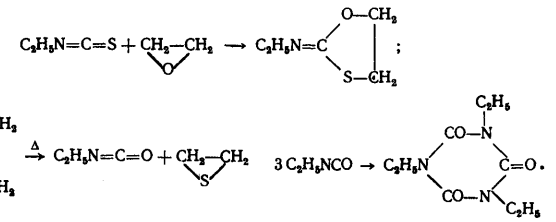
In the presence of tetraethylammonium bromide the anion acts as catalyst:



which catalyses the trimerisation of methyl isothiocyanate. The trimethyl trithioisocyanurate obtained is attacked by the anion at the C=S bond, leading to an anion with a negative charge at the sulphur atom, which closes into a ring by displacing a bromide anion:

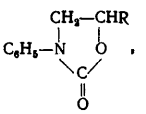


The nearest homologue of methyl isothiocyanate, ethyl isothiocyanate, reacts with ethylene oxide in the presence of tetraethylammonium bromide somewhat differently. In addition to the spiro-compound, triethyl isocyanurate[75] and ethylene sulphide were isolated from the reaction mass; their formation can be represented as follows:

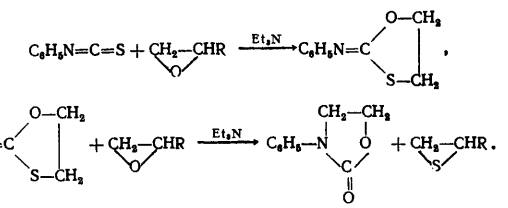


Epoxyalkanes in conjunction with basic compounds are known to bring about trimerisation of isocyanates[54]. Here the trimerisation proceeds under the influence of the sulphur analogue of ethylene oxide — ethylene sulphide — and traces of triethylamine.

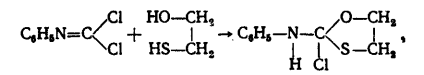
Phenyl isothiocyanate reacts with epoxyalkanes in the presence of triethylamine to form compounds which do not contain sulphur — 3-phenyloxazolid-2-ones[74]:



where R = H, CH_3, or CH_2Cl. The scheme for obtaining oxazolid-2-ones can be represented as follows:



The 2-phenylimino-1-thio-3-oxolan which is formed as an intermediate readily reacts with the epoxyalkane giving an oxazolidone and the corresponding epithioalkane. The possibility of such a reaction taking place is confirmed by the fact that 2-phenylimino-1-thio-3-oxolan is formed from phenylimidocarbonyl dichloride and mercaptoethanol in the presence of triethylamine[75]; ethylene oxide converts the product into 3-phenyloxazolid-2-one. On using pyridine as an acceptor for the hydrogen chloride the above reaction between phenylimidocarbonyl dichloride and mercaptoethanol leads to the production of 2-chloro-2-phenylamino-1-thio-3-oxolan:



which also reacts with ethylene oxide, to form 3-phenyloxazolid-2-one[76]. The reaction probably takes place through the stage of formation of 2-phenylimino-1-thio-3-oxolan.

Hence in the reaction of epoxyalkanes with isothiocyanates, the epoxide opens the C=S bond in the N=C=S system of double bonds.

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