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2-Oxazolidinones

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The synthesis and properties of 2-oxazolidinones and polymers containing 2-oxazolidinone rings are examined. Attention is concentrated on studies devoted to reactions in which the initial monomers are readily available substances produced on a large scale-epoxides and isocyanates. The mechanisms of the formation reactions of oxazolidinones, the catalytic systems employed, and the possible side processes are discussed. The properties and applications of polymers with 2-oxazolidinone rings in the chain are described.
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I. INTRODUCTION

2-Oxazolidinones occupy a special place among heterocyclic compounds in modern organic chemistry. They are widely used in medicine as drugs and pharmaceutical preparations, as intermediates in the paint and varnish industry, as lubricants, and in many other branches of the national economy. In recent years there has been a considerable development of the synthesis of polymers containing 2-oxazolidinone rings, which are used to prepare adhesives, foams, coatings, fibres, and electrically insulating and other materials, which as a rule have effective physicomechanical properties and high thermal stability and heat resistance.

Numerous methods of synthesis of 2-oxazolidinones have been described in the literature. The most promising method, which is of industrial importance, involves the reaction of epoxides with isocyanates[1]. Numerous studies devoted to this reaction and its employment for the synthesis of a large number of polyoxazolidinones with a wide variety of structures have been published.

There are virtually no Russian and foreign reviews dealing with the present state of the chemistry of 2-oxazolidinones. The present review deals with the available data on the methods of synthesis of 2-oxazolidinones, attention being concentrated on studies of the reactions of epoxides with isocyanates having different structures; the physical and chemical properties of 2-oxazolidinones are discussed. A considerable proportion of the review is devoted to a detailed consideration of the synthesis, reaction mechanisms, properties, and applications of poly-2-oxazolidinones—one of the most important fields of practical application of heterocyclic compounds of this type.

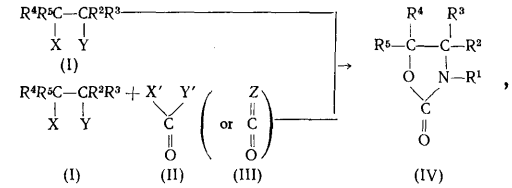
II. THE SYNTHESIS OF 2-OXAZOLIDINONES

The numerous methods of synthesis of 2-oxazolidinones known at the present time can be arranged systematically as follows: (1) cyclisation of β-difunctional compounds in the presence or absence of a cyclising agent; (2) reactions involving the conversion of various (other than epoxides) heterocyclic compounds into 2-oxazolidinones; (3) reactions of epoxides with various compounds.

The reactions are examined below in the same sequence, those of epoxides with isocyanates being dealt with in greater detail, since they are the most promising from the standpoint of practical application.

1. Cyclisation of β-Difunctional Compounds

The reactions involving the synthesis of 2-oxazolidinones from β-difunctional compounds, described in the literature, can be represented schematically in a general form as follows:



where X, Y, X′, and Y′ are functional groups, which are listed in the Table. Hydrogen atoms and aromatic, aliphatic, and alicyclic ligands can be used as substituents R^1, R^2, R^3, R^4, and R^5; R^1 forms part of one of the functional groups of the β-difunctional compound (I).

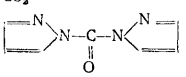
In order to carry out the ring closure reaction, the initial β-difunctional compound (I) is treated with a cyclising agent (II) or (III), which interacts with one of the functional groups of compound (I); this is followed by ring closure with participation of the second functional group. Compound (I) can be cyclised also without adding a cyclising agent, either thermally or under the conditions of acid or base catalysis. The Table presents different versions of the synthesis of 2-oxazolidinones by this method.

The synthesis of 2-oxazolidinone derivatives by the cyclisation of β-hydroxyalkanesulphonic acids (I, X = OH, Y = SO_3H),[40] 1,2-dihalogeno-derivatives (I, X = Y = Hal),[41] β-aminochloroformates (I, X = OCOCl, Y = NH_2),[42] β-hydroxyalkylsemicarbazides [I, X = OH, Y = $N(NH_2)CONH_2$],[43] and nitrenes (I, X = OCO$\ddot{N}$, Y = H) [44] have also been mentioned in the literature.

2. Reactions Involving the Conversion of Various (Other than Epoxides) Heterocyclic Compounds into 2-Oxazolidinones (IV)

Methods of synthesis of 2-oxazolidinones from a series of heterocyclic compounds (mainly three- and five-membered) by their reaction with isocyanates, amines, substituted ureas, carbon dioxide, and other compounds have been described in the literature. In this section we shall consider these reactions with the exception of the conversion of epoxide rings into 2-oxazolidinones.

The synthesis of 2-oxazolidinones (IV) from β-difunctional compounds (I) and cyclising agents (II) or (III).

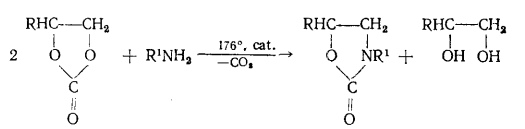
X	Y	Cyclising agent	X′	Y′	Z′	Cyclisation conditions	Refs.
			β-Halogenoamines				
Cl, Br, I	NH_2	Ag_2CO_3	OAg	OAg	—	—	[2]
Cl, Br, I	NH_2	$Na_2CO_3(NaHCO_3)$	ONa	ONa(OH)	—	NaOH	[3]
			β-Halogenoalcohols				
OH	Cl	$COCl_2 + R^1NH_2$	—	—	—	Δ, KOH	[4]
OH	Cl	—	—	—	—	$Na_2NCN + n\text{-}CH_3C_6H_4OCl$	[5]
OH	Cl	$(H_2N)_2CO$	NH_2	NH_2	—	—	[6]
OH	Cl	NCO^-	—	—	—	—	[6]
OH	Br	$R^1NHCOOC_2H_5$	R^1NH	OC_2H_5	—	bases	[7]
OH	Cl	—	—	—	—	isocyanuric acid, NaOH, Δ	[8]
			β-Aminoalcohols				
OH	NH_2, NHR^1	$COCl_2$	Cl	Cl	—	—	[9]
OH	NHR^1	$(C_2H_5O)_2CO$	OC_2H_5	OC_2H_5	—	bases	[10]
OH	NHR^1	ethylene carbonate	—	—	OC_2H_4O	—	[11]
OH	NHR^1	$ClCOOC_2H_5$	Cl	OC_2H_5	—	bases	[12]
OH	NHR^1	$(H_2N)_2CO$	NH_2	NH_2	—	—	[13]
OH	NHR^1	RNCO	—	—	NR	—	[14]
OH	NHR^1	Cl_3COOR	CCl_3	OR	—	$R=CH_3$ C_2H_5	[15]
OH	NHR^1	$ClCO_2CH_3$	Cl	OCH_3	—	CS_2	[16]
OH	NHR^1	CO_2	—	—	O	Δ, P	[17]
OH	NHR^1				—	—	[18]
OH	NHR^1	COS	—	—	S	—	[19]
OH	NHR^1	$CO + S$	—	—	—	—	[20]
OH	NHR^1	—	—	—	—	CCl_4	[21]
OH	NHR^1	—	—	—	—	$BrCN + OH$	[22]
OH	NHR^1	$CO + Se$	—	—	—	$(C_2H_5)_3N$	[23—25]
OH	NHR^1	$CH_3COCH_2COOC_2H_5$	CH_2COCH_3	OC_2H_5	—	bases	[26]
			1,2-Glycols				
OH	OH	$(H_2N)_2CO$	NH_2	NH_2	—	—	[27]
OH	OH	$C_2H_5OCONH_2$	OC_2H_5	NH_2	—	bases	[28]
			Acetylene derivatives				
OH	≡CH	R^1NCO	—	—	NR^1	CH_3ONa	[29]
OH	≡CH	$CO_2 + R^1NH_2$	—	—	O	copper salts	[30]
≡CH	NHR^1	CO_2	—	—	O	—	[31]
			β-Hydroxyisocyanates				
OH	NCO	—	—	—	—	—	[3, 32, 33]
			Urethanes				
Cl, Br, I, NH_2	NR^1COOR	—	—	—	—	Δ or OH	[34]
OH	NHCOOR	—	—	—	—	SO_2Cl, P_2O_5	[35]
			α-Ketols				
OH	=O	R^1NCO	—	—	NR^1	—	[36]
OH	=O	$(NH_4)_2CO_3$	ONH_4	ONH_4	—	KCN	[37]
			α-Aminoketones				
=O	NH_2	CO_2	—	—	O	—	[38]
			β-Aminoethyl diphenylphosphate				
$OPO(PhO)_2$	NH_2	CO_2	—	—	O	—	[39]

(a) The Synthesis of 2-Oxazolidinones from 2-Dioxolans

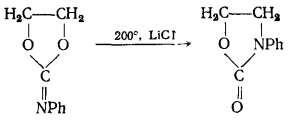
The synthesis of 2-oxazolidinones by the reaction of 2-dioxolans (cyclic carbonates) with isocyanates has been described. Tertiary amines[45], lithium, zinc, and tin chlorides, potassium and sodium carbonates, and sodium hydroxide[46] have been used as catalysts of this reaction. It has been suggested[45] that a molecular complex of the isocyanate and the carbonate is formed as an intermediate, which has been isolated and proved to have a distinct melting point. On heating, this complex decomposed with evolution of carbon dioxide and formation of 2-oxazolidinone. When the reaction of 2-dioxolans with isocyanates was carried out at elevated temperatures, the formation of the complex was not observed.

Substituted 2-oxazolidinones have been obtained by the reaction of cyclic carbonates with formamide[47].

Gulbins and Hamann[48] synthesised 2-oxazolidinones by the reaction of 2-dioxolans with aromatic amines using lithium chloride or alkali (NaOH, KOH) as the catalyst:

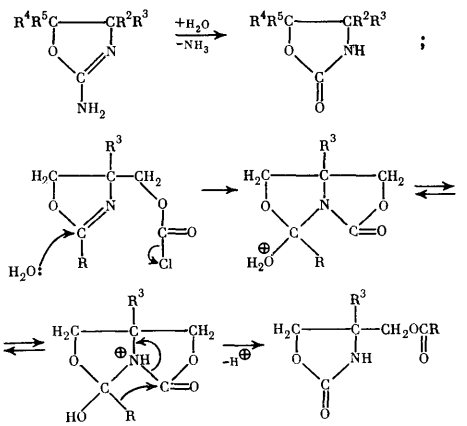


The preparation of oxazolidinones by the reaction of cyclic carbonates with diacylureas[49] and with ammonium carbonate and potassium cyanide[50] and also by the rearrangement of 2-amino-1,3-dioxolans under the influence of lithium chloride[51]:



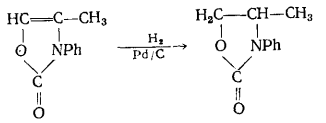
(b) The Synthesis of 2-Oxazolidinones from Oxazolines, Oxazolinones, and Imino-oxazolidinones

2-Oxazolidinones have been obtained by the hydrolysis of 2-amino- and 2-alkyl-2-oxazolines in accordance with the scheme[52,53]

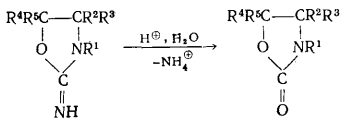


The syntheses of 2-oxazolidinones by the rearrangement of 2-alkoxy-2-oxazolines in inert solvents in the presence of catalytic amounts of alkyl halides have been described in patents[54,55].

The reaction involving the reduction of oxazolinones by hydrogen at atmospheric pressure and room temperature in the presence of a palladium catalyst[56], i.e.



and the hydrolysis of 2-imino-oxazolidones[57], i.e.



belong to methods of synthesis of 2-oxazolidinones without the cleavage of the initial ring.

(c) The Synthesis of 2-Oxazolidinones by the Cleavage of Nitrogen-Containing Heterocycles

The preparation of 4-methyl-2-oxazolidinones by the reaction of propyleneimine with carbon dioxide has been described; polypropyleneimine and polyurethane are formed as side products[58].

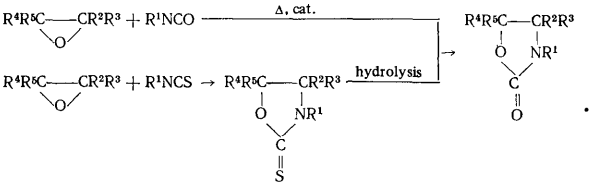
Ikeda and Soga[59] obtained 2-oxazolidinone by the reaction of aziridines having the general formula $\overline{CH_2-CHR^2-NR^1}$ with carbon dioxide; the reaction proceeds in the presence of Lewis acids ($ZnCl_2$, $AlCl_3$) at 60 °C in the course of 50 h.

3. The Reactions of Epoxides with Various Compounds

As mentioned above, one of the most important and promising methods of synthesis of 2-oxazolidinones involves the reactions of epoxides with various compounds (particularly isocyanates), since the initial reactants are in this instance substances produced industrially on a large scale.

(a) The Reactions of Epoxides with Isocyanates and Isothiocyanates

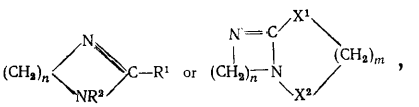
Numerous studies[1,60-77] devoted to the synthesis of 2-oxazolidinones by the reactions of epoxides with organic isocyanates and isothiocyanates have been published. However, there is as yet no unanimous view in the literature concerning either the reaction products or the reaction mechanism. The formation of 2-oxazolidinones can be represented schematically in a general form as follows:



(1)

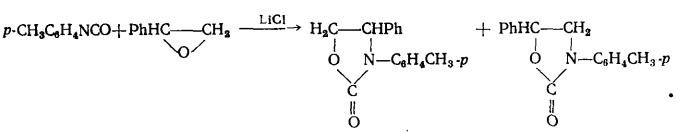
The reaction takes place at elevated temperatures in solvents such as dimethylformamide (DMF), acetonitrile, dioxan[1], and benzene[60] or in the absence of solvents[61], in the presence or absence of catalysts. Secondary[62] and tertiary[63] amines, quaternary ammonium halides[61,64], carboxylate anions[65], zinc, iron[60], and lithium[66] chlorides, the lithium bromide–tributylphosphine oxide complex (or hexamethylphosphoramide),[67] the complexes of aluminium, zinc, and iron halides with ethers, amines, amides, sulphoxides, and phosphines[68], organic derivatives of zinc [R_2Zn and $Zn(OCOR)_2$] and aluminium (AlR_3), with R = alkyl,[69] and Group IIA and IIIA metal alkoxides and phenoxides[70] are used as catalysts. A method of synthesis of oxazolidinones by the reaction of isocyanates with epoxides in the presence of catalysts comprising phosphonium compounds of the type $[R(R^1)(R^2)(R^3)P]^+X^-$, where R^1, R^2 = C_{1-25} alkyl or substituted alkyl, R^3 = alkyl, substituted alkyl, aryl, or substituted aryl, and X = anion of an inorganic or lower aliphatic carboxylic acid [for example, $(n\text{-}C_4H_9)_4PBr$] and with primary and secondary alcohols as cocatalysts has been proposed in a patent[71].

Cyclic amidines having the general formula

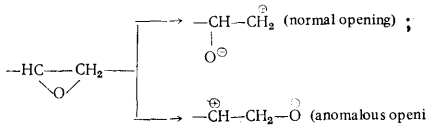


where R^1, R^2 = H, pentyl, or C_{1-8}, X^1, X^2 = alkylene, n = 2–6, and m = 2–11, and their salts have been suggested as catalysts in the synthesis of oxazolidinones[72].

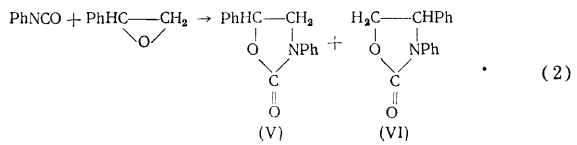
The interaction of isocyanates and epoxides has been investigated[65] in the presence of LiCl as the catalyst. It was found that the reaction results in the formation of a mixture of 3,5- and 3,4-substituted 2-oxazolidinones in proportions of 4 : 1 (by weight):



The formation of two isomers in this reaction is explained by the fact that various ways of opening the epoxide ring are possible:



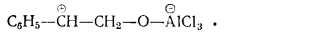
The formation of a mixture of isomers in the reaction of phenyl isocyanate with 2-phenyloxiran (styrene oxide) has been mentioned[73]:



(2)

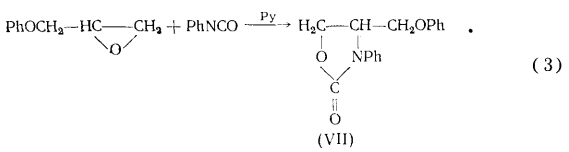
(V) (VI)

It has been established[74] that the reaction of 2-phenyloxiran with phenyl isocyanate in the presence of $AlCl_3$ as the catalyst leads to the formation of a mixture of 3,5-diphenyl-2-oxazolidinone (V) and 3,4-diphenyl-2-oxazolidinone (VI) in proportions of 2:1 [see reaction (2)]. The reaction apparently proceeds preferentially via the formation of the intermediate complex



When $Ca(OC_2H_5)_2$ was used as the catalyst, the formation of only the 3,5-isomer was noted. The authors[74] separated the isomers by fractional crystallisation. They also described[74] the synthesis of various bisoxazolidinones.

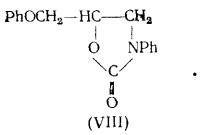
The reaction of glycidyl phenyl ether with phenyl isocyanate in the presence of pyridine (Py) has been investigated[63]:



(3)

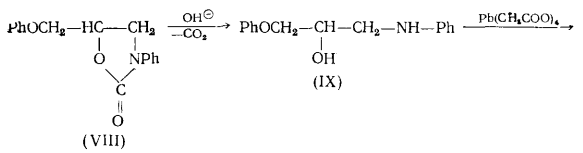
(VII)

The authors[63] concluded that the reaction results in the formation of 4-phenoxymethyl-3-phenyl-2-oxazolidinone (VII), while other workers[60,75] noted that, when the process is carried out under anomalous conditions, the product is 5-phenoxymethyl-3-phenyl-2-oxazolidinone:

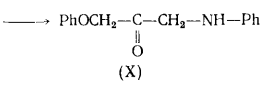


(VIII)

Braun and Weinert[10] also described the synthesis of 5-phenoxymethyl-3-phenyl-2-oxazolidinone (VIII) by reaction (3) in a high yield. Pyridine as well as metal alkoxides and chlorides and $(CH_3)_4Ni$ were used as the catalysts. In order to demonstrate the structure of the resulting 2-oxazolidinone, the authors[10] hydrolysed it. Evidently the hydrolysis of 5-phenoxymethyl-3-phenyl-2-oxazolidinone (VIII) should result in the formation of the secondary alcohol 1-phenoxy-3-phenylamino-2-propanol (IX), which yields the corresponding ketone (X) on oxidation with lead tetra-acetate:

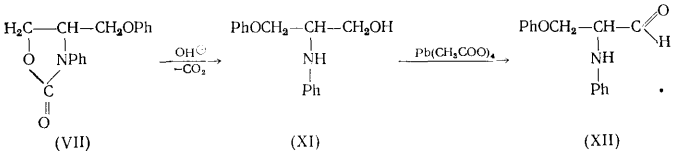


(VIII) (IX)



(X)

The hydrolysis of 4-phenoxymethyl-3-phenyl-2-oxazolidinone results in the formation of the primary alcohol 3-phenoxy-2-phenylamino-1-propanol (XI), which can be oxidised to the aldehyde (XII) by lead tetra-acetate:

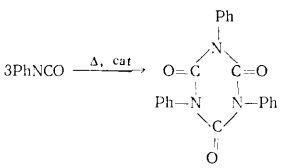


(VII) (XI) (XII)

The infrared spectra of the products of hydrolysis and subsequent oxidation confirmed that the reaction of glycidyl phenyl ether with phenyl isocyanate in the presence of all the catalysts tested (see above) leads to the formation of 5-phenoxymethyl-3-phenyl-2-oxazolidinone (VIII).

Thus inspection of the literature data permits the conclusion that the views of different workers concerning the isomeric products of the reaction of epoxides with isocyanates are extremely contradictory. As a rule the mode of opening of the epoxide ring and hence the formation of a particular isomeric 2-oxazolidinone depend on the catalyst employed and on the nature of the substituent in the epoxide.

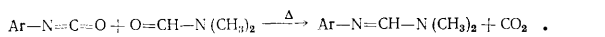
Sandler et al.[61] investigated the relative contributions of the two competing reactions involving the formation of the oxazolidinone [see Scheme (3)] and the cyclotrimerisation of phenyl isocyanate:



(4)

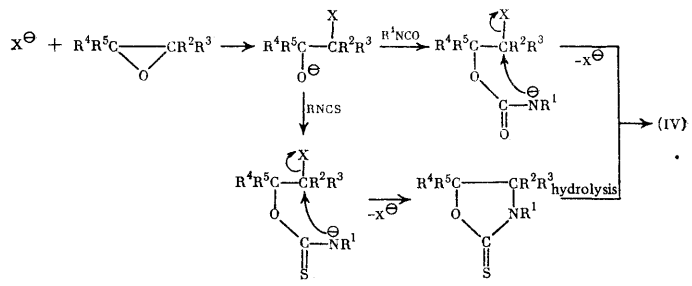
The reaction was carried out in the presence of $(CH_3)_4Ni$ as the catalyst in DMF. The authors[51] showed that oxazolidinone formation reactions take place preferentially in accordance with Eqn.(3) at 140–160 °C, while at 56 °C triphenyl isocyanurate is formed in accordance with reaction (4).

The reaction of epoxides with isocyanates has been carried out in a number of investigations[51,66] in DMF. However, according to Weiner[76], aryl isocyanates react with DMF at an elevated temperature to form formamidines:

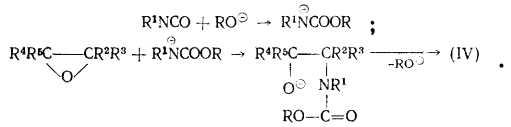


However, Sandler[61] did not point out the possibility of this side reaction. In order to eliminate it, Herweh et al.[66] added the isocyanate to a solution, heated under a reflux condenser, of the epoxide and the catalyst [$(CH_3)_4Ni$ or LiCl] in DMF. However, in the present author's view, this cannot prevent the reaction of the isocyanate with DMF.

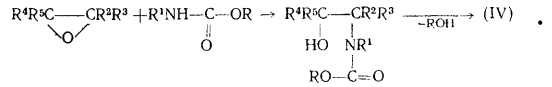
The nature of the catalyst influences the mechanism of the reaction of epoxides with isocyanates. Thus it has been suggested[1] that in the presence of metal halides the epoxide adds directly to the isocyanate (or isothiocyanate) with formation of an activated complex via the reaction



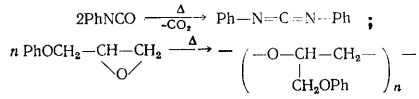
It has been established[77] that, in the presence of alkaline earth metal alkoxides, there is no reaction between the epoxide and the alkoxide and also between the epoxide and the isocyanate. It has therefore been suggested that the oxazolidinone is formed via a stage involving the interaction of the isocyanate with the alkoxide anion followed by the condensation of the urethane anion and the liberation of the alkoxide anion in accordance with the reaction



It has been shown[75] that the formation of oxazolidinones in the presence of quaternary ammonium salts takes place only in the presence of small amounts of an alcohol. Hence, it is believed[75] that oxazolidinones are formed via the condensation of the urethane with the epoxide with liberation of an alcohol and the closure of the oxazolidinone ring. According to the authors[75], the quaternary ammonium salts play the role of compounds which enhance the nucleophilic properties of the urethane nitrogen. The reaction proceeds as follows:



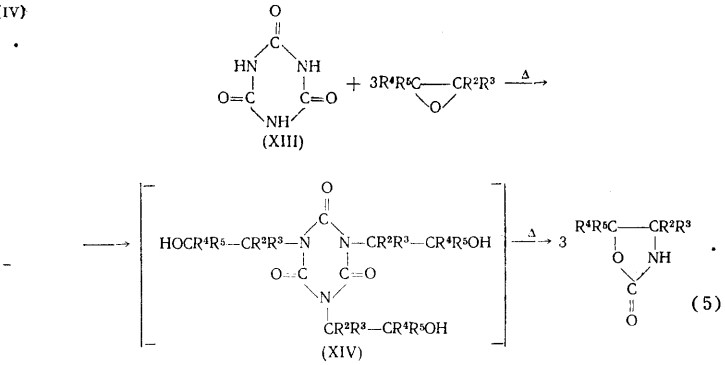
One should note that the reaction of epoxides with isocyanates in the absence of catalysts and solvents has been mentioned in the literature. Thus 5-phenoxymethyl-3-phenyl-2-oxazolidinone has been obtained[61] by heating a mixture of equivalent amounts of phenyl isocyanate and glycidyl phenyl ether at 210 °C for 15 h. Evidently in the absence of a catalyst of the oxazolidinone formation reaction, side reactions occur in the given system, namely the cyclotrimerisation of phenyl isocyanate [see reaction (4)] and also the conversion of phenyl isocyanate into a carbodiimide and linear polymerisation of glycidyl phenyl ether:



(b) The Reaction of Epoxides with Isocyanurates

Since one of the main side processes in the reaction of epoxides with isocyanates involves the formation of isocyanurates, studies on the interaction of the latter with epoxides are of undoubted interest. Thus it has been found in a number of investigations[78–80] that, on treatment with epoxides, the stable isocyanurate ring decomposes with formation of a 2-oxazolidinone.

The reaction of epoxyethane and other epoxides with isocyanuric acid (XIII) has been investigated[78–79]. It has been shown[79] that the reaction proceeds as follows:

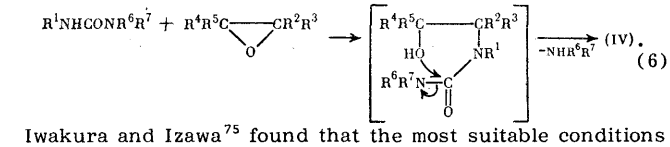


It was carried out in DMF or dimethylacetamide at 100 °C and atmospheric pressure. Pyrolysis of the tris(hydroxyalkyl) isocyanurate (XIV) *in vacuo* at 200 °C or on heating in DMF (150–155 °C) leads to the corresponding 2-oxazolidinone [reaction (5)].

Korshak et al.[80] investigated the reaction of glycidyl phenyl ether and triphenyl isocyanurate in molar proportions of 3:1 (at 230 °C for 10 h) and showed that the only product is 5-phenoxymethyl-3-phenyl-2-oxazolidinone.

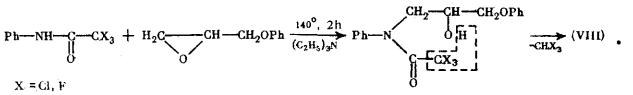
(c) The Reactions of Epoxides with Ureas, Amides, and Urethanes

Apart from their reactions with isocyanates, isothiocyanates, and isocyanurates, epoxides are capable of cleaving the urea, amide, and urethane linkages with formation of 2-oxazolidinones. Thus the reaction of epoxides with urea derivatives to give 2-oxazolidinones has been reported[75–81]:

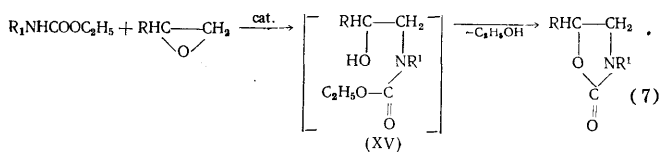


Iwakura and Izawa[75] found that the most suitable conditions for the reactions of di- and tri-substituted ureas with epoxycompounds [see reaction (6)] are a temperature of 90 °C, the absence of a solvent, and the presence of the $(C_2H_5)_3N$ catalyst. A two- or threefold excess of the epoxide is also necessary, since the primary or secondary amines formed rapidly react with epoxides. It is noteworthy that *N*-aryl-*N*,*N'*-disubstituted ureas give rise to oxazolidinones, while *N*-alkyl-*N*,*N'*-disubstituted ureas do not form such compounds.

The same investigators[82,83] studied the interaction of epoxides with acid amides. In particular they studied the reaction of acetanilide and its derivatives with glycidyl phenyl ether and showed that 2-oxazolidinones are formed only from trifluoro- and trichloro-acetanilides, which indicates the necessity for the presence of strong electron-accepting substituents in the acetanilide molecules for the cyclisation to occur:



Urethanes react with epoxides to form oxazolidinones in the presence of nucleophilic catalysts such as KOH,[6] tertiary amines, and quaternary ammonium salts[75]:

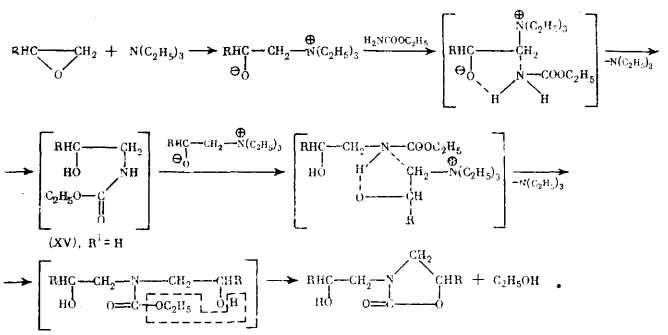


(7)

It has been observed[97] that without a catalyst reaction (7) between a urethane and an epoxide does not take place. When the mixture of the initial components is heated from 0° to 200 °C, only the homopolymerisation of the epoxide is observed. In the presence of $(C_2H_5)_3N$ at 25 °C the reaction takes place quantitatively in 2 h. At 140 °C the reaction terminates after 2–3 min (side reactions were not observed).

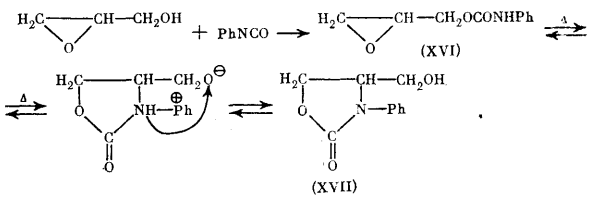
The authors[75] showed that in the presence of solvents (ethanol, benzene, toluene, chloroform and DMF) the reaction occurs at a higher rate than in bulk. *N*-Arylurethanes and *N,N'*-difunctional arylurethanes form oxalidinones on interaction with epoxides, while *N*-alkylurethanes do not undergo the oxazolidinone formation reaction with epoxides (like *N*-alkylureas—see above). According to the mechanism proposed[75], the catalyst is involved in the opening of the epoxide ring and reacts with the epoxide to form an intermediate complex, which then interacts with the urethane; this entails the formation of *N*-(β-hydroxyethyl)urethane (XV), which cyclises with elimination of an alcohol and the formation of a 2-oxazolidinone (IV).

The kinetics of the reaction of an epoxide with *N*-unsubstituted ethylurethane in the presence of $(C_2H_5)_3N$ as the catalyst have been investigated[84]. The mechanism proposed[84] is similar to that described above[75], but the authors[84] believe that the *N*-(β-hydroxyethyl)urethane (XV, R' = H) formed reacts with yet another molecule of the adduct of the epoxide and triethylamine which results in the formation of a hydroxy-2-oxazolidinone:

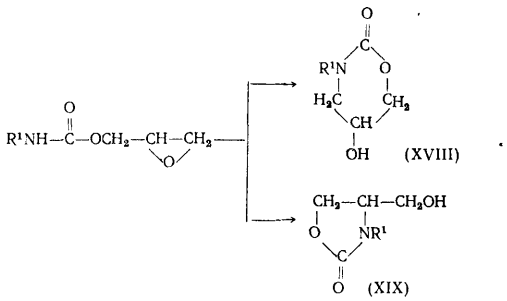


(d) Intramolecular Cyclisation of Glycidyl Esters of *N*-substituted Carbamic Acids

The glycidyl esters of *N*-substituted carbamic acids undergo intramolecular cyclisation on heating with formation of 2-oxazolidinone derivatives. Thus the reaction of phenyl isocyanates with glycidol results in the formation of glycidyl *N*-phenylcarbamate (XVI), which is converted on heating into 4-hydroxymethyl-3-phenyl-2-oxazolidinone (XVII):[85]



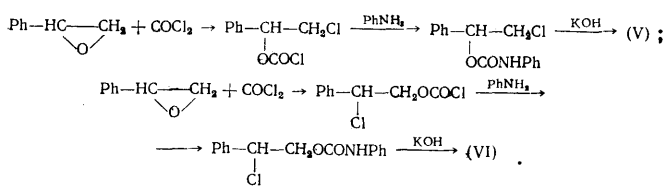
^{1}H NMR spectra[74,85] confirm the location of the hydroxymethyl group in compound (XVII) at the carbon atom adjoining the nitrogen atom of the oxazolidinone ring. However, hitherto there has been no definite view concerning the structure of the cyclisation products. Thus the formation of the six-membered 2-oxazinone ring (XVIII) has been postulated[86], while according to other data[85] the five-membered 2-oxazolidinone ring (XIX) is produced:



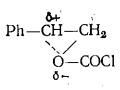
Sorokin and co-workers investigated in a series of studies in recent years[87–92] the intramolecular cyclisation of glycidylurethanes and demonstrated the formation of a five-membered structure (XIX). They showed[87–92] that in proton-donating solvents the reaction takes place at lower temperatures (100 to 140 °C) than in neutral solvents (170–200 °C). Tertiary amines are active cyclisation catalysts. The equality of the molecular weights of the resulting product and of the initial glycidylurethane, the absence of epoxy-groups, and the appearance of hydroxy-groups in an amount corresponding to the cyclisation product indicates the absence of side reactions and the quantitative interaction of the epoxide and urethane groups to form the cyclic compound (XVIII) or (XIX). In order to demonstrate the structure, a study was made[92] of the ^{1}H NMR spectra of the reaction product and it was shown that the signals of the protons in the epoxide and urethane groups are absent and that the signal due to the OH group with δ = 5.2 p.p.m. appears. Its triplet form shows that the hydroxy-group is primary and not secondary and that anomalous opening of the epoxide ring therefore takes place (see above) and the cyclisation product is the five-membered 2-oxazolidinone ring (XIX).

(e) The Interaction of Epoxides with Other Compounds

Irwin and Wheeler[73] investigated the successive interaction of 2-phenyloxiran with phosgene, aniline, and KOH. Two reaction pathways are possible; the products are 3,5-diphenyl-2-oxazolidinone and 3,4-diphenyl-2-oxazolidinone respectively:

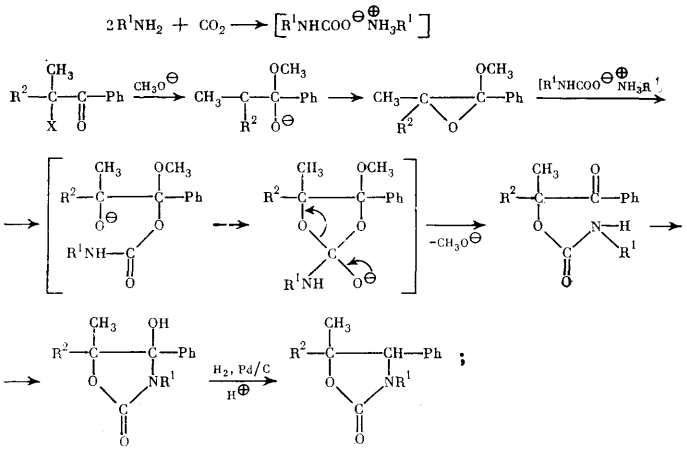


The authors[73] concluded that the oxazolidinone is formed via an intermediate complex:



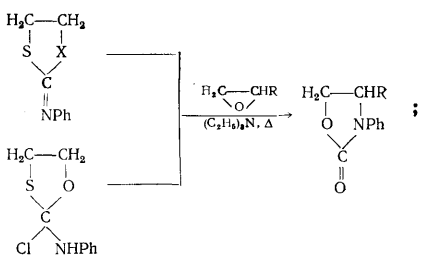
The ^1H NMR spectra confirmed that 3,5-diphenyl-2-oxazolidinone is the main reaction product.

The reactions of 2-methoxyoxirans and of α-halogeno-derivatives of acylphenones with carbon dioxide in aliphatic amines in methanol have been studied[36] and the following reaction mechanism has been proposed:



X = Br, Cl; R^1 = alkyl ; R^2 = CH_3, H .

A series of syntheses of 2-oxazolidinones from epoxides and five-membered heterocycles containing oxygen and sulphur in various combinations have been achieved[93]:



X=O, S; R=H, CH_3, CH_2Cl .

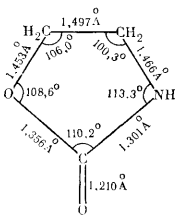
Substituted oxazolidinones have been synthesised[94] by the reaction of epoxides with compounds of the type p-RC_6H_4N = CCl_2 in the presence of $ZnCl_2$ or $SnCl_2$ as catalysts.

III. THE PROPERTIES OF 2-OXAZOLIDINONES

1. The Physical Properties of 2-Oxazolidinones

2-Oxazolidinones are stable heterocyclic compounds whose melting points are in most cases in the range 100–200 °C;[95,96] they are soluble in water and form neutral solutions.

The polymorphism and the mechanochemistry of 5-phenoxymethyl-2-oxazolidinone have been investigated[97] and it has been observed that the oxazolidinone exhibits dimorphism, existing in two independent forms or their mixture.



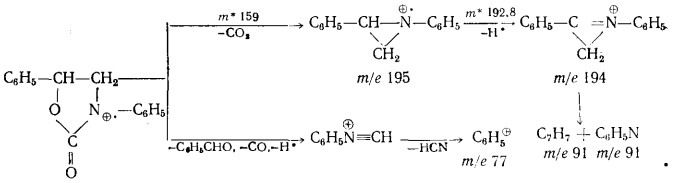
The crystal structure of 2-oxazolidinone

The crystal structure of 2-oxazolidinone has been described[98]. It has a monoclinic three-dimensional crystal lattice with the unit cell dimensions a = 7.313 Å, b = 5.672 Å, c = 9.970 Å, and β = 110.78° (measured at 24 °C). The bond lengths and the angles in the ring are shown in the Figure above.

The infrared spectra of 2-oxazolidinones have been investigated in a number of studies[99–102]. The carbonyl absorption of 2-oxazolidinones is observed in the range 1740–1810 cm^{-1} (usually at 1740–1760 cm^{-1}). 2-Oxazolidinones with an unsubstituted hydrogen atom at the nitrogen atom show an absorption by the N–H group in the range 3200–3500 cm^{-1}.[100]

Several detailed studies on the NMR of 2-oxazolidinones have been made[66,103].

Disubstituted mono- and bis-2-oxazolidinones have been investigated mass-spectrometrically[73,104] and it has been shown that the decomposition of 5-alkyl-, 4-alkyl-, 5-aryl-, and 4-aryl-3-phenyl-2-oxazolidinones takes place as follows: (1) with evolution of CO_2 on β-decomposition; (2) with evolution of CO and the formation of the corresponding aldehyde on α-decomposition. The intense *m/e* 194 peak in the mass spectrum of 5-aryl(or alkyl)-3-phenyl-2-oxazolidinone, characterising the decomposition with evolution of Cl_2, is almost completely absent from the spectrum of 4-aryl(or alkyl)-3-phenyl-2-oxazolidinone, a characteristic feature of which is the cleavage reaction with evolution of CO and the formation of the corresponding aldehyde. For example, the decomposition of 3,5-diphenyl-2-oxazolidinone under the influence of β-irradiation proceeds in accordance with the following scheme:



The dipole moments of 2-oxazolidinones have been published[105] and it has been concluded that the dipolar structure makes a contribution of approximately 21% to the experimental dipole moment (5.04 ± 0.005 D).

Lebedev and Yakshimets[106] investigated the magnetic susceptibility of 2-oxazolidinone and established that the substance is diamagnetic.

Volumetric titration with silver nitrate, spectrophotometry[107,108], calorimetry[107,109], reaction with indole[110], chromatography[107], and methods based on the formation of a phenylhydrazone[111] have been suggested as methods whereby 2-oxazolidinones can be characterised.

2. The Chemical Properties of 2-Oxazolidinones

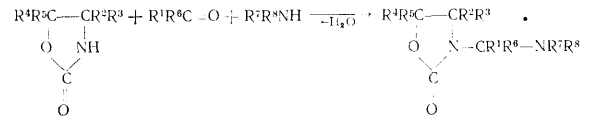
A number of studies have been made on the chemical properties of 2-oxazolidinones. The reactions of 2-oxazolidinones can be divided into the following groups: (a) reactions involving substitution at the ring atoms; (b) ring opening reactions; (c) other reactions involving the ring; (d) reactions of the substituents.

Only the first three groups of reactions, which characterise directly the chemical properties of the oxazolidinone ring, are discussed below.

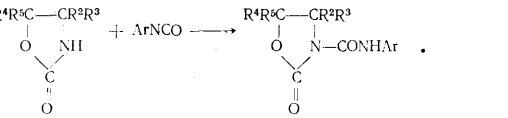
(a) Reactions involving Substitution at the Atoms of the 2-Oxazolidinone Ring

The hydrogen atom linked to the nitrogen atom of the oxazolidinone ring can be substituted by various groups using the following procedures: by reaction with carbonyl compounds, aryl isocyanates, and phosphorus compounds, by alkylation, acylation, carbamoylation, nitration, and amination, by reaction with nitrous acid, etc.

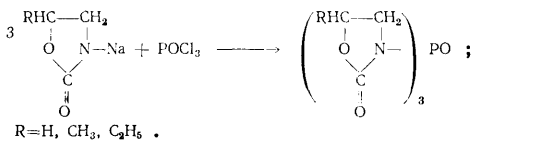
2-Oxazolidinones react with carbonyl compounds in the presence of secondary amines[112]. In the absence of an amine, a second oxazolidinone molecule behaves as an amine (R″R‴NH = $OCOCH_2CH_2NH$). The reaction proceeds as follows:



2-Oxazolidinone-3-carbanilides can be obtained by the reaction of substituted 2-oxazolidinones with aryl isocyanates in the presence of pyridine or triethylamine[113]:



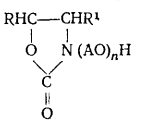
Sodio-derivatives of 2-oxazolidinones react with phosphoryl chloride in DMF in a stream of nitrogen[114]:



R=H, CH_3, C_2H_5.

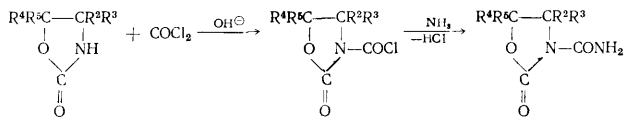
Alkylation is usually carried out in the presence of K_2CO_3, NaOH, CH_3ONa, NaH, and other bases[115]. Organic halides[115,116], olefins[117], and ethers together with benzoic acid and mercury acetate[117] have been proposed as alkylating agents.

The synthesis of a compound having the general formula



(R, R^1 = H, alkyl, or phenyl; AO = C_2–C_5 alkylene oxide group; n = 1–25) by treating 1 mole of 2-oxazolidinone with n moles of an alkylene oxide in the presence of 0.1–10% of a strong basic catalyst (alkali metal hydroxide, sodium salt of 2-oxazolidinone, or a quaternary base) at 90–180 °C and a pressure of 2–10 atm for 2–4 h has been described in a patent[118].

The nitrogen atom has been acylated in alkaline and acid media[119] and carbamoylation has been carried out by treating 2-oxazolidinone with phosgene in an alkaline medium followed by reaction with ammonia[120]:

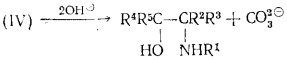


The substitution of the hydrogen atom at the nitrogen atom of the oxazolidinone ring by the NO group has been achieved by the reaction of 2-oxazolidinone with HNO_2 or NOCl.[121]

The nitration of 2-oxazolidinone has been performed by treatment with a mixture of nitric and sulphuric acids or nitric acid and acetic anhydride[122]. The nitro-group can be reduced to the amino-group electrolytically, by hydrogenation in the presence of platinum oxide in an acid medium, or by reaction with zinc and hydrochloric acid[121].

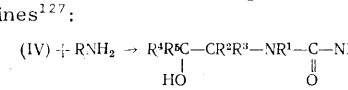
(b) Reactions involving the Opening of the 2-Oxazolidinone Ring

Alkaline hydrolysis of 2-oxazolidinones leads to β-aminoalcohols. It takes place in aqueous[57,116,123] and alcoholic[124] media and in dioxan[125]. It is usually employed to demonstrate the structure and stereochemistry of oxazolidinones[27,37,124,125]. The catalytic conversion of 2-oxazolidinone into the corresponding aminoalcohols by heating the initial compound at 105–200 °C in the presence of bases such as NaOH, KOH, Na_2CO_3, K_2CO_3, and $NaHCO_3$ has been achieved[126]. The reaction takes place in accordance with the following scheme:

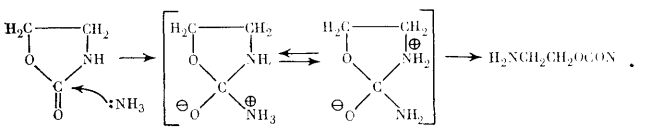


β-Aminoalcohols are also formed on reduction of 2-oxazolidinones with lithium tetrahydroaluminate[27].

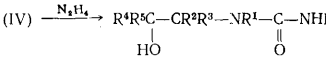
N,*N*′-Disubstituted ureas are the main products of the reaction of 2-oxazolidinones with equimolar amounts of primary aliphatic amines[127]:



2-Oxazolidinone reacts with aqueous ammonia to form β-aminoethyl carbamate[128]:

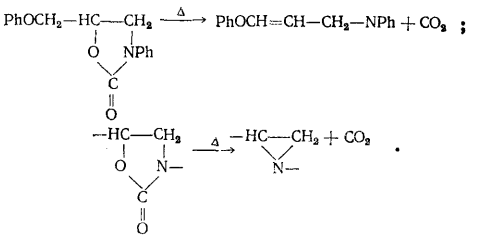


The reaction of 2-oxazolidinones with hydrazine leads to semicarbazides[129]:



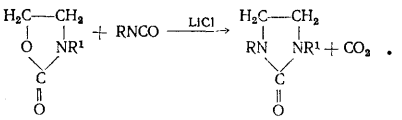
Acid hydrolysis (with concentrated or diluted hydrochloric acid) leads to the formation of the hydrochlorides of β-aminoalcohols[130], while the reaction of 2-oxazolidinone with anhydrous hydrogen chloride results in the formation of β-chloroamine hydrochloride[131].

The thermal stability, the kinetics of the initial stage of the thermal decomposition, and the main decomposition products of 2-oxazolidinones have been investigated[132–134]. It has been shown[133] that heating of 2-oxazolidinones in the absence of air and water is accompanied by autocatalytic decomposition with evolution of CO_2 as the main gaseous reaction product. It was noted that 2-oxazolidinones with alicyclic substituents at the ring nitrogen atom have a higher thermal stability than 2-oxazolidinones with aromatic substituents. Comparison[134] of the thermal stabilities of isocyanurates, oxazolidinones, and carbamates showed that compounds of these classes can be arranged in the following sequence in terms of their thermal stabilities: carbamates < oxazolidinones < isocyanurates. The thermal decomposition of 5-phenoxymethyl-3-phenyl-2-oxazolidinone results in the formation of PhOH, $PhNH_2$, H_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_3H_6 + C_3H_8, and a C_4 fraction. The formation of the possible intermediate thermolysis products is illustrated schematically below:

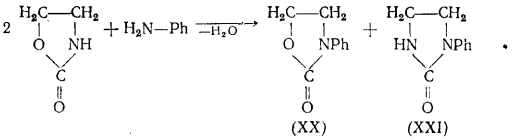


(c) Other Reactions involving the 2-Oxazolidinone Ring

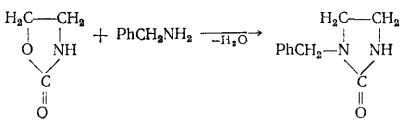
The reaction of *N*-substituted 2-oxazolidinones with organic isocyanates in the presence of lithium chloride leads to *N,N'*-disubstituted 2-imidazolidinones[135]:



It has been noted[136] that the reaction of 2-oxazolidinone with aniline results in the formation of water, 3-phenyl-2-oxazolidinone (XX), and 1-phenyl-2-imidazolidinone (XXI):



The synthesis of 1-benzyl-2-imidazolidinone from 2-oxazolidinone and benzylamine has been described[137]:



IV. THE SYNTHESIS, PROPERTIES, AND APPLICATIONS OF POLYMERS CONTAINING 2-OXAZOLIDINONE RINGS

One of the most important practical applications of 2-oxazolidinones involves the synthesis of polymers containing 2-oxazolidinone rings; recently these polymers have found applications in the preparation of thermostable and heat-resistant foams, coatings, adhesives, fibres, and electrically insulating materials with effective physicomechanical properties.

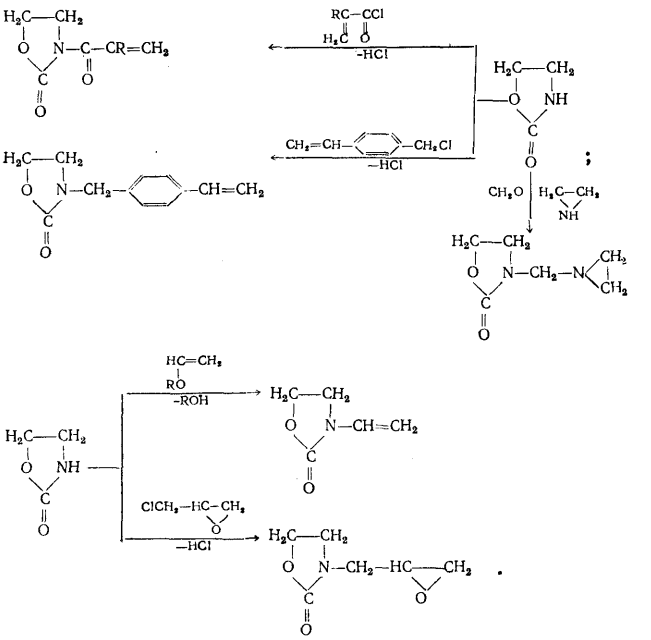
There are virtually no reviews in the Soviet and foreign literature on polymers with oxazolidinone ring. In this section of the present review we shall therefore examine the available information about the synthesis, reaction mechanisms, properties, and applications of polymers in this practically important class.

Numerous methods of synthesis of polymers whose structure incorporates 2-oxazolidinone rings have been described. It is possible to distinguish two fundamentally different types of synthesis of polyoxazolidinones: the first involves the synthesis of the polymers from monomers containing complete 2-oxazolidinone rings in their structure, while in the second the 2-oxazolidinone rings are formed in the course of the synthesis of the polymer. In the former case the products are polymers whose 2-oxazolidinone rings are in a side chain while in the latter case they are in the main chain. They will be examined below in the same order.

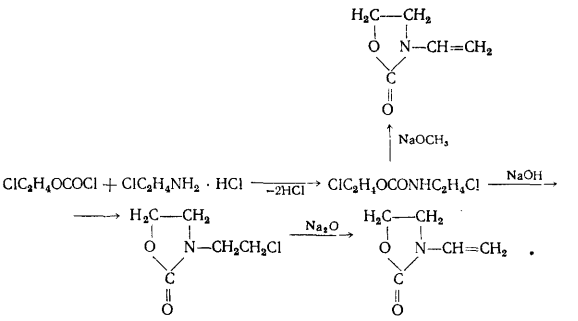
1. Polymers Containing 2-Oxazolidinone Rings in a Side Chain

Polyoxazolidinones based on monomers incorporating complete 2-oxazolidinone rings can be obtained in several ways and contain these rings in a side chain and at the ends of the macromolecules.

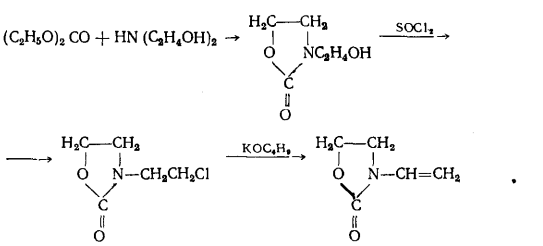
The initial monomers for the synthesis of polyoxazolidinones with side or terminal 2-oxazolidinone rings are obtained by substituting the hydrogen at the nitrogen atom of the oxazolidinone ring by groups capable of polymerisation. A series of syntheses of such monomers are shown schematically below:



The following method of synthesis of *N*-vinyl-2-oxazolidinone has been proposed[138]:

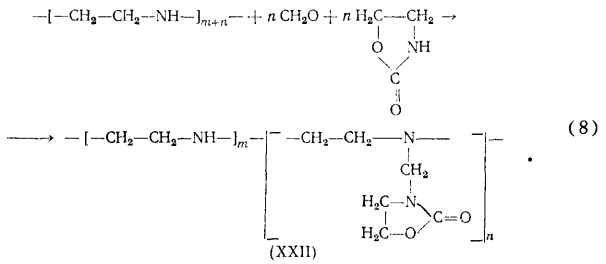


Drechsel[139] obtained *N*-vinyl-2-oxazolidinone by the following procedure:



N-Vinyl-2-oxazolidinones[33,140-142], *N*-isopropenyl-2-oxazolidinones[143], *N*-allyl-2-oxazolidinones[144], 5-methylene-2-oxazolidinones[31], and other 2-oxazolidinones containing unsaturated bonds enter into radical homopolymerisation and copolymerisation reactions with various vinyl and other monomers, such as *N*-vinyl-2-pyrrolidinone[145], *N*,*N*',*N*''-triphenyl-*B*,*B*',*B*''-trivinylborazole[146], maleic anhydride[147], isocyanates[148], acrylonitrile, ethyl acrylate, styrene, methyl methacrylate, vinyl acetate, vinylidene chloride, acrylamide, vinyl chloride, decyl methacrylate[141,142,149,150], monovinyl ethers of glycols having the general formula $HO(C_nH_{2n}O)_x \cdot CH=CH_2$, where $n = 2-4$ and $x = 1-3$,[151] and phthalic anhydride[152]. α,α-Azobisisobutyronitrile is usually employed as the polymerisation catalyst. The polymers and copolymers based on monomeric unsaturated 2-oxazolidinones dissolve in *m*-cresol and acetic, formic and dilute hydrochloric acids, but are insoluble in solvents such as ethanol, acetone, and dioxan. They have fairly high softening temperatures (up to 300° and above) and effective physicomechanical properties, which makes it possible to employ them in various branches of engineering (see below).

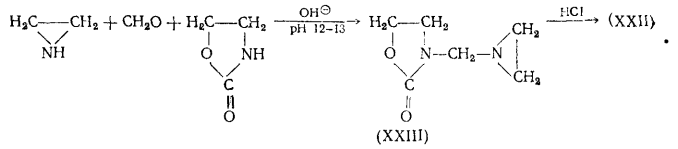
A series of polyethyleneimines containing 2-oxazolidinone rings in the side chains have been synthesised[112] in several ways. The reaction of 2-oxazolidinone with formaldehyde and polyethyleneimine at room temperature in solvents such as water, DMF, and a dioxan–water mixture proceeds in accordance with the following scheme:



(8)

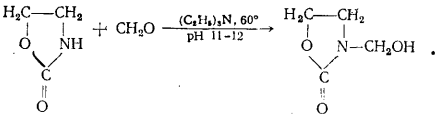
(XXII)

The polymer (XXII) has also been synthesised[112] by the polymerisation of *N*-(1-azirinomethyl)-2-oxazolidinone (XXIII), which had been obtained in its turn from aziridine, formaldehyde, and 2-oxazolidinone:



(XXIII)

In addition, a polymer of type (XXII) had been obtained[112] by the reaction of polyethyleneimine with *N*-hydroxymethyl-2-oxazolidinone in an aqueous medium at room temperature. *N*-Hydroxymethyl-2-oxazolidinone was synthesised from 2-oxazolidinone and formaldehyde by the reaction



The polyethyleneimines described are capable of adsorbing polar substances from aqueous solutions. In an alkaline medium these polymers form complexes with phenol and with toluene-*p*-sulphonic acid; the infrared spectra of the complexes indicate the presence of a hydrogen bond between the CO group of the 2-oxazolidinone ring of the polymer and the hydrogen atom of the phenol or toluene-*p*-sulphonic acid[112].

2. Polymers Containing 2-Oxazolidinone Rings in the Main Chain

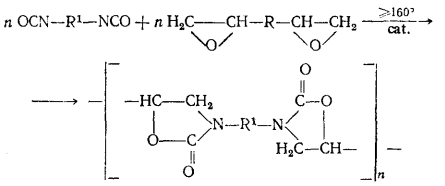
There are literature data on the synthesis and properties of linear, branched, and cross-linked poly-2-oxazolidinones and also polymers containing in their structure other rings and functional groups in addition to the 2-oxazolidinone groups. Studies on the synthesis and properties of linear poly-2-oxazolidinones with 2-oxazolidinone rings in the main chain, hydroxy-2-oxazolidinones, and cross-linked oxazolidinone-isocyanurate polymers are examined below.

(a) Linear Poly-2-oxazolidinones

As mentioned above, one of the most important methods of synthesis of mono- and poly-2-oxazolidinones involves the reaction of epoxides with isocyanates, since these starting materials are readily available industrial products.

Gromakov et al.[153] investigated the reaction of epoxy-resins with di-isocyanates by differential thermal analysis (DTA). The formation of poly-2-oxazolidinones has been observed in the absence of catalysts at temperatures in the range 160 to 250 °C. The same workers[154] investigated by infrared spectroscopy and DTA the reactivities of various epoxy-resins and di-isocyanates. The reactivities of the epoxy-resins increased in the sequence diglycidyl ether of bisphenol A < triglycidyl isocyanurate < diglycidylaniline. The reactivities of the di-isocyanates increase in the sequence 3,3'-dimethyl-4,4'-diphenylmethylene di-isocyanate < 4,4'-diphenylmethylene di-isocyanate < 2,4(2,6)-tolylene di-isocyanate.

High-molecular-weight linear poly-2-oxazolidinones have been synthesised[77] by the slow addition of a di-isocyanate to a solution of a diepoxide and a catalyst (lithium n-butoxide in butanol) in *o*-dichlorobenzene in accordance with the following reaction:



Effective catalysts for the synthesis of elastomeric poly-2-oxazolidinones have been sought in one of the latest studies on the synthesis of linear poly-2-oxazolidinones[155]. The initial di-isocyanate used was polyoxytetramethylene glycol with terminal isocyanate groups and the diepoxide was the diglycidyl ether of bisphenol A. The polymerisation was carried out in bulk. Insoluble catalysts (LiF, $MgCl_2$) proved to be relatively ineffective; the most effective catalysts were the complexes of LiBr, LiCl, LiI, $MgCl_2$ with hexamethylphosphoramide. With increase of temperature from 80° to 150 °C, the yield of the polymer increased by 20%, the reaction occurring over a period of 1 h at 150 °C. The optimum ratio of the initial epoxy-groups and NCO groups is 45 : 55. Hexamethylphosphoramide is a chelating agent, forming coordinate bonds with metal chlorides. In this connection the influence of the coordination number *m* on the polymerisation was discovered and it was shown that $m = 2$ to 4 is preferred. The authors investigated the physicomechanical properties (Young's modulus, tensile strength, relative elongation, tearing energy, the relaxation of stress, and creep) of elastomers containing oxazolidinone and urethane linkages in the main chain. From their results, it was concluded that, together with the high thermally insulating properties of polyester-urethanes and polyoxazolidinones, the polyoxazolidinone has a higher yield point (T_{yield} is 235 to

245 °C for the polyoxazolidinone and 200–220 °C for polyester-urethane) and retains its strength much more effectively after ageing at 170 °C. However, the polyoxazolidinone has a lower strength at a high temperature, while the tearing energy, the relaxation of stress, and creep are virtually at the same level as in polyester-urethane.

Chelate complexes, namely the Mg, Li, Al, Ba, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Hg, Pb, Sn, Be, Mo, and Zr complexes of β-diketones, dimethylglyoxime, salicylaldehyde, α-nitroso-β-naphthol, benzoylacetone, anthranilic acid, etc. have also been proposed in a patent[156] as catalysts of the reaction of polyisocyanates with polyepoxides leading to the formation of oxazolidinones [polyoxazolidinones?]. Complexes of Lewis acids (Al, Zn, and Fe halides) with Lewis bases such as thioesters, amines, (*N*-alkyl)lactams, amides, etc. have been put forward[157–159] as catalysts for the synthesis of polyoxazolidinones.

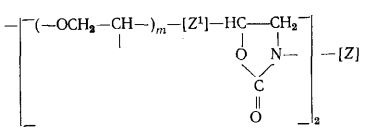
Quaternary ammonium salts of the type $(CH_3)_4NI$, $(C_2H_5)_4NI$, $(CH_3)_4NBr$, and $(C_2H_5)_4NBr$ are very widely used as catalysts of the oxazolidinone formation reaction[160–162].

Linear poly-2-oxazolidinones have been synthesised in DMF in the presence of $(CH_3)_4NI$ at 140–160 °C.[61,64,163]. The possibility of the occurrence of a side reaction of DMF with isocyanates, described by Weiner[76], was not discussed in the above investigations, although it undoubtedly occurs in the given instance.

Herweh and Whitmore[164] synthesised poly-2-oxazolidinones by the 1,3-cycloaddition of diglycidyl ethers and di-isocyanates in the presence of a catalyst (lithium chloride), also in DMF. The reaction was carried out with refluxing in DMF for 12 h. It was found that at 150 °C the side reaction of isocyanates with DMF [76] takes place together with the formation of oxazolidinones. It was noted[164] that the poly-2-oxazolidinones obtained from aromatic di-isocyanates have a lower degree of crystallinity than the polymers obtained from aliphatic di-isocyanates. The authors[164] believe that the amorphous structure of the poly-2-oxazolidinones is due to the irregular structure of the polymer chain and the presence in the latter of isomeric 2-oxazolidinone rings.

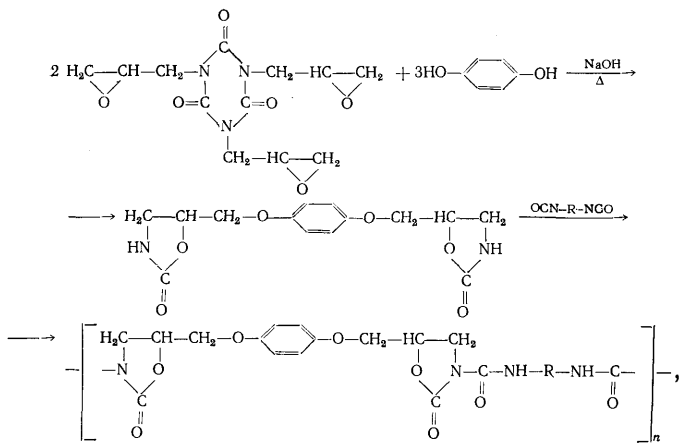
ε-Caprolactam[165], organic compounds of zinc and aluminium[69], cyclic amidines[72], a wide variety of phosphonium compounds[71,166–169], salts of the type BF_3–$C_2H_5NH_2$,[170] tri(ethylaminophenyl) borate[171], and metal compounds containing halogens and the CO_3^{2-}, NO_2^-, ClO_4^-, CN^-, and SCN^- groups with and without neutral ligands[172] have also been proposed as catalysts for the synthesis of poly-2-oxazolidinones.

Novolak epoxy-resins modified by oxazolidinone and having the general formula

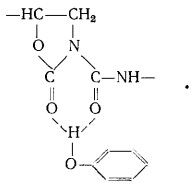


where Z is the organic polyisocyanate residue, Z^1 the epoxy-compound residue, m = 1.5–5.0, have been synthesised[173] by the reaction of polyisocyanates with epoxy-compounds. These polymers are suitable for the preparation of adhesives which are stable under the conditions of high humidity.

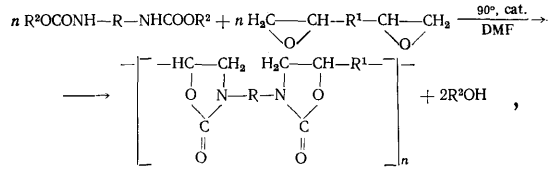
Poly-2-oxazolidinone has been obtained[174] by the reaction of di-isocyanates with bisoxazolidinones in *N*-methylpyrrolidinone at 48 °C in the presence of triethylenediamine. The bisoxazolidinone was obtained by refluxing tris(2,3-epoxypropyl) isocyanurate with hydroquinone in DMF in the presence of NaOH:



where R = alkyl or aryl. The polymers obtained are soluble in *N*-methylpyrrolidinone and *m*-cresol and less so in DMF. The intrinsic viscosities are 0.16–0.64 dl g^{-1} depending on the nature of the di-isocyanate. The presence of the 2-oxazolidinone rings in the polymer is responsible for their ability to form complexes with phenol:



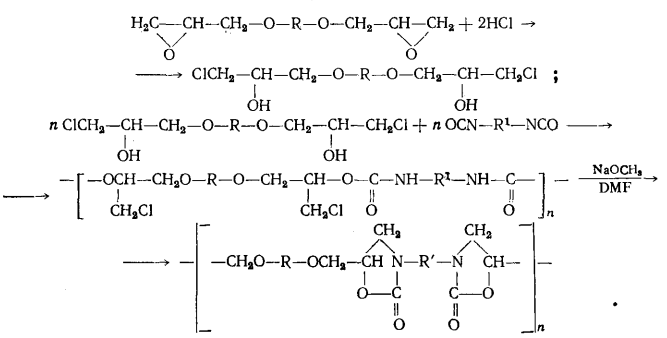
One of the common methods of synthesising poly-2-oxazolidinones involves the reaction of diepoxy-compounds with difunctional urethanes[7,163,175]:



where R = aryl.

It has been shown[175] that the solubilities and melting points of polymers are determined mainly by the structure of the initial diurethane.

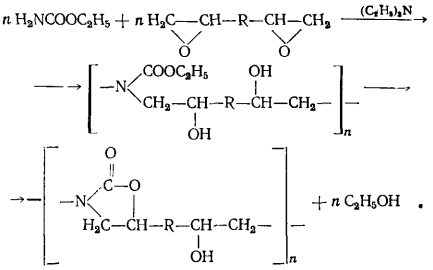
Polyoxazolidinones have been synthesised[176] by the reaction of bischlorohydrins with isocyanates followed by dehydrochlorination and intramolecular cyclisation:



The rate of ring closure depends on the nature of the *N*-substituted polyurethanes. The polyurethanes synthesised from di(4-isocyantophenyl)methane reacts in several

minutes: those obtained from 2,4-tolylene di-isocyanate react more slowly owing to steric hindrance (due to the *o*-methyl group); the cyclisation of the polyurethanes based on tetramethylene di-isocyanate is slower still. The polyoxazolidinones[176] are soluble in DMF and *m*-cresol but are insoluble in acetone, methanol, n-hexane, tetrahydrofuran, dioxan, toluene, and formic acid. The initial polyurethanes with CH_2Cl groups[176] are amorphous substances, while the polyoxazolidinones obtained from them and aromatic di-isocyanates are partly crystalline, and those obtained using aliphatic isocyanates are highly crystalline.

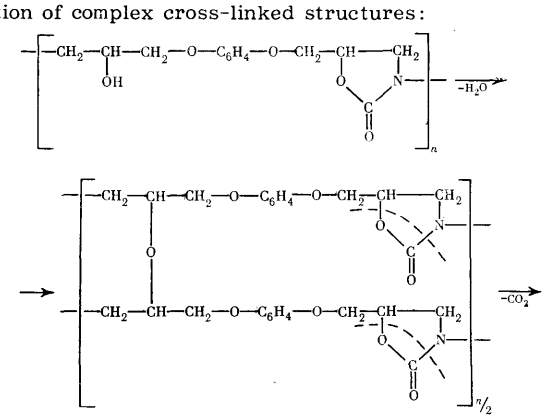
The reaction of ethylurethane with various diepoxy-compounds yielded[177-181] a new class of polymers—linear hydroxylated polyoxazolidinones:

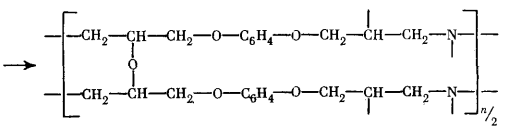


The diglycidyl ethers of hydroquinone, resorcinol, and di(hydroxyphenyl)propane, as well as epoxide oligomers have been used as the diepoxy-component.

The hydroxylated polyoxazolidinones are soluble in the cold in DMF, *m*-cresol, and sulphuric acid. Compared with the usual polyurethanes and hydroxylated *N*-arylpolyurethanes, these polymers have a higher thermal stability, decomposing 260–300 °C above their softening temperatures. The products obtained from the *trans*-forms of the diglycidyl ethers of bisphenols are more resistant to thermal decomposition than the products based on the corresponding *cis*-forms.

The hydroxylated polyoxazolidinones readily react with mono- and di-isocyanates. On oxidation, they give rise to carbonyl compounds, which indicates the presence of secondary hydroxy-groups in their structure. The reactivity of the secondary hydroxy-groups is much higher than that of the second hydroxy-group in isopropyl alcohol, which has been explained[180] by the presence of the oxazolidinone ring nitrogen atom in the β-position relative to them. The hydroxy-groups form intramolecular hydrogen bonds with this atom. The mechanism of the pyrolysis of polymers of this kind has been established by the DTA method in combination with dynamic and isothermal thermogravimetric data[181,182]. It has been observed that the thermal degradation of the oxazolidinone ring is preceded by intermolecular dehydration, which is followed by the decarboxylation of the rings with formation of complex cross-linked structures:



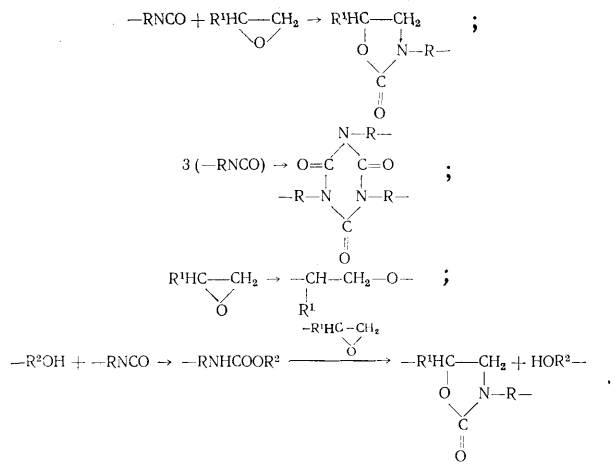


The enhanced reactivity of the hydroxy-groups, the regularity of their arrangement along the polymer chain, and the presence of the thermally stable oxazolidinone rings makes these low-molecular-weight polymers likely to be useful as hardening agents for polyurethane resins[179]. These potential hardening agents can ensure a specified distance between the cross links, which should promote in its turn the reproducibility of properties of the final materials and should improve many mechanical properties. The effectiveness of linear hydroxylated polyoxazolidinones in the hardening of macrodi-isocyanates has been demonstrated[180]. This entails the formation of insoluble and non-swelling very strong polyurethane film materials with good mechanical properties and a higher thermal stability than the polyurethanes hardened by polyols and polyamines.

(b) Cross-Linked Polymers with 2-Oxazolidinone Rings

Several methods of synthesis of cross-linked polymers containing 2-oxazolidinone rings have been described in the Soviet and foreign literature. These are mainly polymers incorporating isocyanurate rings together with 2-oxazolidinone rings.

As already mentioned, the interaction of isocyanates with epoxides involves, apart from the formation of 2-oxazolidinone rings, the competing cyclotrimerisation reaction of the NCO groups. The interaction of epoxide oligomers with di-isocyanates has been investigated[183]. It has been shown that, in the presence of an excess of a di-isocyanate at 160–165 °C, the formation of oxazolidinones is accompanied by the cyclotrimerisation of the isocyanate groups, the homopolymerisation of the epoxy-groups, the reaction of the isocyanates with the compound containing hydroxy-groups, and the reaction between the urethane and the epoxide:



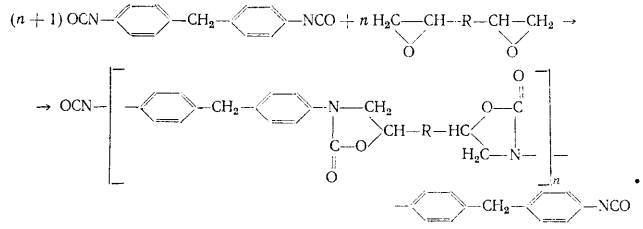
In the synthesis of foam plastics by a single-stage method using an excess of di-isocyanate[60,184] the polymerisation reaction takes place in several minutes and there is virtually no homopolymerisation of the epoxy-groups. The main competing reactions are then cyclotrimerisation and the formation of a urethane.

When tertiary amines are used as catalysts, the epoxide oligomer greatly enhances the catalytic effect in the polycyclotrimerisation of the isocyanate, accelerating thereby this

reaction. The occurrence of competing reactions precludes in this instance the possibility of regulating the distance between the cross links. The considerable brittleness and strain of the foam plastics can be explained by the presence of a large number of isocyanurate rings. The single-stage process takes place[60,184] in the presence of catalysts of the formation of oxazolidinone and cyclotrimerisation, for example, *N,N',N''*-tri[3-(dimethylamino)propyl]hexahydro-*sym*-triazine and the aluminium chloride–hexamethylphosphoramide complex.

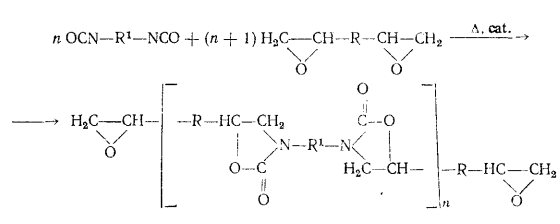
The application of the prepolymer (two-stage) method makes it possible to avoid to a large extent the above difficulties, because cycloaddition (the formation of the oxazolidinone ring) and polytrimerisation (the formation of the polyisocyanurate) take place separately.

Thus the synthesis of an oxazolidinone prepolymer with terminal isocyanate groups has been described[60,185–187]; the synthesis was carried out by the reaction of a diepoxide with an excess of a di-isocyanate at 100–150 °C in the presence of a Friedel–Crafts catalyst ($AlCl_3$, $FeCl_3$, and $ZnCl_2$) for 0.5 to 5 h:



In the second stage the prepolymer is hardened by the polycyclotrimerisation of the terminal isocyanate groups in the presence of catalysts: 2,4,6-tris(dimethylaminomethyl)phenol[185,186] and 2,4,6-tris(dimethylaminoethyl)phenol[60]. However, from our point of view it is doubtful if it is possible to separate clearly and carry out in succession the two reactions—the formation of oxazolidinones and polycyclotrimerisation.

Tanaka et al.[188,189] obtained a prepolymer with terminal epoxy-groups by the reaction of a di-isocyanate with an excess of a diepoxide at 100–200 °C in the presence of catalysts of the formation of oxazolidinones:

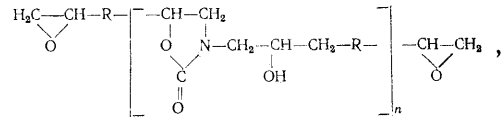


In the second stage an excess of the di-isocyanate was added to the oxazolidinone prepolymer with terminal epoxy-groups and three-dimensional polymers were obtained in the presence of catalysts of the formation of oxazolidinones and polycyclotrimerisation.

Polyisocyanates based on diphenylmethylene di-isocyanate, a mixture of 2,4- and 2,6-tolylene di-isocyanates, and hexamethylene di-isocyanate are usually employed in the synthesis of oxazolidinone-containing polyisocyanurate foam plastics. Among epoxides, applications have been found for epoxide polymers based on 2,2-di(hydroxyphenyl)propane (for example Epon-828 with an epoxide equivalent of 189) and others[60]. Potassium and magnesium ethoxides, aluminium isopropoxide, and iron(III) chloride have been used as catalysts of the formation of oxazolidinones[60].

It has been established[60] that the reaction between unpurified di-isocyanates and the Epon-828 epoxy-resin at 130 °C takes place without the addition of a catalyst. A considerable increase in the viscosity of the reaction medium was observed in the course of the reaction and oxazolidinone rings were formed. However, when purified di-isocyanates were used, a visible increase of viscosity was not observed. The authors[60] explained this by the presence in the unpurified di-isocyanates of admixtures of iron chloride (0.01 wt.%) which catalysed the cycloaddition reaction with formation of oxazolidinone rings.

A method of synthesis of oxazolidinone-containing epoxide oligomers from polyglycidyl ethers of polyols and isocyanuric acid in the presence of catalysts (tertiary amines, quaternary ammonium salts, alkali metal halides and alkoxides, the phosphonium compounds) at 130–180 °C has been described[190]. The reaction takes place with decomposition of the isocyanurate rings and the formation of oxazolidinone rings. The products are oligomers having the general formula



where R is a bivalent residue of the polyglycidyl ether of the polyol and $n = 1–10$. Such oligomers have been synthesised both in bulk and in solvents (DMF, nitrobenzene, *o*-dichlorobenzene, and dioxan). The corresponding derivatives of phenols, bisphenols, Novolak resins, polyoxyalkylene glycols, and aliphatic polyols can be used as the polyglycidyl ethers.

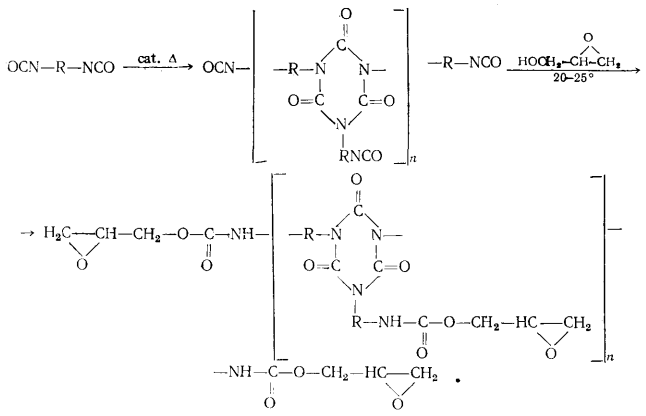
A patent[191] describes the synthesis of thermoreactive resins by the reaction of a polyisocyanate, containing in its structure isocyanurate rings, with a polyepoxide compound, the reaction involving the free isocyanate groups. The resins were hardened at 200–300 °C without a catalyst or at 100 to 185° in the presence of a hardening agent of the amine type.

Oxazolidinone-isocyanurate foam plastics are not very brittle and their combustibility is insignificant. In a study of the influence of the content of the epoxide oligomer in the prepolymer on the physicomechanical properties of oxazolidine-containing foam plastics, it was shown[60,185,186] that an increase of the concentration of the epoxide greatly increases the weight loss in fire tube tests. The content of the epoxide oligomer influences the smoke density particularly when the weight ratio of the epoxide to the isocyanate is greater than 0.1–0.2. An appreciable decrease of the brittleness of the foam plastics is observed when the epoxide : isocyanate weight ratio is approximately 0.05. A further increase of the content of the epoxide entails an insignificant increase of the brittleness[60]. The epoxide : isocyanate ratio (by weight) of 0.05–0.1 may be regarded as optimal.

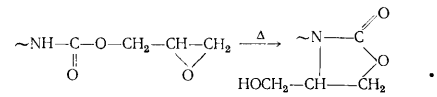
The thermal stability of the foam plastics has been investigated by thermogravimetric analysis (TGA). It was shown[60] that the onset of weight loss is observed at 100 °C and amounts to approximately 30% by 400°. In air, oxazolidinone-isocyanurate foam plastics are more stable than in an atmosphere of nitrogen; in both cases their thermal stability is higher than that of polyurethane foam plastics, evidently owing to the greater stability of the isocyanurate and oxazolidinone rings. It has also been noted[186] that, in contrast to the polyurethane foam plastics and the unmodified polyisocyanurate foam plastics, the mechanical properties of oxazolidinone-isocyanurates are fully isotropic in all directions.

A new method of synthesis of epoxyisocyanurate oligomers has been proposed[92,192–195]. In the presence of polycyclotrimerisation catalysts the initial di-isocyanates were converted into oligoisocyanurates containing isocyanate groups;

then at room temperature the terminal isocyanate groups were made to react with hydroxylated epoxides, for example, with glycidol:



It was shown[192-195] that the hardening of the resulting epoxyisocyanurate oligomers in the presence of hardening agents (acid anhydrides) is accompanied by competing cross-linking reactions involving the epoxy-groups and intramolecular cyclisation with formation of oxazolidinone rings:



However, in the above reports no mention is made of the possibility of the reaction of epoxide rings with isocyanurate rings accompanied by the decomposition of the latter, which has been described in a number of communications[78-80,190].

Hardened epoxyisocyanurates containing 2-oxazolidinone rings have been found to have good physicomechanical properties, to be chemically stable, and to exhibit an effective adhesion in varnish coatings[194]. The temperature of the 10% weight loss by hardened epoxyisocyanurates reached 290 to 300 °C.[88] The ratio of the oxazolidinone rings and cross-links and hence also the physicomechanical and thermal properties can be regulated by the amount of hardening agent and by varying the hardening conditions[88].

3. Applications of Poly-2-Oxazolidinones

Polymers containing oxazolidinone rings are widely used in various branches of modern technology. Their thermal stability and heat resistance are high compared with epoxide materials and polyurethanes and they are more elastic and have more effective physicomechanical properties than polyisocyanurates. By virtue of this set of properties, poly-2-oxazolidinones are used successfully as coatings, varnishes[68,69,156,168,189,190,192,194,196-200], electrically insulating materials[156,188,189,198,201], and binders for various composite materials[156,168,169,190,198,202], in rubber compositions[203], and as adhesives[85,163,168,189,190,197,199], foam plastics[60,68,157-160,184-187,196,204-206], fibres, films[174], corrosion inhibitors[33], etc.[140,144,145,198].

After the manuscript had been sent to the editors, a series of studies on oxazolidinones were published.

Gramain and Remuson[207] described the photochemical oxidation of 2-oxazolidinone which takes place on irradiation by the light of a high-pressure mercury lamp in the presence of O_2 and a 0.1 M solution of Ph_2CO in t-butyl alcohol with formation of oxazolidine-2,4-dione. The study of Itskovich et al.[208] was devoted to the intramolecular cyclisation of diepoxycarbamates with formation of oxazolidinone rings. Kadurina et al.[209] showed that the reactivity of diepoxides in reactions with di-isocyanates decreases in the following sequence: aliphatic diepoxides > aromatic diepoxides > alicyclic diepoxides, the epoxide ring of the alicyclic group altogether failing to react with NCO groups in the absence of a catalyst. According to the authors, steric factors and the lower mobility of the epoxide oligomers with cyclic groups determine their reactivity.

The study of Shukurov et al.[210] was devoted to the synthesis of copolymers of aromatic di-isocyanates and epoxy-resins with high impact strength, hardness, and heat resistance. Sorokin et al.[211] suggest that substituted ureas be used as hardening agents for epoxide oligomers; 2-oxazolidinone rings are then formed in the hardened polymer. Two studies[212,213] were devoted to the synthesis and viscoelastic properties of thermoreactive oxazolidinone-isocyanurate resins. Several patents[214-216] report the synthesis of oxazolidinone-containing polymers. Numata and Kinjo[217] demonstrated the possibility of synthesising oxazolidinone-isocyanurate resins modified by raw rubber. A patent[218] describes the synthesis of 2-oxazolidinone derivatives by the cyclocondensation of substituted β-aminoalcohols with CO_2.

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