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Cyclisation Reactions with Participation of Epoxy-compounds

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The review deals with reactions of epoxy-compounds in which they are involved in the formation of cyclic structures. Intramolecular rearrangements with participation of epoxy-compounds can lead to alicyclic and heterocyclic compounds. Intermolecular condensations of epoxy-compounds with various reagents give rise to heterocyclic structures. The bibliography comprises 307 references.

CONTENTS

I. Introduction 265
II. Intramolecular cyclisations 265
1. Synthesis of carbocyclic compounds 265
2. Synthesis of heterocyclic compounds 269
III. Intermolecular cyclisations 273
1. Condensations in the presence of bases 273
2. Condensations in the presence of acids 275
3. Dimerisation and n-cyclomerisation of epoxy-compounds 278

I. INTRODUCTION

The continuing interest of chemists in epoxy-compounds is due to unusual reactions undergone by compounds of this class. The interest in them increased especially when their significant role in biological processes, where epoxy-compounds are involved as intermediates in the fixation of oxygen by the ethylene bond yielding numerous derivatives in subsequent reactions, became recognised. Many natural products containing the epoxy-ring have been isolated and their number is continually increasing[1].

In recent years a number of reviews dealing with reactions of epoxy-compounds have been published[2-4]. However, the treatment of processes in which epoxy-compounds take part in the formation of cyclic products has been clearly inadequate.

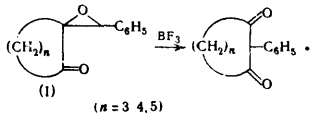
The primary aim of the present review has been to give a systematic account of reactions of this type and to classify them in accordance with common cyclisation mechanisms.

II. INTRAMOLECULAR CYCLISATIONS

1. SYNTHESIS OF CARBOCYCLIC COMPOUNDS

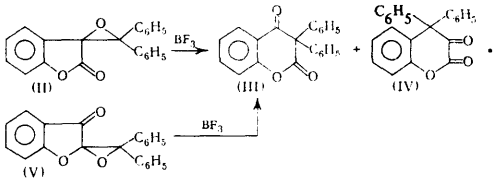
a. Rearrangement on Displacement of an sp^3-hybridised atom

Rearrangements with participation of a carbonium ion. Epoxy-compounds are known to isomerise to the corresponding carbonyl compounds in the presence of acids. The process is accompanied by the migration of the group adjacent to the electron-deficient carbon atom, produced on opening of the ring. In the special case where the epoxy-derivatives of cycloalkenes with an *endo*- or *exo*-double bond are isomerised, the migration of an alkyl group leads to the contraction or expansion of the ring respectively. For example, the epoxy-derivatives obtained from methylenecyclopropane and methylenecyclobutane isomerise to cyclobutanone[5] and cyclopentanone[6] respectively, while the epoxy-derivative of methoxybenzylidenecyclohexane gives 2-anisylcycloheptanone[7]. House and Wasson converted the epoxy-compounds (I) into β-diketones under the action of boron trifluoride in benzene[8]:

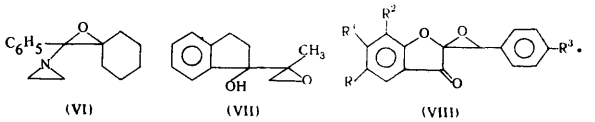


(I) (n = 3 4,5)

Schönberg and Junghans[9] also observed cases of ring expansion in the isomerisation of epoxy-compounds: the epoxy-compound (II) gave a mixture of products (III) and (IV), the former being obtained also in the isomerisation of the epoxy-compound (V):

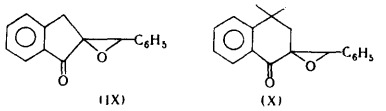


Another example is the conversion of epoxyamines (VI) into cycloheptanone derivatives[10], the conversion of *threo*- and *erythro*-1-(2-hydroxyindolyl)-1-methyloxirans (VII) into a mixture of α- and β-tetralones[11] and also the conversion of the epoxy-compound (VIII) into 4-hydroxycoumarin derivatives[12]:



(VI) (VII) (VIII)

Certain other spirocyclic epoxy-compounds, for example (IX) and (X), undergo similar isomerisation with ring expansion under the action of boron trifluoride[13,14]:

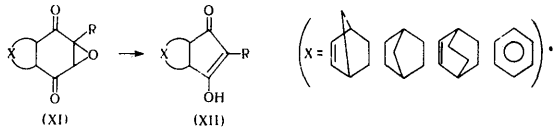


(IX) (X)

The isomerisation of alicyclic epoxy-compounds with ring contraction is observed much more frequently. Thus

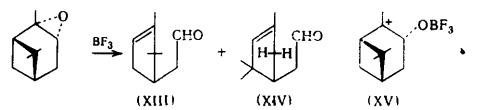
magnesium bromide causes the rearrangement of epoxycyclohexane to formylcyclopentane[15-18], of 1,2-epoxycyclohex-3-ene and 1,2-epoxycyclohex-4-ene to 2- and 3-formylcyclopentenes respectively[19], and of 1,2-epoxy-1-methylcyclohexane to acetylcyclopentane[18]. Under analogous conditions, 4-acetoxy-1,2-epoxy-1-methylcyclohexane rearranges to 1-acetoxy-3-formyl-3-methylcyclopentane[20] and the epoxy-derivative of dihydronaphthalene rearranges to 2-formylindane[21]. The isomerisation of 2,3-epoxycyclohexanone catalysed by boron trifluoride-ether yields 2-formylcyclopentanone[22], and 2-formyl-2-phenylcyclopentanone was obtained by the isomerisation of 2,3-epoxy-3-phenylcyclohexanone[22].

The reaction of epoxycyclohexane with methyl-[23,24], ethyl-[24], cyclohexyl-[25], β-phenylethyl-[26], and phenylmagnesium bromides[27,28] gives alkylcyclopentylmethanols, since the formylcyclopentane formed initially reacts further with the Grignard reagent. Similarly the reduction of 1-methylepoxycyclohexane with the mixed aluminium hydride $AlH_3.2AlCl_3$ yields 1-hydroxymethyl-1-methylcyclopentane[29]. The epoxy-compounds (XI) are isomerised by acid catalysts (BF_3, H_2SO_4) to compounds (XII) as a result of ring contraction and subsequent deformylation[30]:



(XI) (XII)

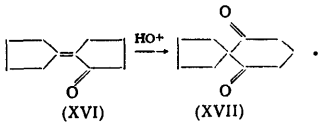
The reactions of epoxy-compounds under acid conditions may be accompanied sometimes by very pronounced changes in the carbon skeleton. Thus the epoxy-derivative of *trans*-cyclo-octene is isomerised by formic acid to hexahydro-*o*-toluic aldehyde[31] and the epoxy-derivative of α-pinene forms campholenic aldehyde under the action of Lewis acids[32-35]. Moreover, apart from campholenic aldehyde (XIII), the mixture contained a certain amount of the aldehyde (XIV), the formation of which can be understood only as a result of non-concerted C-7 and C-2 migration in the carbonium ion (XV)[34]:



(XIII) (XIV) (XV)

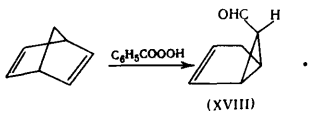
The reactions of the epoxy-derivatives of α- and β-pinenes has been reviewed[36]. The isomerisation of the 3,4-epoxycarane system also provides examples of profound changes in the carbon skeleton[37-39]; the reactions of certain sesquiterpenes[40] and also rearrangements in the steroid series[41-45] catalysed by boron trifluoride-ether have been described.

The oxonium ion formed on co-ordination of the oxygen atom of the epoxy-ring to acids resembles in many respects the structures formed on halogenation and protonation of the ethylene bond; the subsequent rearrangements of this ion with migration of the adjacent group resemble the isomerisation reactions which accompany, for example, the halogenation of a double bond at a quaternary carbon atom[46]. The conversion of a double bond into an epoxy-derivative also includes the formation of an oxonium complex as one of the stages; there are examples of 1,2-alkyl migration in the oxidation of olefins by peracids. In special cases this can cause the contraction or expansion of the carbon ring. The conversion of an exocyclic double bond into an epoxy-group leads to ring expansion[7,47], for example the reaction of a mixture of trifluoroperacetic acid and boron trifluoride with (XVI) yields (XVII):



(XVI) (XVII)

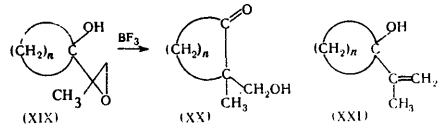
The conversion of an endocyclic double bond into an epoxy-group results in ring contractions: oxidation of norbornadiene with perbenzoic acid gives the aldehyde (XVIII)[48]:



(XVIII)

Certain other examples concerning steroids have been quoted[49].

In the halogenation of a double bond and its conversion into an epoxy-group and in the co-ordination of epoxy-compounds to acids the positive charges at the carbon atoms in the transition states are in general different. This can lead to different final products when account is taken of the possibility of the following competing reactions: (1) internal nucleophilic (in the limit) attack by the oxygen atom in the conversion to an epoxy-group leads to the closure of the epoxy-ring; (2) the migration of the adjacent group yields isomerisation products; (3) the anchimeric assistance of an adjacent group with electron-donating properties (when such is present) can result in the formation of cyclic structures; (4) external nucleophilic attack leads to addition products. In connection with the above, we may note that the epoxy-compounds (XIX) are isomerised by boron trifluoride to the ketones (XX) with ring expansion[50], the reaction of the hydrocarbons (XXI) with hypohalous acids also gives the ketones (XX) while their conversion into epoxy-derivatives yields only compounds (XIX):



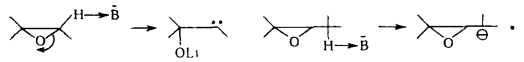
(XIX) (XX) (XXI)

All the cases quoted so far included the formation of a new C–C bond as a result of the migration of an alkyl group to a carbonium ion generated on opening of the epoxy-ring or on its formation. Considerably much less attention has so far been devoted to the reactions of epoxy-compounds with bases. Most of the examples studied included an investigation of the addition of various basic reagents in proton-donating solvents (alcohol, water, dilute acids). However, the latest studies of Cope, Crandall, and Temnikova and coworkers led to the discovery of new interesting reactions of epoxy-compounds in the presence of strong bases.

Anionoid rearrangements. Crandall and coworkers[5] reported certain reactions of epoxy-compounds in the presence of strong bases (R_2NLi, BuLi). A proton may be eliminated from the α- or β-position in the epoxy-compound molecule.† Elimination from the α-position yields a carbene, which can be subsequently inserted intramolecularly in a C–H bond or can add to a C=C bond.

† Here and henceforth Crandall's terminology is used[51].

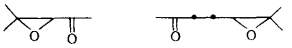
β-Elimination yields a carbanion, the rearrangement of which leads to the isomerisation of the epoxy-compound to an allyl alcohol[51-55]:



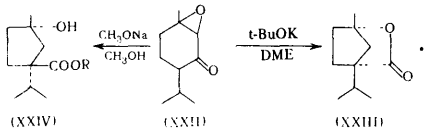
α-elimination β-elimination

The contributions of α- and β-elimination are determined by the presence of a proton in the appropriate positions and the ease of its elimination[51].

Evidently Crandall's mechanism can be supplemented by certain specific cases. Thus, when the molecule of the epoxy-compound contains a powerful electron-accepting group (for example a carbonyl group), elimination of a proton from other positions in the substrate becomes possible and therefore one can speak of γ-elimination, δ-elimination, etc. The most interesting examples of γ-elimination are the rearrangements of αβ-epoxy- and γδ-epoxy-ketones into cyclopropane derivatives:

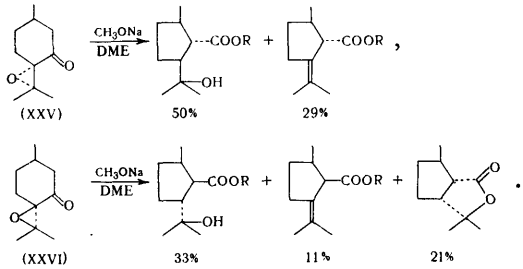


The close analogy between αβ-epoxyketones and α-halogenoketones is quite evident; it is confirmed also by the very similar behaviour of these bifunctional substrates in the Favorskii rearrangement. The intermediate formation of cyclopropanone as a result of a co-ordinated S_Ni attack by the carbanion on the α-carbon atom takes place similarly in both cases. The subsequent cleavage of cyclopropanone under the reaction conditions takes place stereospecifically in non-polar solvents (for example dimethoxyethane) or non-stereospecifically‡ (water, alcohol) and leads to hydroxyacids or lactones. The isomerisation of the epoxy-derivative of piperitone (XXII) yields (XXIII) as a result of a stereospecific Favorskii rearrangement in dimethoxyethane (DME), while in methanol (XXIV) is formed non-stereospecifically[56]:



(XXIV) (XXII) (XXIII)

The *cis*-epoxy-derivative (XXV) and *trans*-epoxy-derivative (XXVI) of pulegone undergo preferential stereospecific rearrangement in the presence of sodium methoxide in dimethoxyethane although in the case of the *trans*-isomer the stereospecificity is weaker[57], as can be seen from the relative amounts of the products:



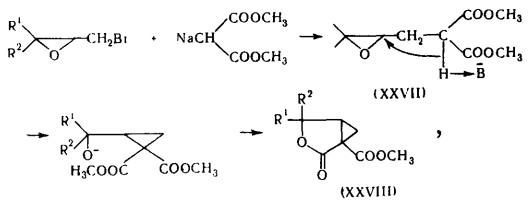
(XXV) 50% 29%

(XXVI) 33% 11% 21%

The study of the reactions of the same epoxy-compounds with sodium methoxide in ethanol or with sodium hydroxide in aqueous ethanol and water showed that in such cases the reaction is stereospecific[61,62]. The Favorskii rearrangement of the epoxy-derivative of isophorone[56] and of αβ-epoxyketones of the steroid series[57] also involves the contraction of a six- to a five-membered ring.

‡ For a discussion of this problem, see Refs. 56-60.

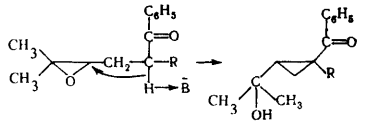
Other interesting examples involving the formation of the cyclopropane ring are provided by the rearrangement of γδ-epoxyketones. Thus the alkylation of dimethyl sodiomalonate with α-bromo-derivatives of epoxypropane, 1,2-epoxy-2-methylpropane, 1,2-epoxybutane, 2,3-epoxybutane, and 2,3-epoxy-2-methylbutane gave the γ-lactone of 1-hydroxymethyl-2-methoxycarbonylcyclopropane-2-carboxylic acid and its homologues according to the following mechanism[63,64]:



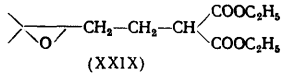
(XXVII) (XXVIII)

where R^1 = H and R^2 = H or CH_3 or R^1 = CH_3 and R^2 = CH_3.

The mechanism is confirmed by the finding that the epoxy-compound (XXVII) obtained in a different way isomerises to (XXVIII)[64]. The products of the alkylation of the sodio-derivatives of acetophenone and benzyl methyl ketone with 1-bromo-2,3-epoxy-3-methylbutane in toluene undergo a similar rearrangement[65,66]. The epoxyketones formed in the first stage isomerise in an alkaline medium to cyclopropane structures via the intramolecular attack by the nucleophilic carbon atom of the epoxy-ring according to the mechanism[66]

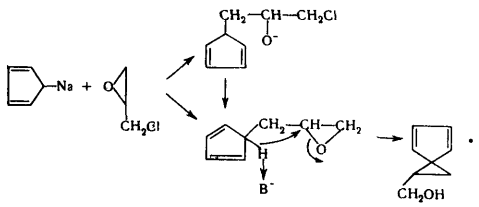


where R = H or C_6H_5. We may note that the epoxy-compound (XXIX) (synthesised by an independent method), the chain of which contains one carbon atom more than in (XXVII), is not converted into the corresponding cyclobutane[67]:



(XXIX)

The interaction of epichlorohydrin with cyclopentadienylsodium leads to the formation of cyclopropane as a result of the attack by the carbanion on the epoxy-ring according to the mechanism[68]

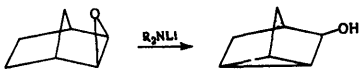


The authors do not state which pathway is actually followed. For information about the preparation of cyclopropane by the rearrangement of 1,2-dicyano-oxiran, see Ershov et al.[69]

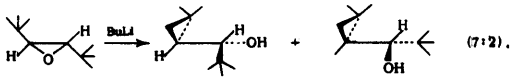
b. Reactions with Participations of a Carbene

The elimination by strong bases of a proton from epoxy-compounds without electron-accepting functional

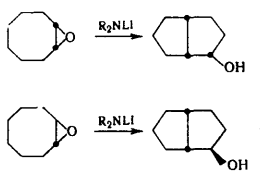
groups involves, as already stated, competition between α- and β-elimination. In the vast majority of cases β-elimination is observed[51]. There are, however, cases, where the formation of a carbene predominates or constitutes the sole reaction of epoxy-compounds in the presence of bases. For instance, epoxynorbornane rearranges to a nortricyclanol via the intermediate formation of a carbene, because the elimination of a proton from the β-position is impossible[70]:



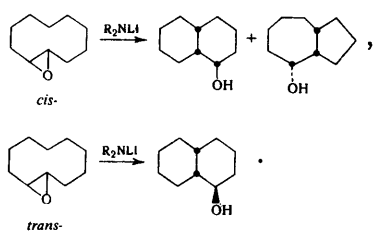
1,2-Di-t-butylepoxyethane yields two products of the insertion of a carbene in the C–H bond[71]:



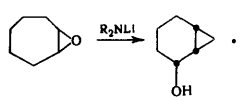
The formation of a considerable amount of the second isomer is evidence of the incomplete stereospecificity of the insertion reaction and can probably be accounted for by the existence of the carbene as a discrete entity. On the other hand, the configurational mobility of the carbon chain leads to a mixture of products. In contrast to aliphatic epoxy-compounds, the epoxy-derivatives of cycloalkanes (n = 7, 8, or 10) undergo stereospecific *trans*-annular insertion of the carbene. The closeness of the atoms in medium rings leads to the preferential interaction of the carbenes with the C–H bond at the opposite end of the molecule. The epoxy-compounds derived from *cis*- and *trans*-cyclo-octenes undergo a stereospecific rearrangement to the corresponding bicyclo-octanols[72,73]:



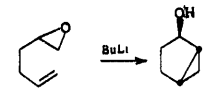
The epoxy-compounds derived from *cis*- and *trans*-cyclodecenes are converted into bicyclodecanols also as a result of a stereospecific *trans*-annular insertion of the carbene in a C–H bond[73,74]:



The rearrangement of epoxy-cycloheptane takes place similarly[51]:

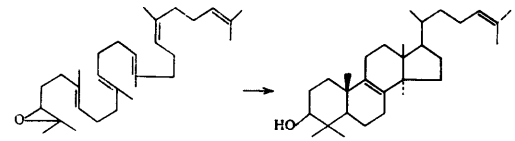


The stereospecificity of reactions involving the *trans*-annular insertion of carbenes into medium rings and also the predominance of α-elimination in such cases have been explained[51,71,75]. We shall only note an interesting example of intramolecular addition of a carbene to a double bond in the rearrangement of the monoepoxy-compound derived from diallyl[71]:

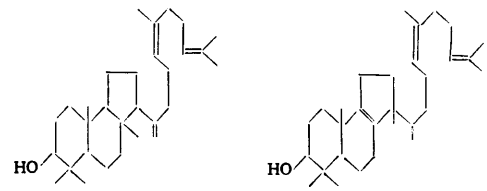


c. Nucleophilic Participation of the C=C bond in the Rearrangement of Epoxy-Compounds

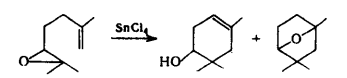
A study of the rearrangement of the electron-deficient carbon atom in the opening of the epoxy-ring gives rise to the following natural question: whether the alkyl group migrates synchronously as the charge of the carbon atom in the oxonium complex increases or whether the coordination of the epoxy-compound molecule to acids with subsequent ring opening involves a discrete carbonium ion. Probably this question can be solved in a concrete form as a function of the reaction conditions and the object investigated[76,77]. In particular, there are a number of examples where the rupture of the C–O bond in the epoxy-ring takes place synchronously with formation of the new bond, with the adjacent group playing the role of a donor. This leads ultimately to cyclic products. This process can be aided by the nucleophilic effect of a hetero-atom (O, N, etc) or groups with a relatively high electron content, for example, a multiple bond. The nucleophilic involvement of the C=C bond in enzyme- and acid-catalysed reactions of epoxyolefin systems attracted very considerable attention in recent years as a model of the biosynthesis of natural products (terpenes, steroids). The most interesting example of this kind is the conversion of squalene-2,3-oxide into lanosterol steroids, which has been achieved enzymically under laboratory conditions[78–81]:



Certain homologues of squalene-2,3-oxide and its derivatives have also been converted into lanosterols[82–86]; by varying the enzymes, it proved possible to obtain under laboratory conditions fusidic acid[87] and pentacyclic products: β-amyrin[88] and cycloartenol[89]. Non-enzymic cyclisation of 2,3-oxidosqualene with stannic chloride yielded only tricyclic products[90]:

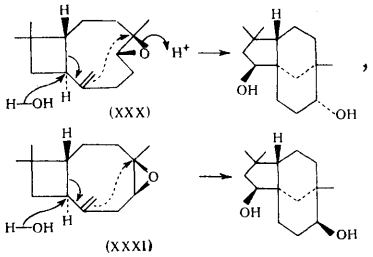


One of the first studies in this series involved an investigation of the cyclisation of the monoepoxy-derivative of geraniolene as a model compound in the synthesis of 3-hydroxy-derivatives of polycyclic systems (steroids, terpenes)[91]:



The yield of these cyclic products in the presence of boron trifluoride as a catalyst (both in benzene and in

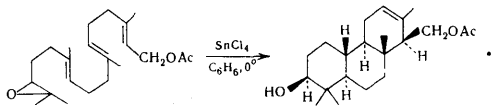
ether)[92] was smaller than in the presence of $SnCl_4$. Pyrethrosin undergoes a cyclisation of a similar type yielding a tricyclic product[93]. The epoxy-compounds derived from caryophyllene (XXX) and isocaryophyllene (XXXI) cyclise[94,95] to the corresponding glycols by the mechanisms



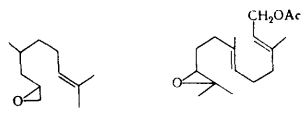
(XXX)

(XXXI)

A similar process takes place when geranylgeranyl acetate is treated with stannic chloride[96]:



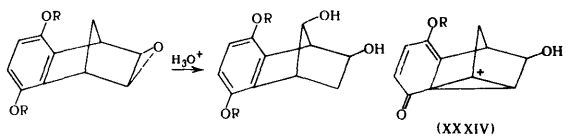
Goldsmith et al.[97] studied the reaction of stereoisomeric epoxy-derivatives of citronellal (XXXII), and the stereochemistry of the cyclisation of the epoxy-derivatives of farnesyl acetate (XXXIII) has been discussed by van Tamelen and coworkers[98,99]:



(XXXII) (XXXIII)

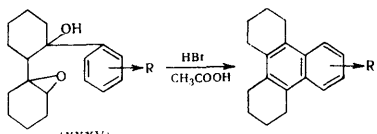
The conversion of certain epoxyolefins into carbocyclic compounds has also been described[100-102].

The involvement of a double bond, formerly included in a benzene ring, in the acid-catalysed hydrolysis of epoxy-groups in the benzonorbornene series yields anomalous water addition products. The formation of a new C–C bond in the intermediate structure (XXXIV) is postulated, as shown in the mechanism below[103-105]:



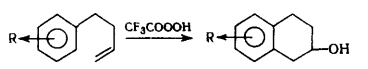
(XXXIV)

The epoxy-compound (XXXV) reacts similarly; under these conditions, the cyclic product is dehydrated[106]:



(XXXV)

An unusual example of the involvement of the C=C bond is quoted by Davidson and Norman[76]. The conversion of butenylbenzenes (XXXVI) into epoxy-derivatives with trifluoroperacetic acid leads to 1,2,3,4-tetrahydronaphthols in yields of 7% (R = H) and 25% ($R = OCH_3$):



(XXXVI)

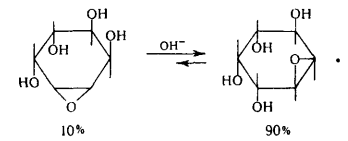
It is surprising that in the presence of boron trifluoride epoxy-compounds derived from unsaturated hydrocarbons do not yield naphthols.

2. SYNTHESIS OF HETEROCYCLIC COMPOUNDS

The previous section quoted certain examples of the reactions of epoxyolefins with the nucleophilic participation of the carbon–carbon double bond and formation of carbocyclic products. In this section we shall discuss cases of the formation of heterocyclic compounds such as the intramolecular nucleophilic involvement of the heteroatom in the base- and acid-catalysed rearrangements of epoxy-compounds with functional groups.

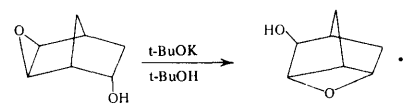
a. Attack by the Heteroatom on the Epoxy-ring without Incorporation of the Oxygen Atom into the Cyclic System

The simplest example of processes of this kind is the so called migration of the epoxy-group, which in the case of sugars, for example, can lead to an equilibrium mixture of isomers[107]:

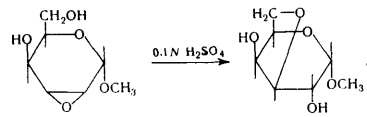


10% 90%

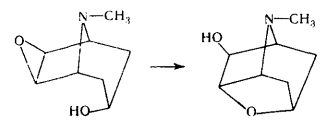
Some examples of reactions of this type have been reviewed by Newth[108] and Lemieux[109]. Similar cases of migration of the epoxy-group have been observed by Payne[110] for epoxyalcohols[110] and Akhrem and coworkers for steroids[111,112]. All these reactions take place under mild alkaline conditions involving the formation of an oxy-anion. The participation of such anions can lead to a strained oxacyclobutane system[113]:



If, owing to steric factors, the participation of an O^- or OH group is impossible, then furans and pyrans are readily formed when the epoxy-ring is opened. The acid hydrolysis of methyl-2,3-anhydro-D-hexopyranosides leads to 3,6-anhydropyranosides[114]:

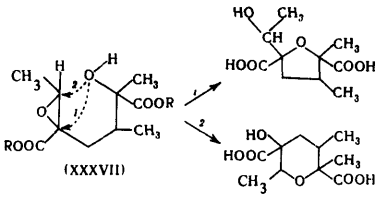


This cyclisation, which takes place most readily under mild alkaline conditions, has been described in the literature for 2,3-anhydro-derivatives[114-118] and 5,6-anhydro-derivatives[119]. Reactions of a similar kind are encountered among alkaloids: for example, scopine is converted into scopoline[120]:



The alkaloid jacobine (XXXVII) is converted into a mixture of substituted tetrahydrofuran and tetrahydropyran

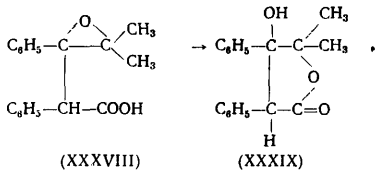
derivatives[121] (in the formulae below R = R = H or R = R = retronecine residue):



(XXXVII)

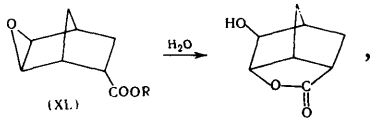
Many other examples of O-5 and O-6-involvement of the hydroxy-group in acid- and base-catalysed reactions of epoxy-derivatives of the terpene series, leading to the formation of furan and pyran derivatives, have been found in recent years[122-126].

Examples of the nucleophilic involvement of the carboxy-group in the isomerisation of epoxyacids are rarely encountered in a pure form. In particular, we may note that the $\beta\gamma$-epoxyacid (XXXVIII) is readily converted into the lactone (XXXIX) in the presence of *p*-toluenesulphonic acid[127]:



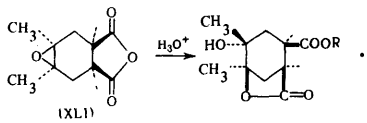
(XXXVIII) (XXXIX)

In most cases it is difficult to decide, because of a deficiency of data, whether the epoxy-ring opens with participation of the adjacent group or whether the epoxy-group is first hydrolysed to a glycol and the lactone is formed as a result of the interaction between the hydroxy- and carboxy-groups. This is illustrated by the conversion of the epoxyester (XL) into a hydroxylactone[113]:



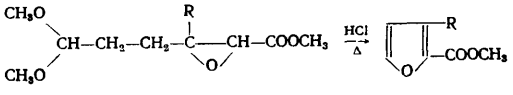
(XL)

or the conversion of the epoxyanhydride (XLI) into a hydroxylactone on hydrolysis[128]:

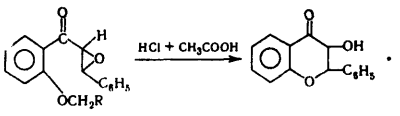


(XLI)

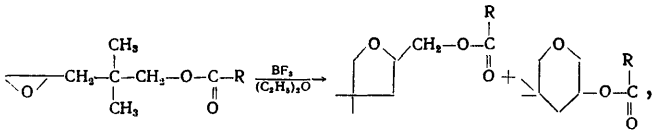
Excellent examples of translactonisation occurring on opening of the epoxy-ring in epoxylactones subjected to hydrolysis or reduction with lithium aluminium hydride have been given by Conroy[129,130] and Nazarov et al.[131] Cases of the participation of the oxygen atom in ether, ester, and epoxy-groups following the opening of the epoxy-ring in the corresponding epoxy-compounds under acid conditions are very numerous. In particular, the cyclisation of δ-acetals of glycidic esters leads to 3-substituted furans[132]:



and epoxy-derivatives of 2'-hydroxychalcone yield 3-hydroxyflavanone[133]:



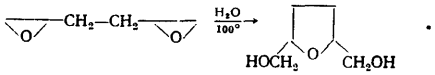
The rearrangement of 4,5-epoxy-2,2-dimethylpentyl acetate catalysed by boron trifluoride gave a mixture of furan and pyran derivatives[134]:



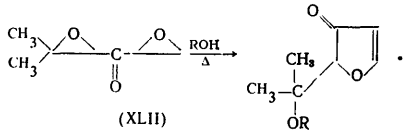
where R = CH_3.

Only the furan derivative was isolated after the reaction of 4,5-epoxy-2,2,4-trimethylpentyl isobutyrate[134].

The nucleophilic co-operation with the epoxy-oxygen atom in the opening of the second epoxy-ring in diepoxy-compounds is also well known. For example, the diepoxy-compound derived from hexa-1,5-diene forms a tetrahydrofuran derivative in the presence of acids[135]:

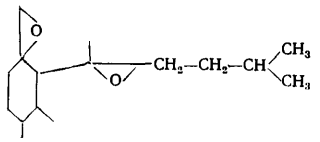


On heating in the presence of alcohol, the epoxy-compound (XLII) isomerises to dihydrofuranone[136]:



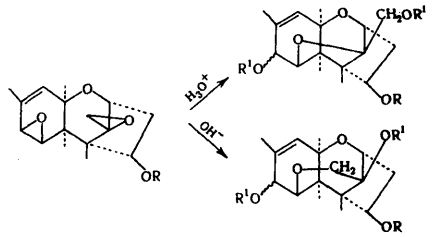
(XLII)

Klein and coworkers[137,138] described the conversion of diepoxy-derivatives of geraniol, nerol, and linalo-ol into furan and pyran derivatives under mild alkaline conditions. In the course of experiments designed to elucidate the structure of fumagillin (XLIII), Tarbell[139] observed various reactions of this compound due to the presence of two epoxy-groups:



(XLIII)

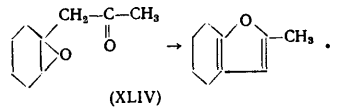
Crotocin, an antimildew antibiotic, also contains two epoxy-groups, the interaction of which is different under acid and alkaline conditions[140], leading to furan or pyran derivatives:



Similar reactions have been described also for certain other diepoxy-compounds[126,141].

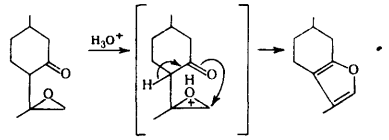
The intramolecular interaction of carbonyl and epoxy-groups can take place in two different ways. Under

alkaline conditions, there is a possibility of the formation of a mesomeric enolate anion, the intramolecular interaction of which with the epoxy-ring leads to carbocyclic products (cyclopropanes, cyclobutanes, etc) in the case of *C*-alkylation or to oxiran (oxetan, tetrahydrofuran, etc.) derivatives in the case of *O*-alkylation. In an acid medium the epoxy-group activated by co-ordination to the catalyst can cause a displacement via a field effect of the electrons from the carbonyl group (or the hydroxy-group of the enol if such is formed), which leads to the formation of cyclic products, as in *O*-alkylation in an alkaline medium. For example, the ketoepoxy-compound (XLIV) is cyclised by dilute sulphuric acid to furan[142]:

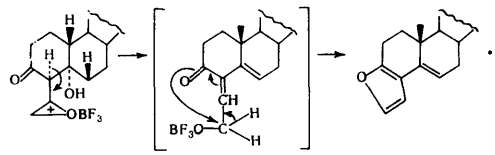


(XLIV)

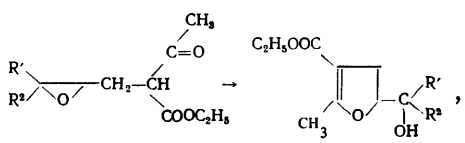
The epoxy-derivative of isopulegone undergoes a similar reaction, menthofuran being formed under very mild conditions, close to those obtaining in biological systems[143]:



Epoxyketols of the cholestane series also tend to undergo similar reactions; the reaction is catalysed by boron trifluoride which behaves at the same time as a dehydrating agent[144,145]:



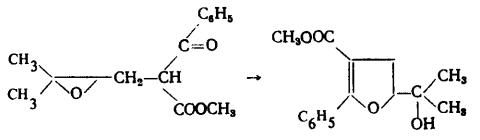
Much attention has been devoted to the problem of the biosynthesis of furans from natural products, in particular from epoxy-derivatives[144,146]. Interesting results were obtained in the alkylation of metal derivatives of carbonyl compounds by α- and β-bromoepoxy-compounds. In most cases the alkylation products formed initially undergo a rearrangement as a result of attack by the enolate anion on the epoxy-ring. In the interaction of sodioacetoacetic ester with 1-bromo-2,3-epoxybutane and 1-bromo-2,3-epoxy-3-methylbutane, compound (XLV), formed as an intermediate, rearranges to dihydrofuran[147,148]:



(XLV)

where $R^1 = R^2 = CH_3$ or $R^1 = H$ and $R^2 = CH_3$.

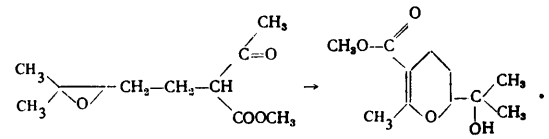
Similarly, compound (XLVI), formed as an intermediate in the reaction of methyl benzoylacetate with 1-bromo-2,3-epoxy-3-methylbutane in methanol also yields a dihydrofuran[149]:



(XLVI)

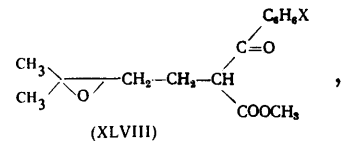
Dihydrofurans have also been obtained in the alkylation of the sodio-derivatives of benzyl phenyl ketone, benzoylacetone, and acetylacetone with 1-bromo-2,3-epoxybutane as a result of rearrangement under the reaction conditions of the $\gamma\delta$-epoxyketones formed[150,151].

In the alkylation of methyl acetoacetate with 1-bromo-3,4-epoxy-4-methylpentane the intermediate (LVII) isomerised to dihydropyran[152,153]:



(XLVII)

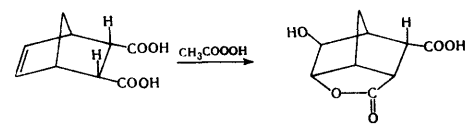
The epoxy-compounds (XLVIII) synthesised by an independent procedure are also converted into dihydropyran in the presence of bases[154]:



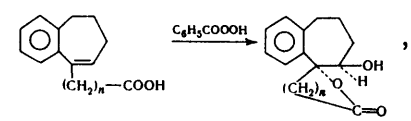
(XLVIII)

where X = *p*-CH_3O, *p*-CH_3, H, or *p*-NO_2.

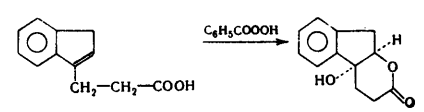
The nucleophilic involvement of an oxygen atom may be reflected not only in the opening of the epoxy-ring but also in its formation. Thus in the conversion into epoxy-derivatives of unsaturated compounds containing hydroxy-, carboxy-, ester, ether, or epoxy-groups the reaction is anomalous. The reaction of peracetic acid with 2,3-di-*endo*-carboxybicyclo[2,2,1]hept-5-ene gives a lactone[155]:



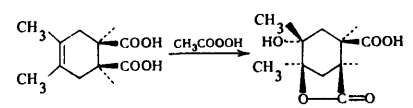
Lactones are formed similarly from the derivatives of benzocycloheptene[156]:



indene[157]:



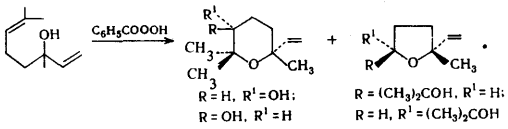
and 4,5-dimethyl-Δ^4-cyclohexene-*cis*-1,2-dicarboxylic acid[128]:



Interesting examples of the formation of a mixture of γ- and δ-lactones in the oxidation of *trans*- and *cis*-*o*-carboxystilbenes with perbenzoic acid have been quoted by Berti and Bottari[158-160] (see also Nazarov et al.[131] and Mousseron et al.[161]).

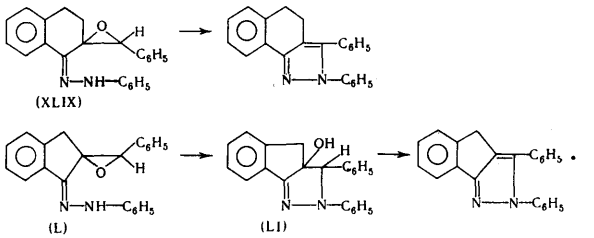
The most numerous examples of the participation of the hydroxy-group have been found in the Prilezhaev oxidation of hydroxyolefins with formation of furans and pyrans. For example, the conversion of 2-allylphenols into

epoxy-derivatives leads to benzofurans[162,163]. Benzofurans have also been obtained by the oxidation of 2-propenylcresols[164]. The conversion of linalo-ol into an epoxy-derivative over phthalic acid yields a mixture of stereoisomeric tetrahydropyrans[165,166]:

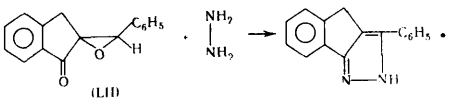


More detailed studies showed that the mixture contained also stereoisomeric tetrahydrofurans[125,167]. The formation of furan and pyran derivatives in the conversion to epoxy-derivatives of diallyl[168], octadeca-9,10-trienecarboxylic, octadeca-11,12-trienecarboxylic, and octadeca-13,14-trienecarboxylic acids[169], and other compounds[170,171] has been described.

Few data have been published on the intramolecular cyclisation of epoxy-compounds with participation of a nitrogen atom, probably owing to the difficulty of the synthesis of such bifunctional compounds. Cromwell showed that epoxyphenylhydrazones of type (XLIX) and (L), which are formed in the reaction between the corresponding $\alpha\beta$-epoxyketones with phenylhydrazine, are readily converted into pyrazoles[13,172]:



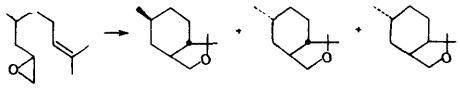
Since the rates of cyclisation of epoxyphenylhydrazone (L) into pyrazoline (LI) and its subsequent dehydration are comparable, it proved possible to isolate all three products. The interaction of the epoxy-compound (LII) with hydrazine leads directly to a pyrazole[13]:



Certain other examples of the formation of pyrazoles in the interaction of $\alpha\beta$-epoxyketones with hydrazine have been described[173-176].

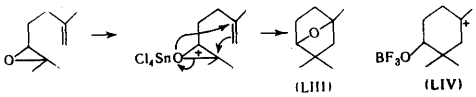
b. Cyclisation with Incorporation of the Oxygen Atom of the Epoxy-compound into the Cyclic System

Most of the examples considered above involved an intramolecular nucleophilic attack on the epoxy-ring with inversion at the carbon atom attacked. In reactions in an alkaline medium the group eliminated (the oxy-anion) was stabilised by abstracting a proton from the medium. In acid-catalysed processes the oxygen atom of the epoxy-group was bound to a proton or a Lewis acid. The molecule was then stabilised either by splitting off the catalyst and forming a carbonyl compound or by the fixation of the oxygen atom as a hydroxy-group as a result of hydrolysis by the reaction medium. It is quite evident that this mechanism is oversimplified. Indeed, if the molecule is fairly complex, in the rearrangement in the presence of bases the liberated oxy-anion may attack any other electrophilic centre in the same molecule (if allowed by the geometry). Such a case has already been mentioned (p. 267). Another example is provided by acid-catalysed rearrangements of epoxyolefins. The isomerisation of the epoxy-derivative obtained from citronellal leads to bicyclic products[97]:



The cyclisation of the mono-epoxyderivative obtained from geraniolene (p. 268) and the epoxy-derivative from geranylgeranyl acetate takes place similarly[96]:

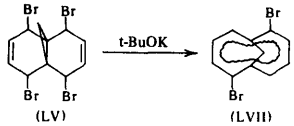
The fact that the yield of the cyclic products was higher in the catalysis by $SnCl_4$ than in the catalysis by BF_3 is striking[91,92]. As a catalyst, $SnCl_4$ is a weaker Lewis acid than BF_3 and the rupture of the C–O bond of the epoxy-ring requires a higher degree of nucleophilic co-operation by an adjacent (geometrically suitable) C=C bond. Consequently in this case the cyclisation process is more synchronous. As the C–O bond is broken, the interaction of the π electrons of the double bond with the positive charge generated at one of the carbon atoms of the epoxy-ring becomes intensified simultaneously with the intensification of the nucleophilic interaction between the oxygen atom and the carbon of the multiple bond. The entire process may be represented by the following mechanism:-

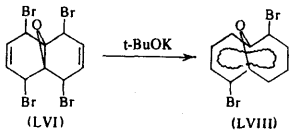


In the presence of boron trifluoride the carbonium cation structure of the transition state in the opening of the epoxy-ring is more pronounced and therefore the process is less synchronous and the yield of the cyclohexane derivative is lower. The bicyclic product (LIII) is also formed in a small amount, because the significant weakening of the nucleophilicity of the oxygen atom increases the probability of a competing process—the stabilisation of (LIV) by the elimination of a proton. We believe that the greater resemblance to a carbonium cation of the transition state in the BF_3-catalysed reaction of epoxy-compounds is indicated by the formation of fluorohydrins in this reaction, which has been known for a long time. On the other hand, in the reaction catalysed by $SnCl_4$ the formation of chlorohydrins has not been observed.

c. Valence Tautomerism of Epoxy-compounds

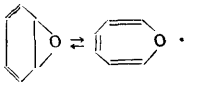
The valence tautomerism of acyclic and alicyclic dienes and their cyclopropyl analogues, involving 1,5-dienyl or homodienyl migration of hydrogen, has been described fairly adequately[177]. A certain similarity in the state of the bonds in the cyclopropane and oxiran rings is reflected in a number of rearrangements of vinyl-substituted cyclopropanes and oxirans. For example, dehydrobromination of (LV) and (LVI) with potassium t-butoxide in ether at 10°C leads to (LVII) and (LVIII) respectively[178]:



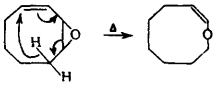


(LVI) (LVIII)

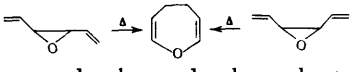
The monoepoxy-derivative of benzene is in equilibrium with its monocyclic tautomer—oxepin; in iso-octane their ratio is 3 : 7, while in aqueous methanol epoxycyclohexadiene predominates[179]:



Crandall and Watkins reported 1,5-migration of hydrogen in epoxycycloalkenes[180]:



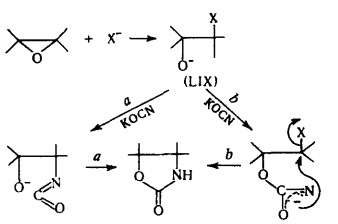
This rearrangement has also been observed in the acyclic series. When the epoxy-derivatives obtained from *cis*- and *trans*-1,2-divinylethylenes are heated, 4,5-dihydro-oxepin is formed. The *trans*-isomer of the epoxy-compound reacts under more severe conditions and is usually present in a mixture with 4,5-dihydro-oxepin[181,182]:



Certain other examples have also been described[183-185].

III. INTERMOLECULAR CYCLISATIONS

All the cases of the formation of cyclic products in the condensation of epoxy-compounds with various reagents described below involve the formation of five-membered rings. Huisgen[186] suggested that these reactions of epoxy-compounds can be classified as 1,3-dipolar addition processes in which the molecule of the epoxy-compound in the transition state is regarded as a 1,3-dipole, (i.e. $^-O-C-C^+$). The expansion of the oxiran ring in the presence of bases evidently does not include such a dipolar structure, since in the first stage the nucleophilic agent attacks the least substituted carbon atom with formation of an intermediate oxy-anion, the existence of which has been demonstrated in many cases[187]. The interaction of the oxy-anion with the electrophilic agent completes the cyclisation when the electrophilic centre is also part of the attacking agent. Epoxy-compounds react in this way with carbanions. The reactions of epoxy-compounds with molecules having multiple bonds (cyanates, isocyanates, isothiocyanates, etc.) probably involve a different mechanism. As will be shown below, in all cases a catalyst must be present (metal and ammonium halides and certain others). The role of the catalyst reduces to the formation of the oxy-anion (LIX), the interaction of which with the condensing agent can occur via two pathways:



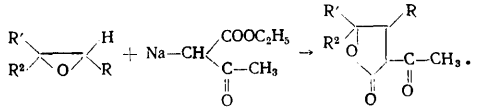
The kinetic data for reactions of epoxyalkanes with carbon dioxide catalysed by potassium, sodium, and ammonium halides support pathway *b*[188,189]; the alternative pathway *a* has been considered by Dyen and Swern[190]. The acid-catalysed condensation of epoxy-compounds with compounds having multiple bonds has been investigated purely empirically. Here the role of the acid probably reduces to the activation of the epoxy-ring (the formation of an oxonium complex) and, on the other hand, to the activation of the multiple bond, which becomes polarised as a result of co-ordination to the catalyst.

For a number of reasons, it is difficult to classify the intermolecular reactions. For example, pyridine, tribenzylamine, $ZnCl_2$, $FeCl_3$, LiCl, alkalis, etc. have been suggested as catalysts for the reactions of epoxy-compounds with isocyanates[191-193]. The site of the opening of the epoxy-ring is known to depend also on the presence of even traces of acids and therefore it is evident that pyridine and zinc chloride catalysts will lead to different reaction products. Moreover, the primary condensation products sometimes undergo pronounced changes under the reaction conditions, which also hinders the classification. Nevertheless, we believe it useful to consider separately reactions occurring in the presence of acids and bases. To simplify the task, the interaction of epoxy-compounds with the simplest inorganic molecules (CO_2, CS_2, COS, SO_2) will not be considered; this problem is discussed in detail in a recent review[4].

1. CONDENSATIONS IN THE PRESENCE OF BASES

a. Attack of the Epoxy-ring by Carbanions

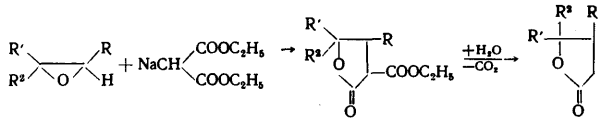
The most numerous examples of this type of interaction are the reactions of epoxy-compounds with α-dicarbonyl compounds, which lead to γ-lactones. The latter are formed, for example, in the reaction of sodioacetoacetic ester with epoxyethane[194], epoxypropane, epoxyethylbenzene[195], epichlorohydrin[196,197], the propyl, isopropyl[198], ethyl, and phenyl[199] ethers of glycidol, and $\beta\beta$-dimethyl- and α-phenyl-glycidic esters[200], the epoxy-ring being opened on the side of the least substituted carbon atom in all the cases enumerated:



1,2-Epoxybut-3-ene[195], 2,3-epoxypent-4-ene[201], and 1,2-epoxypent-3-ene[201] form a mixture of lactones, the products obtained as a result of the attack by the nucleophilic agent on the unsubstituted carbon atom predominating. Two lactones were isolated also in the interaction of sodioacetoacetic ester with 3-chloro-1,2-epoxybutene[202], the product ratio (4 : 1) illustrating the preferential ring opening in accordance with Krasusskii's rule. The reaction of epoxyethane[203] and epichlorohydrin[196,203] with methylsodioacetoacetic ester also leads to the corresponding lactones; epoxyethane reacts similarly also with benzoylacetic ester[204].

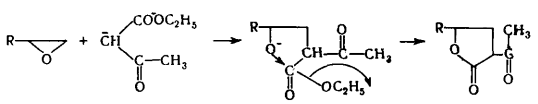
The least substituted carbon atom is also attacked in the reaction between sodiomalonic ester and epichlorohydrin[205], epoxyethylbenzene[206-208], 2,3-epoxybutene[206], epoxycyclohexane[209,210], epoxymethylcyclohexane, the epoxy-derivative from menthene[209], $\beta\beta$-dimethyl-[200,211], $\beta\beta$-dialkyl-[212], and β-phenyl-glycidic esters[213], the ethyl

and phenyl ethers of glycidol[199], and 3-dialkylamino-1,2-epoxypropanes[214], as a result of which γ-lactones are again formed:



It has been shown recently that sodiomalonic ester reacts with epoxyethylbenzene attacking the rings at two different carbon atoms[215] and not exclusively at the primary carbon atom, as was claimed in early investigations[206,207]. Cristol and Osman[216] also confirmed that epoxyethylbenzene is attacked preferentially and *p*-(epoxyethyl)nitrobenzene entirely at the secondary carbon atom. Similar results were obtained by de Puy et al.[217], who established that epoxyethylbenzene is attacked to the extent of 60% at the secondary carbon atom and to the extent of 40% at the primary carbon atom.

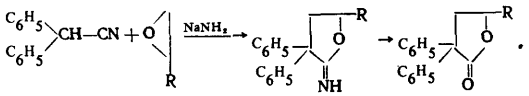
Lactones were also obtained in the reaction of sodiomalonic ester with the epoxy-derivative of dihydronaphthalene[209] and in the reactions of sodioethylmalonic ester with the ethyl and phenyl ethers of glycidol[199] and of methylsodiomalonic ester with 1,2-epoxy-3,4-dihydronaphthalene[218]. The mechanism of the above condensations was examined in the reaction with sodioacetoacetic ester by Adams and Vander-Werf[195] (see also Chelintsev[219]):



The condensation of epoxy-compounds with sodioacetoacetic and sodiomalonic esters takes place with high yields and can be used for preparative purposes[3,220].

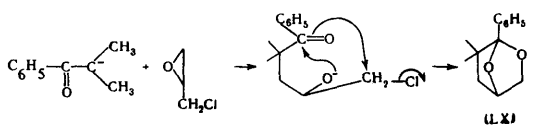
γ-Lactones are formed also in the reaction of epoxy-compounds with sodiocyanoacetic ester. In the presence of sodamide epoxyethylbenzene and 2,3-epoxybutene[221] give rise to stereoisomers of α-cyano-γ-lactones; under these conditions, as in the interaction between sodiocyanoacetic ester with ethyl and phenyl ethers of glycidol[199], the unsubstituted carbon atom of the epoxy-compound is attacked. Glickman and Cope[222] showed that epoxyethane reacts similarly, forming α-cyano-γ-butyrolactone[222].

Imidolactones, which are subsequently readily hydrolysed to γ-lactones, were obtained in the reaction of diphenylacetonitrile with a number of epoxy-compounds in the presence of sodamide[223,224]:



Under these conditions too, the carbanion attacks the primary carbon atom (see also Temnikova and Kovalevskaya[225]).

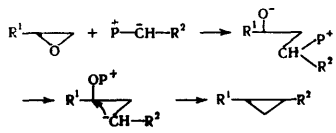
The interaction of epoxy-compounds with Ivanov's reagent also leads to γ-lactones[226-228]. The reaction of the sodio-derivative of isobutyrophenone with epichlorohydrin takes place in an interesting way[229]:



(LX)

The bicyclic product (LX) had been isolated earlier but its structure had not been demonstrated[230].

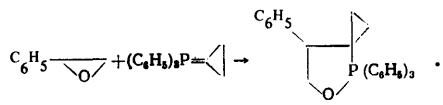
The interaction of epoxy-compounds with phosphorus ylides takes place in an unusual manner[231]. The reaction mechanism probably involves substitution in the epoxy-ring with subsequent rotation about the C–C bond and the closure of a five-membered ring, the subsequent rupture of which leads to the formation of cyclopropane in the following way[232-234]:



(LXI)

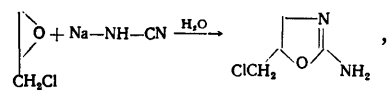
where R^1 = H or alkyl, P = Ph_3P, $(RO)_2PO$, or R_2PO, and R^2 = CN or COOR.

The formation of cyclopropanes by the above mechanism takes place only with reagents of the type $P^+-C^-H-R^2$, where R^2 is an electronegative group (CN, $COOC_2H_5$). The stabilisation of the carbanion (LXI) by these reagents favours the rupture of the intermediate five-membered ring[232-236]. The interaction of cyclopropylidenetriphenylphosphorane with certain epoxy-compounds gives rise to stable ring compounds[237], for example:

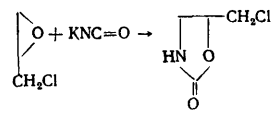


b. Attack of the Epoxy-ring by a Nitrogen Atom

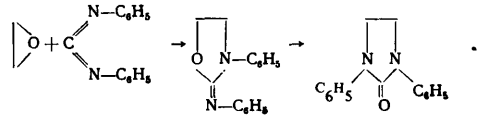
Epichlorohydrin and sodiocyanamide react in the cold in aqueous solution to form 2-amino-5-chloromethyloxazoline[238-239]:



while potassium isocyanate and ei ichlorohydrin give 5-chloromethyl-2-oxazolidinone[240]:

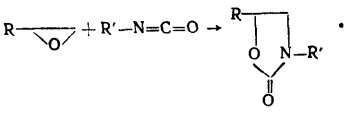


i.e. in such cases the primary carbon atom of the epoxy-ring is attacked. Pyridine, triethylamine, and lithium chloride catalyse the reaction of epoxyethane with carbodi-imides. The imino-oxazolidine formed initially rearranges under reaction conditions to 1,3-diphenyl-2-imidazolidinone[223]:

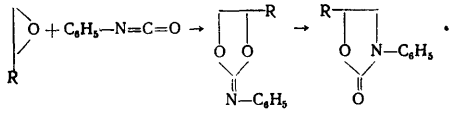


The interaction of epoxyethane, epoxypropane, epoxydodecane with phenyl and ethyl isocyanates in dioxan, dimethylformamide, and acetonitrile at 160–200°C [catalyst $(C_2H_5)_4NBr$ and KBr] leads to 2-oxazolidinones.

In this case the reaction involves the unsubstituted carbon atom[241]:



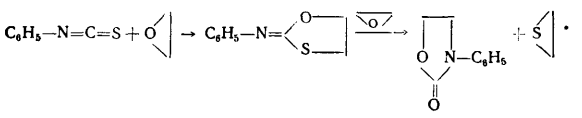
Dimethylbenzylamine catalyses the condensation of benzylepoxyethane and the phenyl ether of glycidol with phenyl isocyanate to the corresponding 2-oxazolidinones in yields up to 45%[242]. Pyridine, tribenzylamine, metal (zinc, lithium, and iron) chlorides, alkalis, etc. were used as catalysts for the reaction of aliphatic, aliphatic-aromatic, and alicyclic epoxy-compounds with phenyl isocyanate[191-193]. 2-Oxazolidinones were also obtained in the absence of a solvent at 180–200°C. Gulbins and Hamann[223,243] suggested that the initial products of this reaction are 2-phenylimino-1,3-dioxolans which isomerise to 2-oxazolidinones under the reaction conditions:



The occurrence of such isomerisation has been demonstrated by the conversion of 2-imino-1,3-dioxolans into 2-oxazolidinones at 200°C in the presence of lithium chloride (under conditions identical to those indicated above). However, this does not mean that dioxolans must necessarily be the primary products in all cases. Their formation is more evident under conditions of acid catalysis when the secondary carbon atom of the epoxy-ring in the oxonium complex is attacked and the nucleophilic centre in the phenyl isocyanate molecule is the oxygen atom. In the presence of basic catalysts, normal ring opening takes place and 2-oxazolidinones may be formed directly. Numerous examples of the synthesis of 2-oxazolidinones by the condensation of epoxy-compounds with cyanates, cyanuric acid, organic isocyanates, and urea and its derivatives, have been discussed in detail by Dyer and Swern[190,244].

c. Cyclisation with Participation of a Sulphur Atom

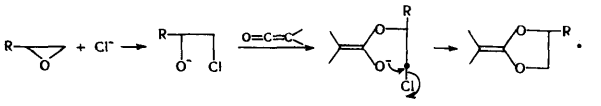
The interaction of epoxy-compounds with isothiocyanates takes place in a more complex manner than with isocyanates and is accompanied by various side processes: for example, epoxyethane and phenyl isothiocyanate give 2-oxazolidinone according to the mechanism[245]



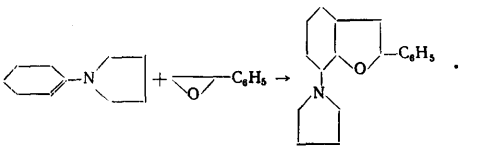
The reaction with alkyl isothiocyanates is even more complex. Without considering this process in detail, which is analysed in the review by Grobov et al.[4], we shall only mention that the epoxy-ring is attacked by the more highly polarised sulphur atom with subsequent S → O migrations[246].

d. Certain Other Cases

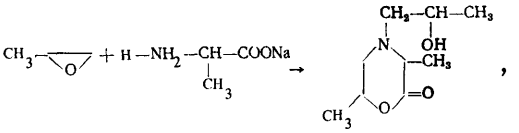
There are no data on the base-catalysed condensations of epoxy-compounds with carbonyl components. The formation of ketals in the interaction between epoxy-compounds and diphenylketen is noteworthy[223] and may be explained by the following mechanism:



The interaction of epoxyethylbenzene with enamines leads to cyclic products[247]:



Morpholone derivatives are obtained in the interaction between epoxypropane and certain aminoacids[248]:

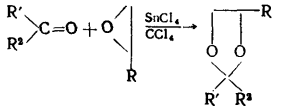


2. CONDENSATIONS IN THE PRESENCE OF ACIDS

The interaction of the epoxy-ring with polar groups having multiple bonds (carbonyl, cyano-, azomethine, etc.) might constitute a good method for the synthesis of new heterocyclic compounds. However, the small number of experimental data and almost total absence of any attempt to discover the laws governing these processes preclude for the moment the use of this method on an adequate scale.

a. Synthesis of 1,3-Dioxolans

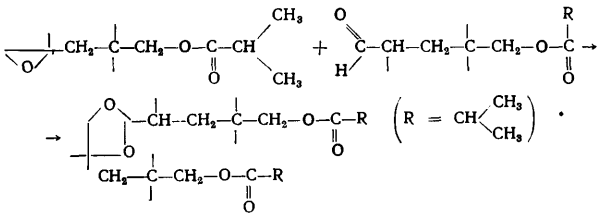
In 1861 Wurtz attempted for the first time to prepare 1,3-dioxolan by the direct condensation of epoxyethane with acetaldehyde[249]. The formation of 1,3-dioxolan as a side product was observed in 1906 in the catalytic synthesis of dioxan from epoxyethane[250]. It was suggested that the acetal is formed from epoxyethane and acetaldehyde formed by the isomerisation of the epoxy-compound. This was confirmed by the work of Bogert and Roblin[251], who obtained 1,3-dioxolans by the condensation of epoxyethane and epoxypropane with a number of aldehydes and ketones (benzaldehyde, hexanal, hexyl ethyl ketone, acetophenone):



$SnCl_4$, $SnCl_4.4H_2O$, $ZnCl_2$, $FeCl_3$, $SbCl_3$, $AlCl_3$, and $CaCl_2$, as well as HCl, H_2SO_4, and $POCl_3$ were chosen as catalysts. Best results were obtained with $SnCl_4$. In recent years the reaction of carbonyl compounds with epoxy-compounds has been applied to some extent in the synthesis of new 1,3-dioxolans. The interaction of epichlorohydrin and epibromohydrin with aliphatic aldehydes (acetaldehyde, propionaldehyde, butyraldehyde, crotonaldehyde, chloral) and also with ketones (diethyl

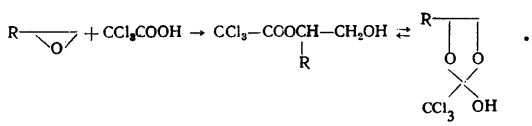
ketones, cyclopentadecanone, bromoacetophenone, benzophenone[252,253]), of epoxyethane, epoxypropane, epoxybutane, and epoxy-derivatives obtained from pseudo- and iso-butenes with a wide variety of aldehydes and ketones[254,255], and of glycidol ethers, 2,3-epoxybutene, and epoxyethylbenzene with acetone[256,257] has been investigated. Certain 1,3-dioxolans have been obtained as intermediates in the synthesis of antispasmodic compounds by the condensation of epichlorohydrin and epibromohydrin with various aromatic ketones[258,259]. The interaction of acetylenic epoxy-compounds with acetone, ethyl methyl ketone[260], cyclopentanone, and cyclohexanone[261] has been described.

1,3-Dioxolans may be formed also as side products in the intramolecular reactions of epoxy-compounds. House observed their formation in a study of the isomerisation of *cis*- and *trans*-2,3-epoxybutanes in the presence of $MgBr_2$ and BF_3.[262] The isomerisation of 4,5-epoxy-2,2,4-trimethylpentyl isobutyrate to a tetrahydrofuran derivative under the influence of boron trifluoride-ether is accompanied by the formation of dioxolan, which is probably obtained as a result of the interaction between the initial epoxy-compound and an aldehyde[134]; the formation of the latter under the reaction conditions has been demonstrated:



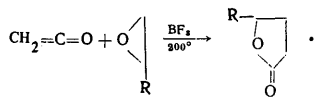
In the presence of inorganic acids (HCl, H_2SO_4) benzoin reacts with epichlorohydrin, and epoxyethane and epoxypropane react with formaldehyde, yielding 1,3-dioxolans[263,264]. The preparation of certain ketals containing a silicon atom or a triple bond in the 4-position of the ring has been described[265-267].

Aldehydes and ketones are usually employed as the carbonyl components in the synthesis of acetals and ketals, but Hibbert[268,269] and Meerwein[270,271] attempted to extend the applications of this reaction. In Meerwein's report on the preparation of 2-hydroxy-1,3-dioxolans by the condensation of di- and tri-chloroacetic acids with epoxyethane, epichlorohydrin, and glycidic ester at room temperature, it is stated that the reaction product can exist as a tautomeric mixture of cyclic and linear compounds. The cyclic structure is indicated by the stability of the product in the presence of alkalis and the ease with which it is hydrolysed by acids, which is typical for a ketal:

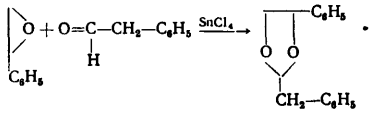


Under the same conditions, monochloroacetic and acetic acids yield the half-esters, e.g. $CH_2Cl-COOCH_2CH_2OH$.

The possibility of using ketens for the synthesis of 2-methylene-1,3-dioxolans appears to be attractive but only one such example is described in the literature. Diphenylketen was allowed to react in a sealed tube with epoxyethane at 200°C for 4–5 h, forming a dioxolan (catalyst LiCl).[223] The interaction of keten with epoxyethane, epoxypropane, and epichlorohydrin under acid conditions (BF_3) leads to the corresponding γ-lactones[272]:

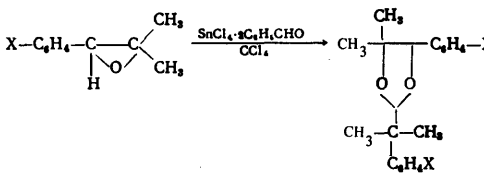


The behaviour of epoxy-derivatives obtained from substituted styrenes is striking. The attempt to condense epoxyethylbenzene with acetophenone did not give the desired results even in the presence of a large excess of epoxy-compound: the main reaction product was 2-benzyl-4-phenyl-1,3-dioxolan[273,274], probably formed as a result of the interaction between the epoxy-compound and phenylacetaldehyde (an isomerisation product of the epoxy-compound):



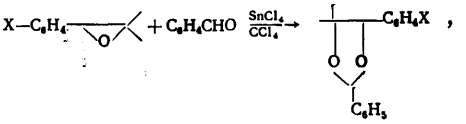
2-Benzyl-4-phenyl-1,3-dioxolan formally corresponds to the dimer of epoxyethylbenzene; previously the structure of 1,4-dioxan was attributed to the dimer, which is formed from the epoxy-compound[275] or the corresponding glycol[276,277] under acid conditions.

The behaviour of the epoxy-derivatives obtained from *para*-substituted $\beta\beta$-dimethylstyrenes in the condensation with benzaldehyde in the presence of $SnCl_4$ was investigated[278]. It was found that, for epoxy-compound : benzaldehyde : catalyst ratios of 2 : 2 : 1 (under these conditions, the benzaldehyde is fully bound in a complex with $SnCl_4$), only the so called "dimers" of epoxy-compounds—2-benzyl-1,3-dioxolans—are formed:



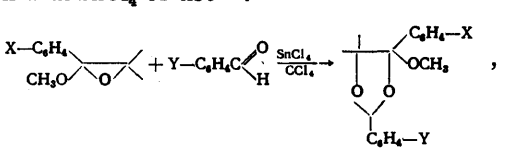
where X = Cl, H, or CH_3.

In the presence of an excess of the carbonyl compound (aromatic aldehyde) normal products are formed:



where X = Cl, H, or CH_3.

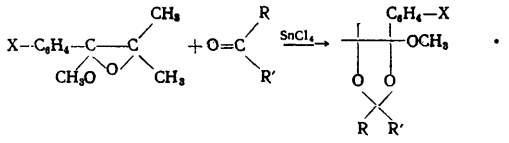
However, the epoxy-derivatives obtained from α-methoxy-$\beta\beta$-dimethylstyrenes condense with aromatic aldehydes regardless of whether the aldehyde is bound in a complex with $SnCl_4$ or not[279]:



where X = Cl, H, CH_3, or CH_3O and Y = Cl, H, or CH_3.

The very sharp difference between the behaviour of the epoxy-compounds can be accounted for by the different stabilities of the carbonium ions generated on opening of the ring.

Temnikova and Gontarev obtained a large amount of 4-methoxy-1,3-dioxolans by the condensation of methoxy-derivatives of epoxy-compounds with various aldehydes and ketones [280-283]:

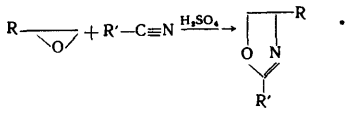


The presence in the products obtained of a system of acetal bonds may prove to be of significant interest.

An adequate mechanism has not been proposed [251,252,278] for the condensation of epoxy-compounds with carbonyl compounds.

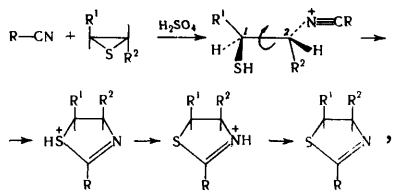
b. Synthesis of 2-Oxazolines and 2-Oxazolidines

Oda et al. [284] were the first to isolate 2-oxazolines by condensing epoxyethane, epoxypropane, and epichlorohydrin with acetonitrile, phenylacetonitrile, benzonitrile, and isobutyronitrile in concentrated sulphuric acid:



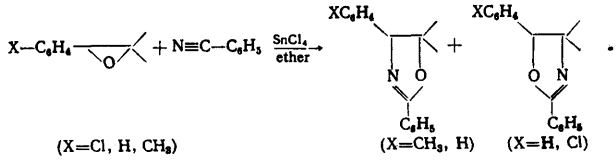
After the interaction of epoxypropane and acetonitrile, they succeeded in isolating two oxazolines: 2,2-dimethyl- and 2,5-dimethyl-Δ^2-oxazolines in proportions of 7 : 3, i.e. the opening of the epoxy-ring at the secondary carbon atom predominates. Unfortunately, the systems investigated do not allow an interpretation of the stereochemistry of the reaction.

The interaction of episulphides, which are very close in their properties to epoxy-compounds, with nitrile in concentrated sulphuric acid takes place according to the mechanism [285,286]



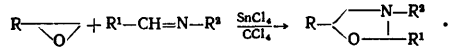
i.e. involves nucleophilic attack from the rear with formation of a nitrilium salt and subsequent rotation of the C^1-C^2 bond and ring closure. The validity of extending this mechanism to epoxy-compounds has not yet been proved.

Temnikova and Zhesko were the first to isolate a 4-methoxy-Δ^2-oxazoline by the reaction of 1,2-epoxy-1-methoxy-2-methyl-1-phenylpropane with benzonitrile in the presence of $SnCl_4$ in carbon tetrachloride [287]. They suggested the structure of 4-methoxy-Δ^2-oxazoline for this product in accordance with the usual rule governing the rupture of the epoxy-ring in methoxy-derivatives of epoxy-compounds under acid conditions. The epoxy-derivatives obtained from *para*-substituted $\beta\beta$-dimethylstyrenes did not yield appreciable amounts of oxazolines in the condensation with benzonitrile under these conditions [288]. When carbon tetrachloride was replaced by butyl ether, the desired products were obtained, the *para*-substituents in the molecule of the epoxy-compound having a decisive influence on the mode of attack on the epoxy-ring by the nitrile. The mechanism below shows that, with X = Cl, benzonitrile attacks the tertiary carbon atom and, with X = CH_3, the secondary carbon atom:



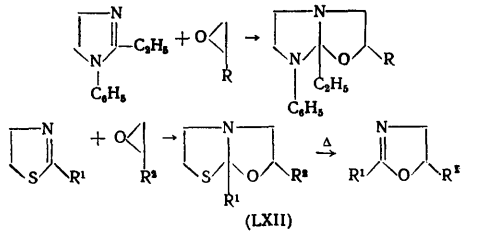
The unsubstituted epoxy-compound gives two products.

The condensation of Schiff bases with epoxyethane, epoxypropane, and epichlorohydrin in the presence of $SnCl_4$ leads to oxazolidines [289]. The reaction is carried out in carbon tetrachloride at 10–20°C. The yield of the final product greatly depends on the structure of the substrate and as a rule decreases when BF_3 is employed instead of $SnCl_4$:



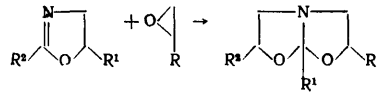
The interaction with t-butylazomethine does not require a catalyst, the introduction of which only reduces the yield.

The condensation of epoxy-compounds with certain imidazolines and thiazolines with C=N bonds in the ring gives rise to bicyclic products [290,291]:

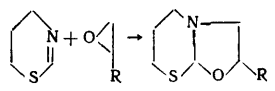


(LXII)

In the case of thiazolines the product (LXII) is unstable under the reaction conditions and is converted into oxazoline, which reacts with a further molecule of the epoxy-compound:

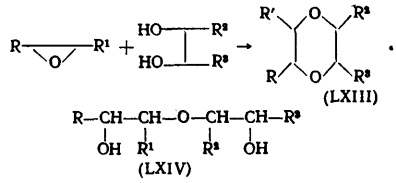


This mechanism is confirmed by the isolation of stable bicyclic products in the condensation of epoxy-compounds with thiazines [290]:



c. Certain Special Cases

The interaction of epoxyalkanes with glycols [292-294] yields dioxans (LXIII). The reaction proceeds via the intermediate formation of (LXIV), further reaction of which giving rise to dioxan:

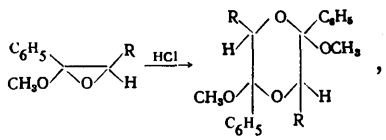


(LXIII)

(LXIV)

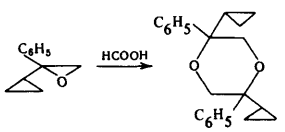
3. DIMERISATION AND n-CYCLOMERISATION OF EPOXY-COMPOUNDS

Numerous data have been published on the formation from epoxy-compounds of dimeric products to which the structure of 1,4-dioxans has been attributed. The industrial manufacture of 1,4-dioxan from epoxyethane is generally known; epoxypropane gives dimethyldioxan[295]. More detailed studies of the polymerisation products of epoxypropane, 1,2-epoxybutane, and epichlorohydrin initiated by BF_3, $SnCl_4$, and triethyloxonium fluoroborate showed that the low-molecular-weight products obtained from epoxy-propane, for example, consist of a mixture of dimers (*cis*- and *trans*-isomers of 2,5- and 2,6-dimethyl-1,4-dioxans), tetramers, pentamers, and hexamers[296,297]. It appears likely that the dimers are formed from methoxy-derivatives of the epoxy-compounds in acid media by the mechanism[298-300]:

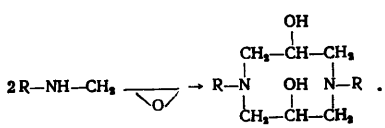


where R = CH_3, C_2H_5, or C_6H_5.

The reactions of epoxyethylbenzene in the presence of acids are usually accompanied by the formation of a high-boiling product to which the structure of 1,4-dioxan was attributed initially[275]. Summerbell and coworkers[273,274] showed that the main product of the reaction of epoxy-ethylbenzene in the presence of $SnCl_4$ is 2-benzyl-4-phenyl-1,3-dioxolan with only a slight admixture (up to 5%) of the isomeric 2,5-diphenyl-1,4-dioxans (see also Pasika[301]). Tiffeneau and Levy[302,303] proposed the 1,4-dioxan structure also for the dimerisation product of epoxy-$\beta\beta$-dimethyl-ethylbenzene, but the latter proved to be in fact a derivative of 2-benzyl-1,3-dioxolan[278]. Of the other examples available, mention may be made of the dimerisation of epoxy-α-methylethylbenzene to 2,5-dimethyl-2,5-diphenyl-1,4-dioxan[304] and of the work of Oda and coworkers on the synthesis of 1,4-dioxan by the cleavage of 1-cyclopropyl-1,2-epoxyethylbenzene with formic acid[305]:



Alkyl-2,3-epoxypropylamines are converted into cyclic dimers—1,5-dialkyl-1,5-diazacyclo-octane-3,7-diols[306,307]:



Mixed condensation of two glycidylamines is also known to occur.

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