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Base-catalysed Rearrangements of Epoxides

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The principal characteristics of the rearrangements of epoxides due to the elimination of α-, β-, γ-, δ-, and ε-protons under the influence of bases have been considered.
The bibliography includes 135 references.

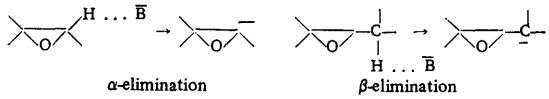
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I. INTRODUCTION

Numerous monographs and reviews have been devoted to the reactions of epoxides[1-7]. Two types of reactions—addition and isomerisation—are the most characteristic of epoxides. Until recently, the study of the chemistry of epoxides was confined in most cases to reactions in which nucleophilic agents added to them and to their acid-catalysed isomerisations to carbonyl compounds. Recently new reactions of epoxides catalysed by strong bases were discovered. This review is a first attempt at a systematic account of the data which have accumulated on the isomerisation of epoxides in the presence of strong bases, i.e. processes which are not accompanied by the intermolecular addition of any external agents to the epoxides.

In a study of a base-catalysed isomerisation of the so called "non-functional" epoxides, i.e. epoxides without any other functional groups, Crandall showed that, depending on the reaction conditions, strong bases abstract a proton from the α- or β-position in relation to the oxygen atom of the epoxy-ring[8,9]:

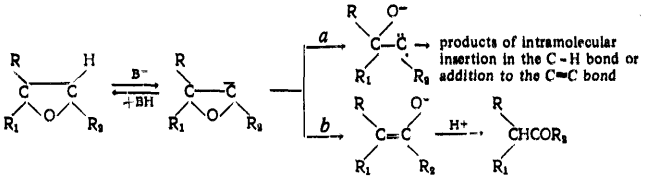


α-elimination β-elimination

When the epoxide molecule contains an electron-accepting functional group, there is a possibility of the elimination of the proton from the carbon atom adjoining this group (processes involving the elimination of a proton from a heteroatom in the functional group are not discussed in this review). In general one can consider the elimination of α-, β-, γ-, δ-, and ε-protons, etc. and the various reactions of epoxides due to these processes.

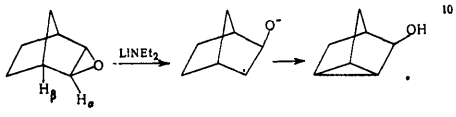
II. ELIMINATION OF AN α-PROTON

The majority of the cases of elimination of the α-proton described hitherto have been observed with non-functional epoxides or epoxides having aromatic substituents, since the introduction of any functional group into the side chain of the epoxide favours the removal of a proton from other parts of the molecule. The α-elimination results in the formation of an epoxide anion which subsequently isomerises according to a carbenoid (*a*) or an anionic (*b*) mechanism†, depending on the reaction conditions and the structure of the initial epoxide:



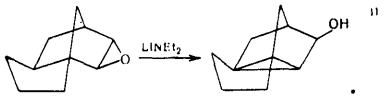
In the presence of hydrogen atoms in the α- and β-position, β-elimination takes place as a rule. Two cases constitute exceptions.

1. The approach of the base to the β-proton is greatly hindered as a result of which α-elimination takes place. For example, epoxynorbornane (I) isomerises to a nortricyclanol as a result of the intramolecular insertion of β-alkoxycarbene in the C — H bond[10], so that the approach of the base to the β-H atom is sterically hindered:



(I)

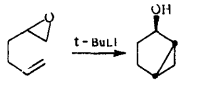
The epoxide (II) reacts similarly:



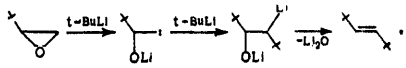
(II)

2. α-Elimination is observed with epoxycycloalkanes containing 8 — 10 carbon atoms in the ring. A characteristic property of such rings is transannular reactions owing to the closeness in space of the opposite carbon atoms[12,13]. Thus the epoxy-derivatives of *cis*- and *trans*-cyclo-octenes isomerise on treatment with $LiNEt_2$ to the corresponding bicyclo-octanols as a result of a transannular carbenoid insertion[14,15].

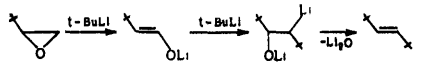
The attempt to trap the carbene in an intermolecular reaction involving addition to the C=C bond was unsuccessful, while the analogous attempt in the intramolecular reaction succeeded[16]:



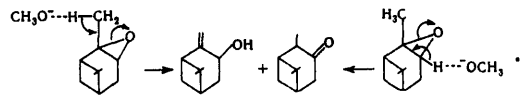
Crandall and coworkers[17] observed that, when t-butyl-epoxyethane is treated with t-butyl-lithium, *trans*-di-t-butylethylene is formed in high yield. The authors explain this finding by the formation of a carbene and its subsequent insertion in the t-butyl-lithium molecule:



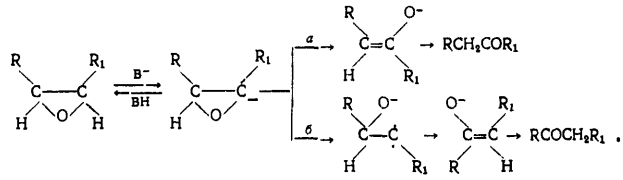
The simpler pathway for the formation of di-t-butylethylene via the intermediate formation of the product of the addition of t-butyl-lithium to the epoxide is rejected, since the product of this reaction (an alcohol) would not be dehydrated under the reaction conditions. We believe that the recently observed[18] enhanced tendency of lithium alkoxides derived from allyl alcohols to undergo addition reactions with lithium alkyls makes it unnecessary to postulate the insertion of a carbene in the t-butyl-lithium molecule, since the reaction can take place according to the mechanism



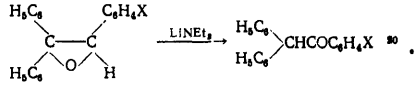
The isomerisation of alkyl-substituted epoxides in the presence of strong bases to allyl alcohols (β-elimination, see p. 405) is usually accompanied by the formation of ketones as a side reaction. For example, the isomerisation of the epoxy-derivative of α-pinene in the presence of sodium methoxide leads to pinocarveol and pinocarvone[19]:



A control experiment showed that pinocarveol isomerises only slightly to pinocarvone under the reaction conditions. Similar results were obtained also in a few other cases[8,16]. All these findings suggest that ketones are formed mainly via a pathway involving the initial elimination of the α-proton from the epoxide[8]. Further conversion of the epoxidecarbanion into the ketone can theoretically take place via two mechanisms:

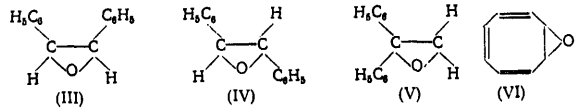


As a rule the reaction follows pathway *a*, as can be seen from the following example:



However, it is noteworthy that aryl substituents may stabilise the carbanion.

Carbonyl compounds are the main products of the base-catalysed isomerisation of the epoxides (III) — (VI)[20-22]:

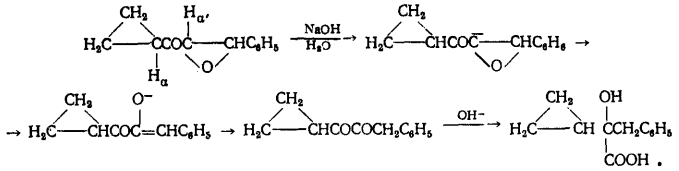


(III) (IV) (V) (VI)

The isomerisation of α-ketoepoxides in an alkaline medium does not usually stop at the stage involving the

† The mechanisms quoted do not imply that a "free" carbene or carbanion is formed during the isomerisation. The reactions are classified on the basis of the final products.

formation of a α-diketone[23-29], since the latter undergoes the benzil rearrangement under the reaction conditions[29]:

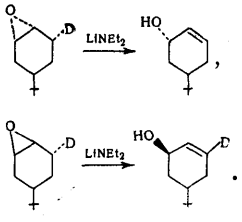


Of the two possible pathways for the conversion of the ketoepoxide—the Favorskii rearrangement (with the abstraction of a proton from the α-carbon atom as the initial stage) and the benzil rearrangement (with the abstraction of a proton from the α'-carbon atom as the initial stage)—in the above example the second actually occurs, owing to the greater mobility of the hydrogen atom in the α'-position.

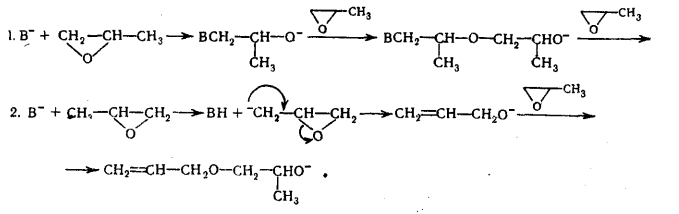
In conclusion we may note a unique case of the isomerisation of epichlorohydrin and its homologues to α-chloroketones as a result of the elimination of the α-proton under the influence of lithium orthophosphate. β-Elimination products were not detected in these reactions. According to Sheng[30], this is evidence of a considerable increase of the mobility of the proton linked to the carbon atoms in the epoxy-ring under the influence of the adjacent chloromethyl group.

III. ELIMINATION OF A β-PROTON

In a study of the mechanism of the base-catalysed isomerisation of the epoxy-derivatives of *cis*- and *trans*-oct-4-enes (labelled with deuterium in 4- and 5-positions) to allyl alcohols, Cope and Heerin demonstrated unambiguously that the first reaction stage is the abstraction of a proton from the β-position of the epoxide[31]. However, it is not clear whether the process proceeds via the intermediate formation of a carbanion or via a concerted mechanism. A further step towards the understanding of the β-elimination mechanism was taken by Thummel and Rickborn[32], who showed that the conversion of epoxides into aryl alcohols is a *cis*-elimination reaction:

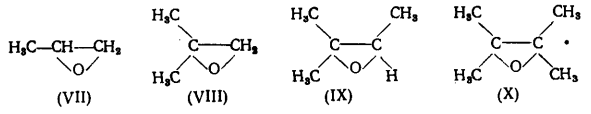


A study of epoxide polymers obtained in the presence of alkaline catalysts revealed a high content of unsaturated terminal groups[33]. It has been suggested[34] that the initiation and propagation of the polymer chain may be represented by mechanism (1), while the unsaturated terminal groups are formed as a result of the competing reaction (2):



The latter leads to a lowering of the molecular weight, since the abstraction of a proton from the β-position of the monomer by the growing polymer chain leads to chain termination[35].

In a study of the polymerisation of epoxides in dimethyl sulphoxide catalysed by potassium t-butoxide, Price and Carmelite[36] showed that the yield of the polymer and its molecular weight decrease in the series of epoxides (VII) > (VIII) > (IX) > (X). The yield of allyl alcohols increases simultaneously in the same sequence:



The ratio of the addition and β-elimination products is determined to a large degree by the basicity of the alkaline agent. As a rule, the stronger the base the lower the yield of the addition product. For example, in the presence of n-propyl-lithium or n-butyl-lithium epoxycyclohexane isomerises to cyclohex-3-enol and a small amount of 2-alkylcyclohexanol, while in the presence of allylsodium and allylmagnesium bromide, only the alkylation products were obtained[37] (see also Bedos[38,39]).

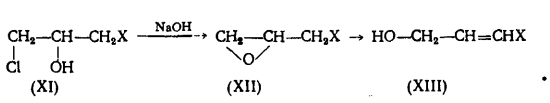
A comparative study of the effects of base strength on the relative amounts of the alkylation and β-elimination products from epichlorohydrin was made by Fabris[40].

The bulk of the base and the steric accessibility of the reaction centre have a considerable influence on the proportions of the addition of β-elimination products. It has been shown[41] that the rates of abstraction of a proton from primary, secondary, and tertiary alkyl groups decrease in the series primary $\gg$ secondary $\gg$ tertiary. The introduction of a methyl group into the epoxy-ring greatly facilitates the conversion of these epoxides into allyl alcohols. The epoxy-derivatives of 1-methylcycloalkenes[42], α-pinene[8,43-46], Δ^3-carene[44-47], β-diisobutene[8], and many others[48,49] isomerise in this way.

Methyl-substituted epoxides can isomerise to allyl alcohols under very mild conditions, for example in chromatography on alumina[50-54] and on treatment with aluminium alkoxides[55,56] and di-isobutylaluminium[57] and methoxyaluminium[58] hydrides.

The isomerisation of a series of epoxycycloalkanes to allyl alcohols as a result of the elimination of a β-proton has been described[8,43,59-64].

The elimination of a β-proton is greatly facilitated in the presence of an electron-accepting substituent in the methylene (or methylidyne) group attached to the epoxy-ring. It was noted long ago that the principal products of the dehydrohalogenation of the chlorohydrins (XI), where X = SO_2Ar,[65] CN,[66] $COOCH_3$,[67] and C≡C – R[68-72], are not the epoxides (XII) but the alcohols (XIII):

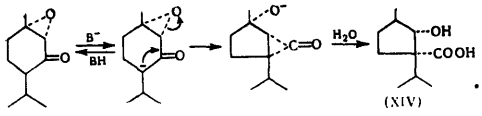


It has been shown in a number of studies that epoxides of type (XII), where X = Cl [40] (c.f. Sheng[30]), NO_2,[73] PR,[74] and CH = CHR [75] also readily isomerise to allyl alcohols.

IV. ELIMINATION OF A γ-PROTON

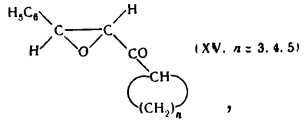
The base-catalysed abstraction of a proton from the carbon atoms in the epoxy-ring (α-elimination) is facilitated by the presence in the ring of a heteroatom and the shift of electron density towards it. Since the epoxy-ring exhibits an *I* effect[76-79], the relative ease of β-elimination is understandable. The abstraction of a proton from a carbon atom in the side chain of the epoxide is particularly easy when an adjoining electronegative group is present (C = O, CN, COOR). Rearrangements of "functional" epoxides of this kind will be considered in the present section.

The Favorskii rearrangement of α-epoxyketones is a well known example of the base-catalysed isomerisation of epoxides as a result of the elimination of a γ-proton. For example, it has been shown in a number of investigations[80-86] that, in the presence of bases (OH^-, OR^-), the epoxy-derivative of piperitone rearranges to the hydroxy-acid (XIV):



(XIV)

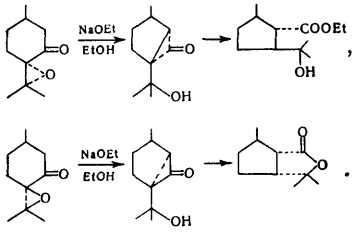
Analogous reactions of the epoxy-derivatives of isophorone and α-epoxyketones of type (XV),



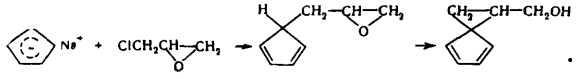
(XV, n = 3, 4, 5)

have been described[29,86].

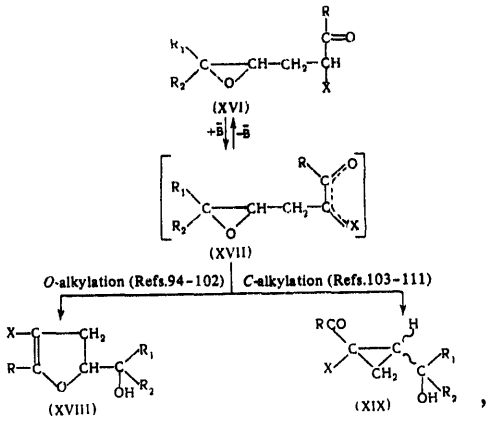
The study of the Favorskii rearrangements of the epoxy-derivatives of *cis*- and *trans*-pulegones showed that in both cases the process is stereospecific[87-90]:



Yet another example of the base-catalysed isomerisation of an epoxide as a result of the elimination of a γ-proton has been described[91]:

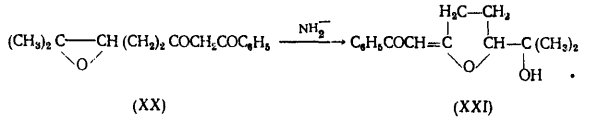


In a series of studies, Temnikova, Ershov, and coworkers investigated in detail the isomeric conversions of epoxides of type (XVI) containing in the side chain the RCO — CH — X fragment, which is capable of mesomerism. Depending on the nature of the substituents R and X, in an alkaline medium the epoxides (XVI) isomerise as a result of the intramolecular *O*-alkylation of the RCO — CH — X fragment with formation of 4,5-dihydrofurans (XVIII) or the *C*-alkylation products of the same fragment—derivatives of cyclopropane (XIX)‡:



where R = CH_3, XC_6H_4, OCH_3, or OC_2H_5, X = C_6H_5, CH_3 H, OCH_3, OC_2H_5, CN, $COCH_3$, or COC_6H_5, and R_1, R_2 = H, CH_3, or XC_6H_4.

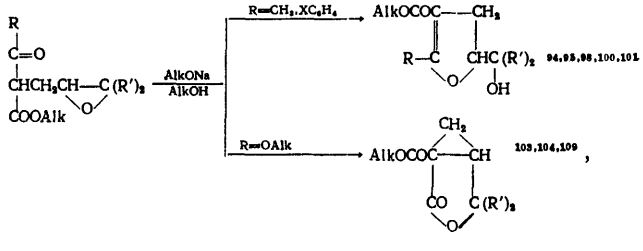
The base-catalysed isomerisation of the γε-diketo-epoxide (XX) results in the formation of exomethylene-tetrahydrofuran (XXI)[112]:



(XX) (XXI)

In contrast to the analogous intermolecular processes leading exclusively to *C*-alkylation products[3], intramolecular alkylation in systems of type (XVI) results as a rule in the formation of *O*-alkylation products[94-102,112,113-116]. This can be accounted for by the dominant role of steric factors in the above intramolecular reactions[118,119], since the steric requirements which must be met by the geometry of the transition state in *O*-alkylation are usually less rigorous than in *C*-alkylation; moreover, *O*-alkylation leads to less strained systems than does *C*-alkylation.

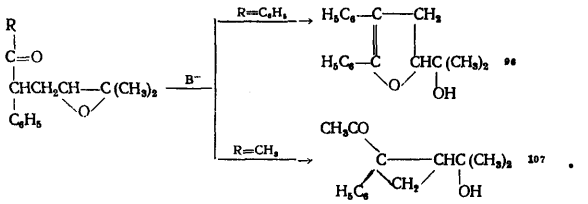
Another important factor determining the mode of intramolecular alkylation in systems (XVI) with a similar structure is the degree of delocalisation of the charge in the intermediate carbanion (XVII). A high degree of delocalisation of the charge in the anion leads to the formation of *O*-alkylation products, i.e. in this case alkylation takes place at the most electronegative reaction centre[117]:



94,95,98,100,101
103,104,109

‡ The possibility of the base-catalysed isomerisation of cyclopropyl ketones to 4,5-dihydrofurans has been discussed[92,93].

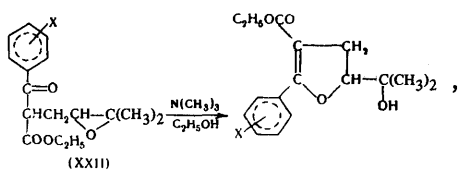
where R' = CH_3 or XC_6H_4 and Alk = CH_3 or C_2H_5.



Experimental data agree qualitatively with the calculations by the LCAO-MO method[120].

The mode of base-catalysed isomerisations of epoxides (XVI) is determined mainly by internal (structural) factors. A change in external conditions (the solvent, the basic catalyst, and temperature) does not as a rule affect the site of intramolecular alkylation.

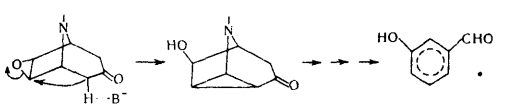
Kinetic studies on the mechanism of the isomerisation reaction[121]



(XXII)

where X = H, *p*-CH_3, CH_3O, Br, or *m*-Cl, show that the reactions of epoxides (XXII) having electron-donating substituents (particularly with X = *p*-CH_3O) involve predominantly a relatively non-polar transition state and a synchronous mechanism including the abstraction of a proton from the carbon atom of the keto-form (XXII) with the subsequent intramolecular *O*-alkylation accompanied by a transfer of the reaction centre. In the case of epoxides (XXII) with electron-accepting substituents, a proton is abstracted in the first stage from the oxygen atom of the enolic form of the β-ketoester (XXII); subsequently the oxygen atom of the enolate anion formed attacks the carbon atom of the epoxy-ring. A characteristic feature of the last transition state is the *cis*-orientation of the negatively charged oxygen atom and the residue containing the epoxy-rings§.

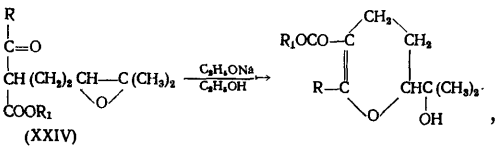
The above reactions include certain rearrangements in the benzonorbornene series and certain alkaloids[123-125]. For example the alkaloid skopinone (XXIII) is converted into *m*-hydroxybenzaldehyde in the presence of bases. It is suggested that the initial stage in this rearrangement is the elimination of a γ-proton with subsequent intramolecular *C*-alkylation[124,125]:



(XXIII)

V. ELIMINATION OF δ- AND ε-PROTONS

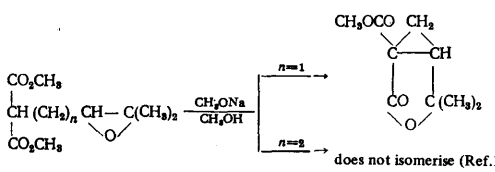
Temnikova, Ershov, and coworkers showed that epoxides of type (XXIV) isomerise in an alkaline medium as a result of intramolecular *O*-alkylation with formation of 5,6-dihydro-1,4-pyrans[113-116,126]:



(XXIV)

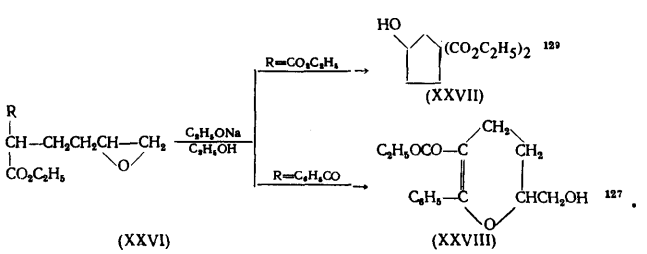
where R = CH_3 or XC_6H_4 and R_1 = CH_3 or C_2H_5.

According to a kinetic study, the first stage of the process is the elimination of a δ-proton under the influence of the base. This results in the formation of a mesomeric carbanion, which isomerises to the corresponding dihydropyran[127]. Derivatives of cyclobutane or cyclopentane, i.e. *C*-alkylation products, were not detected in the reactions investigated[113-119]. Nor are they formed on treating with bases under severe conditions the epoxide (XXV, *n* = 2), the homologues of which, for example (XXV, *n* = 1), isomerise under analogous conditions to cyclopropane derivatives[103,104,109]:



(XXV)

Another homologue of the epoxide (XXV, *n* = 2), namely (XXVI, R = $COOC_2H_5$), readily rearranges to a substituted cyclopentane (XXVII), while the epoxide (XXVI, R = C_6H_5CO) isomerises under analogous conditions as a result of intramolecular *O*-alkylation with formation of the dihydropyran (XXVIII):



(XXVI) (XXVII) (XXVIII)

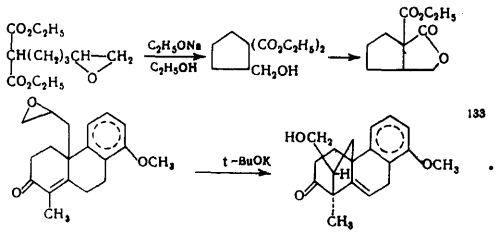
This difference in the mode of isomerisation emphasises yet again the relation between the degree of delocalisation of the charge in the intermediate mesomeric anion and the mode of isomerisation of epoxides with mobile hydrogen atoms in the carbon side chain[118] (cf. p. 406).

The difference between the reactivities of the epoxides (XXV, *n* = 2) and (XXVI, R = $COOC_2H_5$) may be accounted for by steric hindrance to cyclisation. It is noteworthy that derivatives of cyclobutane are not formed in either case owing to the comparative difficulty of the formation of a four-membered ring[130].

Several examples of the isomerisation of epoxides to allyl alcohols as a result of the elimination of a δ-proton have been described[131,132].

§ ^1H NMR spectroscopic data indicate rotation about the C=C bond in the enolate anions of carbonyl compounds even at comparatively low temperatures[122].

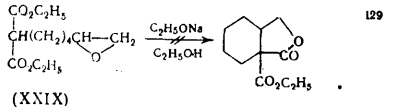
The elimination of a ϵ-proton with subsequent intramolecular *C*-alkylation leads as a rule to the formation of cyclopentanes[129,133-135]:



133

In the examples quoted intramolecular attack is directed to the sterically more hindered secondary carbon atom of the epoxy-ring. These results agree with kinetic studies[130], according to which the rate of formation of a five-membered ring in the intramolecular *C*-alkylation reaction is approximately 1000 times faster than the rate of formation of a six-membered ring.

The difficulty of the formation of a six-membered ring is demonstrated by the unsuccessful attempts at the isomerisation of the epoxide (XXIX):



129

(XXIX)

In conclusion we may note that the study of the base-catalysed rearrangements of epoxides is not only of purely chemical interest, since epoxides are biogenetic precursors of many natural products[131-135]. The isomeric transformations discussed above can probably serve as models of certain natural processes.

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