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Molecular Rearrangements in the Series of Carane Derivatives

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The available information about the molecular rearrangements of carane derivatives in addition, elimination, and substitution reactions are examined and the structural and steric principles which determine the nature of the rearrangements are analysed. A systematic account is given of data concerning the changes in the carane structure in various reactions involving rearrangements with participation of three-membered and six-membered rings.
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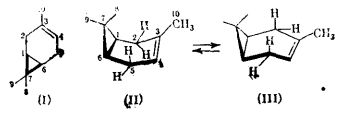
I. INTRODUCTION

Extensive factual data have now accumulated on the chemistry of bicyclic terpene derivatives of the carane series. Since the beginning of the 1960's, the stereochemistry of carane derivatives has been investigated vigorously, largely as a result of the application of various physical methods for the study of steric structure and the principles of conformational analysis. In the course of this research, numerous stereoisomeric carane derivatives have been synthesised, their configurations and conformations have been elucidated, and extensive information has been obtained about their reactivities. Data concerning the transformations of carane derivatives in various reactions have been partly surveyed in a number of reviews[1,2], but the results of stereochemical investigations on caranes have not yet been described systematically.

The present review deals with publications in the last ten years containing information about the molecular rearrangements of carane derivatives in addition, elimination, and substitution reactions, and analyses the structural and steric principles which determine the nature of the rearrangements.

II. THE STERIC STRUCTURES AND STEREOISOMERISM OF CARANE DERIVATIVES

The results of studies on the photosensitised oxygen-transfer reaction and an examination of Dreiding models have led to the hypothesis[4,5] that 3-carene (I)† molecules can exist in an equilibrium 1 : 1 mixture of two "boat" forms (II) and (III):



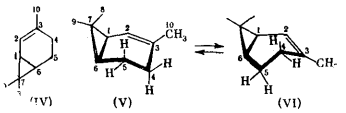
(I) (II) (III)

It follows from electron diffraction data[6] that the *syn*-boat conformation (II) exists. Examination of the ^{1}H NMR spectra demonstrated the possibility that 3-carene molecules exist as a mixture of two conformers, again with the *syn*-boat form (II) predominating[7,8].

† In this review the carane system is numbered in accordance with the IUPAC nomenclature[3].

On the basis of the results of a study of the conformational structure by the method of molar Kerr constants and of calculations of the energy difference between the conformers, taking into account steric and electrostatic interactions, Vereshagin and Vul'fson[9] concluded that conformer (II) predominates (to an extent of at least 90%) in the equilibrium mixture of (II) and (III). Despite its being sterically "filled" from the inner or β-side, the stability of form (II) has been accounted for[7] by the absence of a rigid interaction between the non-bonded 8-CH_3 group and the β-hydrogen atoms at $C_{(2)}$ and $C_{(5)}$, which is present in the boat form (III).

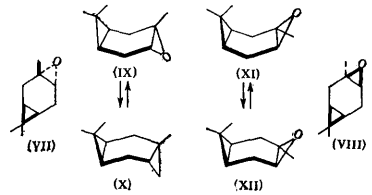
The conformation of the isomeric 2-carene (IV) was determined in a similar way. Of the two possible conformations (V) and (VI), the partial boat form (V) is preferable[7,10]:



(IV) (V) (VI)

It is seen from Dreiding models that the interatomic distance between 8-CH_3 and 4β-H in conformer (VI), amounting to 0.2 Å, is responsible for the steric hindrance in the molecule, which makes this conformation unfavourable. The results of the analysis of the steric interactions of the atoms on the basis of the correlations between the spin–spin coupling constants and the dihedral angles led to the adoption of conformation (V) also for 2-carene and its 4-substituted derivatives[11]. Arbuzov et al.[12] explained why conformation (V) is preferable by analysing the relative chemical shifts of the protons of the *gem*-dimethyl groups using dipole moments and molar Kerr constants.

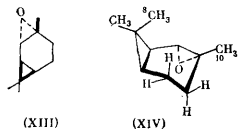
The configurations and conformations of the stereoisomeric 3,4-epoxycaranes (VII) and (VIII) and of 2,3-epoxycarane (XIII) have been determined with the aid of the same set of methods for the investigation of steric structure[8,9,12-16].



(VII) (IX) (XI) (VIII) (X) (XII)

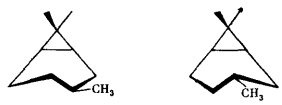
As for the corresponding olefin (I), conformations with the six-membered ring in the *syn*- and *anti*-boat forms are possible for the stereoisomeric 3,4-epoxycaranes. Form (IX) predominates in the equilibrium mixture of the conformers of the α- or *trans*-isomer (VII)(with respect to the steric orientation of the three-membered ring relative to the plane of the cyclohexane ring)[8,15]. Completely unanimous conclusions have not been reached concerning the choice of the preferred conformation of the β- or *cis*-isomer (VIII).[8,15-17]

α-2,3-Epoxycarane (XIII) has the partial boat conformation (XIV):[12]



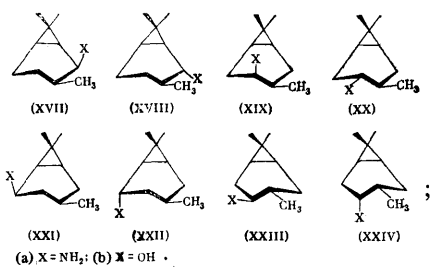
(XIII) (XIV)

It is evident from an examination of Dreiding models and ^{1}H NMR spectra of the stereoisomeric saturated *cis*- and *trans*-caranes‡ that their most probable steric structures must be the half-chair conformations (XV) and (XVI) with the equatorial (*e*) 10-CH_3 group[18]:



(XV) (XVI)

It has been shown by ^{1}H NMR spectra that the amines of the *cis*-carane series, stereoisomeric with respect to the position of the NH_2 group and the carbon atoms of the six-membered ring, have the half-chair conformation (XVIIIa–XXIIa), with rare exceptions[19]:

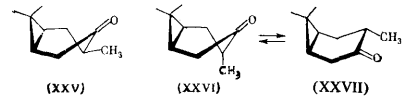


(XVII) (XVIII) (XIX) (XX)

(XXI) (XXII) (XXIII) (XXIV)

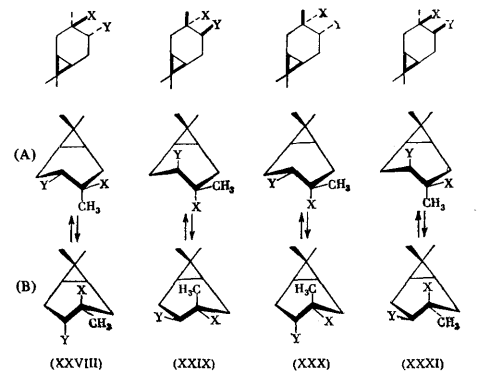
(a) X = NH_2; (b) X = OH.

In studies on the stereochemical structures using both physical and chemical methods, the half-chair conformation with the *e*-10-CH_3 group (XVIIb–XXIIb) was assigned to the isomeric secondary alcohols of the *cis*-carane series[20]. Preferred half-chair conformations have been found also for the stereoisomeric *trans*-4-caranols (XXIIIb, XXIVb).[14] Different conformations have been proposed for the two stereoisomeric 4-caranones (based on the results of studies by ^{1}H NMR and optical rotatory dispersion[14], dipole moment, and Kerr effect[21] methods and an examination of models): half-chair with the *e*-10-CH_3 group [form (XXV)] for the *cis*-isomer and a conformer intermediate between the half-chair with an axial (*a*) 10-CH_3 group [form (XXVI)] and a boat with the *e*-10-CH_3 group for the *trans*-isomer:



(XXV) (XXVI) (XXVII)

Calculations (based on Kitaigorodskii's mechanical model) on the equilibrium optimal conformations of the four isomers of carane-3,4-diol[22], two *trans*-3,4-dichlorocaranes[23], and *trans*-4-bromo-3-hydroxycarane[24], also led to the assumption that the half-chair conformation is preferred for the six-membered carane system of these compounds and it has been shown that 3,4-disubstituted caranes (XXVIII–XXXI) can exist in the form of equilibrium mixtures of conformers (A) and (B).



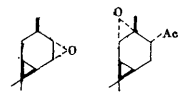
(XXVIII) (XXIX) (XXX) (XXXI)

(a) X=Y=OH; (b) X=Y=Cl; (c) X=OH, Y=Br; (d) X=OH, Y=OAc; (e) X=OH, Y=OTs; (f) X=Hal, Y=OAc; (g) X=Y=Br; (h) X=OH, Y=Cl.

Similar results were obtained in a study of 3,4-dihalogencaranes from dipole moments and Kerr effects[25,26] and of carane-3,4-diols, their monoethers, and ketols by infrared spectroscopy (an intramolecular hydrogen bond was detected)[27,28].

The conclusions concerning the steric structure of carane derivatives agree with the steric relations governing the occurrence of the corresponding reactions. In this respect carane derivatives have proved to be convenient objects for the elucidation of the stereochemical aspects of particular reactions, for the investigation of reaction mechanisms, since they make it possible to make comparative estimates of the influence of electronic, configuration, and conformation factors.

One of the characteristic features of the stereochemistry of carane derivatives is the stereospecificity of electrophilic addition to isomeric carenes having a double bond within the tricyclic system. In all the reactions investigated hitherto the double bond of carenes is attacked by the electrophilic species in the *trans*-position (or from the "α-side") with respect to the *endo*-condensed cyclopropane ring. Thus the only products of epoxidation by peracids are the *trans*-isomers (with respect to the mutual orientation of the three-membered rings) of epoxycaranes[11,12,14,29-33] (VII), (XIII), and (XXXII) and 4α-acetyl-2α, 3α-epoxycarane[34] (XXXIII).



(XXXII) (XXXIII)

Reactions involving photosensisised oxygen transfer to carenes[4,32], oxidative hydroboration of carenes[10,14],

‡ The conformational relations of carane derivatives are determined, on the one hand, by the mutual disposition of the 10-CH_3 group and the three-membered ring relative to the plane of the cyclohexane ring and, on the other hand, by the steric orientation of the functional groups in relation to the three-membered ring. Carane derivatives can be divided into two series, with *cis*- and *trans*-carane structures, on the basis of the type of the hydrocarbon skeleton.

hydroxylation with $KMoO_4$ and OsO_4–H_2O,[8,22,35] Friedel–Crafts acetylation, and the Prins reaction[11] lead to the formation of products with the α- (or *trans*-) orientation of the functional groups. Such stereospecificity of the attack on the double bond of carenes is caused, as can be seen from Dreiding models, by the hindered approach by the bulky electrophilic agents from the β-side shielded by the 8-CH_3 group.

A second distinctive feature of the behaviour of carane derivatives is a tendency towards a rearrangement of the hydrocarbon skeleton of the carane in different reactions.

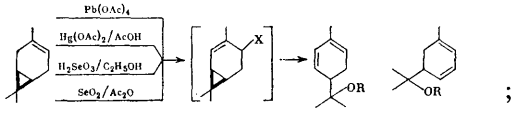
III. MOLECULAR REARRANGEMENTS OF THE CARANE STRUCTURE

The possibility of skeletal rearrangements due to the involvement of both rings is inherent in the very structure of the carbon system of carane, which contains condensed alkyl-substituted six- and three-membered rings.

1. HOMOALLYL REARRANGEMENTS

(a) Rearrangement Involving the Conjugated System of a Double Bond and the Cyclopropane Ring

The first evidence for the possibility of an allyl type of rearrangement of 1,3-diene systems in the series of carane derivatives was obtained in a study of the oxidation of 3-carene by $Pb(OAc)_4$, $Hg(OAc)_2$, and H_2SeO_3 under various conditions[36–39]. In all cases one of the main reaction products proved to be the ester of the dienol of the *p*-methane series (XXXV); the reaction with $Pb(OAc)_4$ also gave the ester of the dienol of the *m*-menthane series (XXXVIb):



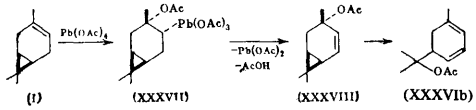
(I) (XXXIV) (XXXV) (XXXVI) ;

(1) X=Pb(OAc)$_3$
(2) X=HgOAc
(3 and 4) X=SeO_2H

(a) R=H
(b) R=Ac
(c) R=Et .

The conversion of 3-carene into *p*-menthadienol derivatives under the influence of these agents has been explained by postulating the intermediate formation of allyl-substituted 2-carene derivatives of the elements of type (XXXIV), the solvolysis of which is accompanied by the allyl rearrangement with participation of the vinyl cyclopropane fragment.

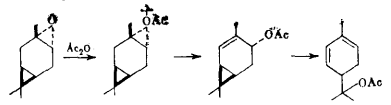
In order to convert olefins into acetates derived from allyl alcohols under the influence of $Pb(OAc)_4$, one can use also another pathway, involving the formation of an adduct of the olefin and $Pb(OAc)_4$ as an intermediate[40]. Accordingly, the oxidation of 3-carene with $Pb(OAc)_4$ should lead to the acetate of *m*-mentha-4,6-dien-8-ol (XXXVIb) [41,42] via the mechanism of the "4-carene → *m*-mentha-4,6-diene" rearrangement:



(I) (XXXVII) (XXXVIII) (XXXVIb) .

According to Whitham[43], $Pb(OAc)_4$ forms a *cis*-adduct with olefins. The adduct (XXXVII) is converted, with liberation of $Pb(OAc)_2$ and an AcOH molecule, into the acetate of *cis*-car-4-en-*trans*-3-ol (XXXVIII), which rearranges to (XXXVIb) under the reaction conditions.

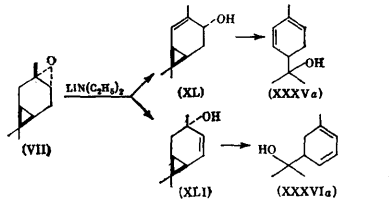
The formation of compound (XXXVb) from α-3,4-epoxycarane (VII) in the reaction with acetic anhydride has been explained similarly[44,45]:



(VII) (XXXIX) (XXXVb)

The identification of car-2-en-*trans*-4-ol (XXXIX) together with compound (XXXVb) in the products of these reactions was regarded as evidence for the possibility of the "2-carene → *p*-mentha-1,5-diene" rearrangement. The two isomeric products (XXXVb) and (XXXIX) were also identified in the products of the reaction of 3β,4α-dihalogenocaranes with AgOAc in acetic acid[46,47].

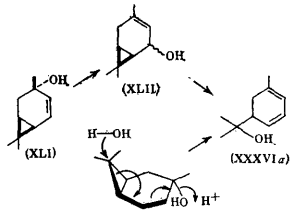
Presumably the rearrangement investigated occurs in the reaction of the allylic carenols (XL) and (XLI) (the products of the isomerisation of α-3,4-epoxycarane by a base[49]) with phthalic anhydride[49]; the rearranged alcohols were identified in the reaction mixture.



(VII) (XL) (XXXVa) (XLI) (XXXVIa)

Thus in the examples quoted above the allyl rearrangements involving the vinylcyclopropane fragment were observed only indirectly. The "4-carene → *m*-mentha-4,6-diene" rearrangement has been achieved directly.

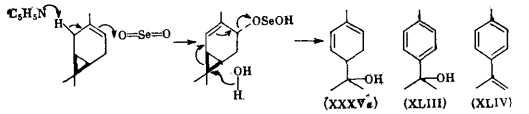
Gollnick et al. [50] showed that car-4-en-*trans*-3-ol (XLI) is converted quantitatively into *m*-mentha-4,6-dien-8-ol (XXXVIa) on refluxing with water and under the influence of acetic or dilute sulphuric acid at room temperature.



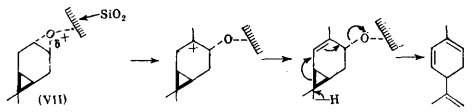
Gollnick et al.[50] suggested that this transformation can occur either as a concerted process or via car-3-en-5-ol (XLII), which undergoes a homoallyl rearrangement with participation of the cyclopropane ring under the reaction conditions.

According to the latest report by Cocker and coworkers[51], the oxidation of 3-carene by SeO_2 in pyridine (after refluxing for 3 h) with subsequent steam distillation of the reaction products yields preferentially compounds of the *p*-menthane series (XXXVa) (50%) and its degradation and

dehydration products 2-(*p*-tolyl)-2-propanol (XLIII) (11%) and *p*-isopropenylmethylbenzene (XLIV) (11%). The authors explain their formation from 3-carene by the "interference" of the "2-carene → *p*-mentha-1,5-diene" rearrangement occurring analogously[50] to the concerted mechanism:

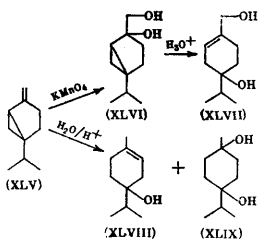


There is an interesting interpretation[52] of the transformations of α-3,4-epoxycarane (VII) under the influence of silica gel, which is regarded as a matrix with an electron-accepting surface responsible for the carbonium mechanism of the process; one of the pathways in the reactions involves a rearrangement similar to that already described above



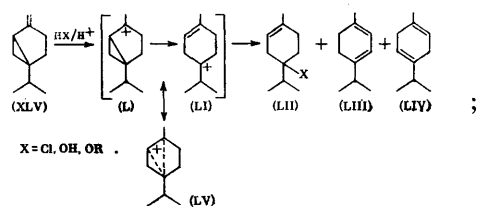
(b) Homoallyl Rearrangement with Participation of the Cyclopropane Ring

The homoallyl rearrangement in the series of bicyclic terpenes was observed previously for derivatives of bicyclo[3,1,0]hexane with a system of condensed three- and five-membered rings. Thus Semmler[53] found that the hydroxylation of Sabinene (XLV) by $KMnO_4$ leads to the diol (XLVI), which readily isomerises to the diol (XLVII) under the influence of dilute H_2SO_4 in the cold:



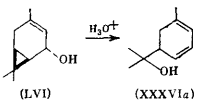
The hydration of sabinene (XLV) with 10% H_2SO_4 also leads to the monocyclic products (XLVIII) and (XLIX).[54]

Goryaev and coworkers[55-57] obtained analogous results in the study of the transformations of sabinene (XLV) in reactions with HCl—the hydration and alcohol addition reactions in an acid medium:

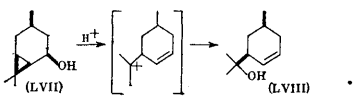


It is evident from the above scheme that the formation of monocyclic products is the result of the rearrangement of the cyclopropylmethyl ion (L) to the homoallylcyclohexyl ion (LI) and the stabilisation of the latter by the attack of a nucleophile to give the terpenen-4-ol ether (LII) or the ejection of β-H^+ leading to the hydrocarbons (LIII) and (LIV). The authors also believe that the hydration of sabinene via the non-classical ion (LV) is probable.

In the carane series, the rearrangement of the cyclopropylmethyl derivative to the homoallyl compound was also achieved somewhat later by the conversion of car-3-en-*trans*-5-ol (LVI) into *m*-mentha-4,6-dien-8-ol (XXXVIa):[32]

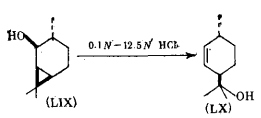


According to the data of Cocker and coworkers[58], *cis*-caran-*cis*-5-ol (LVII) partly isomerises to *cis*-*m*-menth-4-en-8-ol (LVIII) under the influence of dilute hydrochloric acid at room temperature or on heating with acetic acid in sealed tubes:

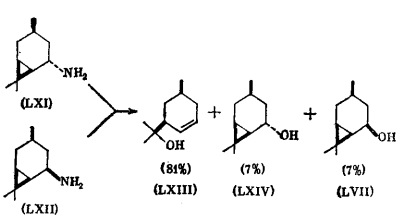


The rearrangement (LVII) → (LVIII) has also been noted under the conditions of the oxidation of compound (LVII) with chromic acid, particularly in oxidation in 75% acetic acid; in acetate buffer (pH 2.24), the rate of rearrangement is insignificant[20].

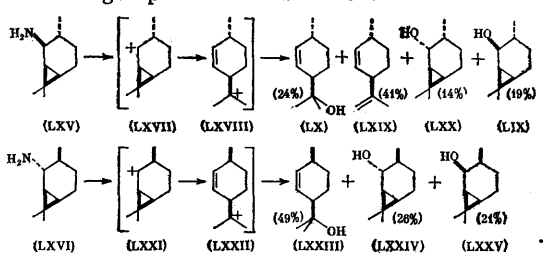
The homoallyl rearrangement has also been observed for *trans*-caran-*cis*-2-ol (LIX),[59] which is converted into *trans*-*p*-menth-2-en-8-ol (LX) under the conditions mentioned above for *cis*-caran-*cis*-5-ol (LVII):



More complete data on the rearrangement of cyclopropylmethyl derivatives were obtained by Cocker and coworkers in a study of the deamination of stereoisomeric amines of the carane series[60]. The deamination of the epimers (LXI) and (LXII) leads preferentially to the rearrangement of the product (LXIII), the composition of the deamination products being independent of the configuration of the initial amine:



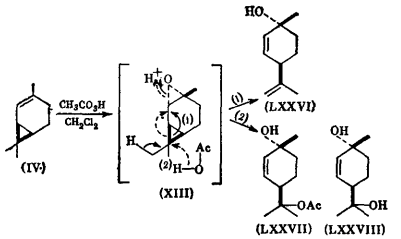
Stereoisomeric 2-amines with the *trans*-carane structure (LXV) or the *cis*-carane structure (LXVI) give a mixture of products having various compositions (different from those obtained previously); in this case the content of the rearranged products is smaller.



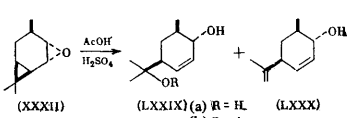
The authors explain the difference on the hypothesis that steric and electronic factors influence the ease of the rearrangement. While the formers promote to an equal extent the rearrangement of the corresponding α-cyclopropylcarbonium ions, with migration of the carbonium ion centre to a side chain, the influence of the electronic factors must be different, Owing to the +*I* effect of the 10-CH_3 group in compounds (LXVII) and (LXXI), which stabilises the positive charge on the 2-C atom, there is an increase of the possibility of the formation of the non-rearranged products (LIX), (LXX), (LXXIV), and (LXXV). For the isomeric amines (LXI) and (LXII), the formation of the rearranged product (LXXIII) should be the dominant process.

Thus expansion of the range of isomeric carane derivatives investigated and the extension to them of the reactions accompanied by the formation at some stage of an electron-deficient centre in the α-position relative to the cyclopropane ring made it possible to observe directly in a number of instances their homoallyl rearrangement. The observations were used to elucidate the mechanism of the reactions, the pathways followed in the formation of particular products, and hence individual reaction pathways.

In an attempt to synthesise α-2,3-epoxycarane (XIII) by the epoxidation of 2-carene with peracetic acid, Gollnick and Schade[32] isolated *cis*-*p*-mentha-2,8-dien-1-ol (LXXVI), which they regard as the product of the acid-catalysed isomerisation of the α-2,3-epoxycarane (XIII) formed initially:

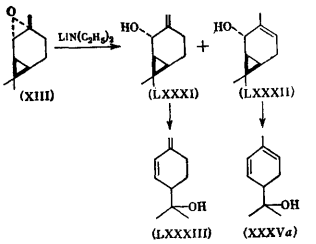


The rearrangement of α-2,3-epoxycarane (XIII) under the conditions of the epoxidation of 2-carene (IV) by a solution of peracetic acid in a mixture of acetic acid and methylene chloride buffered with sodium acetate was reported somewhat later[61]. The reaction products consisted of a mixture of compound (LXXVI) and the monoacetate of *cis*-*p*-menth-2-ene-1,8-diol (LXXVII). The diol (LXXVIII) was isolated as the sole product of the hydration of the epoxide (XIII) by 1% sulphuric acid[62]. It has been shown[32,61,63] that α-4,5-epoxycarane (XXXII) can be obtained by the epoxidation of *cis*-4-carene, which rearranges just as readily under the influence of acids; in the reaction with acetic acid, even in the cold (0°C), it gives the monoacetate of *m*-menth-4-ene-6,8-diol (LXXIXb) and *cis*-*m*-mentha-4,8-dien-6-ol (LXXX) as the main products:

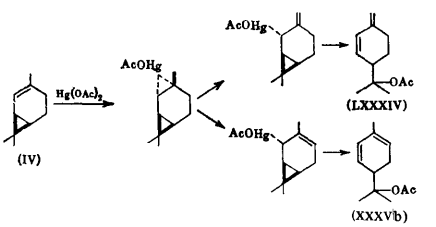


The diol (LXXIXa) has been obtained by Chabudzinski and coworkers[61,63] by treating the epoxide (XXXII) with 1% sulphuric acid, although the authors regarded it as carane-4,5-diol.

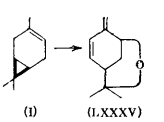
It is interesting to note that both allyl and homoallyl alcohols (LXXXI) and (LXXXII), the products of the isomerisation of α-2,3-epoxycarane (XIII) by $LiN(C_2H_5)_2$, rearrange even under the conditions of gas–liquid chromatography in a column with 10% of polyethylene glycol adipate on refractory brick at 140°C.[64] The carenols (LXXXI) and (LXXXII) rearrange rapidly in boiling water:



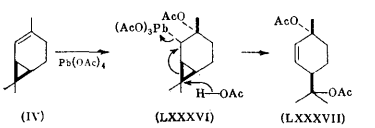
A study of the oxidation of 2-carene (IV) by $Hg(OAc)_2$ in acetic acid[65] showed that the formation of *p*-menthadienyl acetates (XXXVb) and (LXXXIV) involves a similar rearrangement at the stage where allylmercury acetates are solvolysed:



One cannot rule out the possibility that the formation of 2,8-oxy-*p*-mentha-1(7),5-diene (LXXXV) from 3-carene (I) when the latter is oxidised by SeO_2 in acetic anhydride[39,66] is also associated with the homoallyl rearrangement in the α-cyclopropylmethyl system:



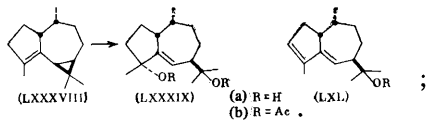
Assuming the homoallyl rearrangement at the stage involving the decomposition of allylic organolead intermediates, one can explain also the formation of the association complexes of the acetates (XXXVb) and (LXXXIV) in the oxidation of 2-carene (IV) by $Pb(OAc)_4$ in benzene[62]. As already mentioned, in agreement with the proposed mechanism[40], the oxidation of 2-carene by $Pb(OAc)_4$ can also proceed via another pathway involving an intermediate adduct (LXXXVI) of the olefin and $Pb(OAc)_4$. During its subsequent reactions, conditions also arise for the homoallyl rearrangement with opening of the cyclopropane ring and the formation of a monocyclic adduct:



In this case the acetate of *cis*-*p*-menth-2-ene-1,8-diol (LXXXVII) was identified in the reaction products.

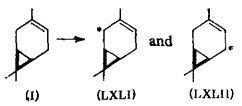
It is of interest to compare the reactions involving the epoxidation and oxidation by $Pb(OAc)_4$ and SeO_2 of 2-carene (IV) and α-gurjunene (LXXXVIII), which contains

the same vinylcyclopropane fragment as 2-carene (IV), but the latter is located in neighbouring rings[67-69]:



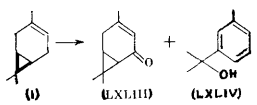
Comparison of the products of the above reactions of compounds (LXXXVIII) and (IV) demonstrates their fairly complete similarity.

Under the influence of "allylic" oxidants, the "cyclopropylmethyl" fragment may arise in the 3-carene molecules in two ways:



Presumably investigators encountered the rearrangement of the bicyclic 3-carene system to the *p*-menthadiene system, i.e. the rearrangement "2-carene → *p*-mentha-1,5-diene", already in the study of the catalytic autoxidation of 3-carene[70-72]. On the other hand, the structures of the corresponding rearranged reaction products were not finally elucidated, although it was shown subsequently that *p*- and *m*-menthadienols (XXXVa) and (XXXVIa) are formed as a result of the homoallyl rearrangement of the corresponding 3-carenyl derivatives (LXLI) and (LXLII) under the reaction conditions or during the separation of the reaction mixtures.

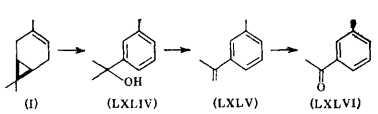
Cocker and coworkers[73], who investigated the oxidation of 3-carene by $KMnO_4$, found that the neutral products contain, apart from the main component car-3-en-5-one (LXLIII), also 8-hydroxy-*m*-cymene (LXLIV):



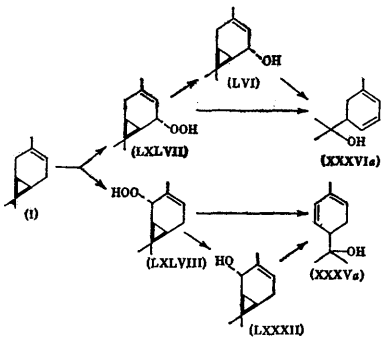
According to the results of Cocker and coworkers[74], compound (LXLIV) constitutes the bulk of the neutral oxygen-containing products of the oxidation of 3-carene by CrO_3 in acetone. However, when an acetone solution of CrO_3 buffered by sodium acetate is used, the yield of compound (LXLIV) is reduced by a factor of 2 and in pyridine by a factor of 4. Consequently, in an acid medium the stage responsible for the formation of compound (LXLIV) may involve the homoallyl rearrangement with opening of the three-membered ring.

The same dependence of the yield of the rearranged products on the acidity of the medium was found in a study of the oxidation of 3-carene by t-butyl chromate[75,76].

The oxidation products of the *m*-series are represented by 8-hydroxy-*m*-cymene (LXLIV), 1-isopropenyl-3-methylbenzene (LXLV), and 3-methylacetophenone (LXVI). Their overall content in the reaction products reaches 70% when the oxidation reaction is carried out in a mixture of benzene, acetic acid, and acetic anhydride.



The autoxidation of 3-carene in the presence or absence of a catalyst (cobalt stearate), using several methods for the reduction of the mixture of hydroperoxides formed initially, has been reinvestigated in detail by Baines and Cocker[51]. The products of the homoallyl rearrangement are represented by the *p*- and *m*-menthadienols (XXXVa) and (XXXVIa), their ratio depending primarily on the autoxidation reaction conditions: in the presence of a catalyst, a 1 : 4 mixture is formed, while in its absence the product is a 4 : 5 mixture with an increase of the overall yield of the two isomers by a factor of 2. Thus the preferential formation of products of the *m*-menthane series is evidence for the preferential attack on the 5-CH_2 group of 3-carene. The homoallyl rearrangement can occur in the reduction of carenyl hydroperoxides (LXLVII) and (LXLVIII):

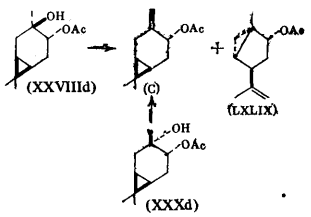


There is also the possibility of a rearrangement of the carenols (LVI) and (LXXXII) under the influence of an acid medium.

2. REARRANGEMENT WITH TRANSANNULAR CYCLOPROPYL PARTICIPATION

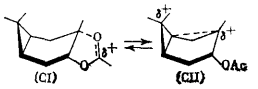
As in the homoallyl rearrangement, data concerning the transannular cyclopropyl participation in the chemistry of carane compounds have been obtained comparatively recently, although many such instances are known for the related bicyclic derivatives of the thujane series[77,78].

In 1966, Kropp[8,79] found that one of the products of the degradation of the monoacetate of carane-3-β,4α-diol (XXVIIId) by $POCl_3$ in pyridine has the structure of the acetate of 4-isopropenyl-1-methylbicyclo[3,1,0]-hexan-*trans*-2-ol (LXLIX):

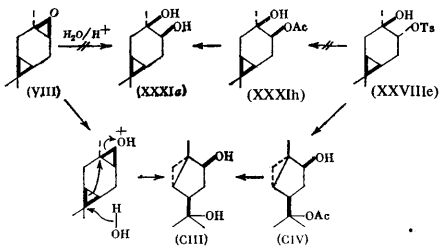


The degradation of the monoacetate of the stereoisomeric carane-3α,4α-diol (XXXd) under the same conditions yields only the acetate of car-3(10)-en-*trans*-4-ol (C) without appreciable admixtures of compound (LXLIX). Having compared the dehydration products of the two carane-3,4-diol ethers epimeric with respect to the 3-C atom, Kropp suggested that the condition determining the rearrangement with 1,3-transannular cyclopropyl participation is the *cis*-orientation of the eliminated OH group with respect to the cyclopropane ring. However, the absence of a rearrangement in the analogous dehydration of "model" epimeric alcohols, i.e. *trans*- and *cis*-3-caranols, showed that this condition alone is insufficient.

The formation of compound (LXLIX) and hence the occurrence of the rearrangement was interpreted by Kropp on the assumption of the equilibrium conformation (CI) ⇌ (CII) for the intermediate homocyclopropyl derivative in which the involvement of the cyclopropyl group is facilitated by the presence of the acetoxy-group, which "fixes" the six-membered ring of (CI) in the *syn*-boat conformation:



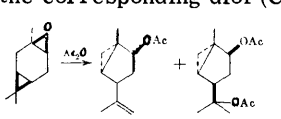
Having analysed the data available at the time on the transformations of the carane structure, Kropp concluded that the rearrangement constitutes the "first 'documented' example of the transannular cyclopropyl participation in the chemistry of carane". However, this rearrangement was presumably achieved in 1962 by Chabudzinski and Kuczynski[80] (who failed to notice it) in the hydration of β-3,4-epoxycarane (VIII) in an acid medium:



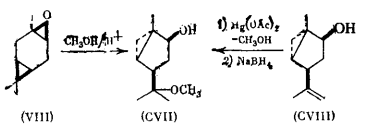
They erroneously attributed the structure of carane-3β,4β-diol (XXXIa) ("*cis*-carane-3,4-diol") to one of the two diols obtained in this reaction, having "confirmed" it by synthesis via the acetolysis of the monotosylate of carane-3β,4α-diol (XXVIIIe). It was subsequently found by the present authors[81] that the relevant diol has the structure of 4-(α-hydroxyisopropyl)-1-methylbicyclo-[3,1,0]hexan-*cis*-2-ol (CIII). Consequently a rearrangement with the 1,3-transannular cyclopropyl participation occurred in both the hydration of β-3,4-epoxycarane (VIII) and in the acetolysis of the monotosylate (XXVIIIe); because of this coincidence, the rearrangement was not noticed.

In connection with the elucidation of this finding, it became necessary to reanalyse the experimental data of the studies where "*cis*-carane-3,4-diol" had been identified[80]. As a result, the rearrangement with transannular cyclopropyl participation was observed in the reactions of 3β,4α-dibromocarane with Ag_2O,[82,83] or 3β,4α-dichlorocarane with AgOAc,[47] and of β-3,4-epoxycarane with $NaHSO_3$ in an aqueous solution[84].

In a study of the reaction of β-3,4-epoxycarane (VIII) with acetic anhydride, it was found[85,86] that approximately 50% of the mixture of reaction products consists of the acetates of 4-isopropenyl-1-methylbicyclo[3,1,0]hexan-*cis*-2-ol (CV) and the corresponding diol (CVI):

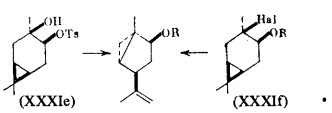


According to the results of Arbuzov et al.[87], the reaction of β-3,4-epoxycarane with methanol in the presence of an acid gives a low yield of the monoether (CIII) of the diol (CVII); the structure of compound (CVII) was confirmed by a synthesis involving hydration using the method of Arbuzov et al.[89]:

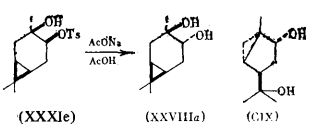


It is therefore of interest to note that one of the adducts of β-3,4-epoxycarane with methanol, obtained by Kropp[8], to which the latter attributed the structure of the monoether of "*cis*-carane-3,4-diol" by analogy with "*cis*-carane-3,4-diol itself", also has the structure of compound (CVII).[80]

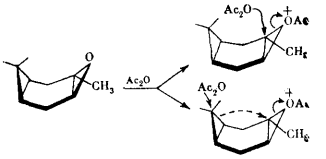
The formation of derivatives of the alcohol (CVIII) was likewise demonstrated in reactions of β-3,4-epoxycarane with sodium acetate in acetic acid[90], by the dehydration of the monotosylate of carane-3β,4β-diol (XXXIe),[91] and by the dehydrohalogenation of ethers of *cis*-3-halogeno-4-hydroxycaranes (XXXIf) under the influence of bases[92,93]:



The acetolysis of compound (XXXIe) with subsequent hydrolysis leads to the diol (CIX),[94] but with an appreciably lower yield than that of the epimeric diol (CIII) in the acetolysis of the monotosylate of carane-3β,4α-diol (XXVIIIe):



Comparison of the steric structures of 3,4-disubstituted caranes, the reactions of which are accompanied by a rearrangement with transannular cyclopropyl participation, permits the conclusion that a precondition for the rearrangement is the *cis*-configuration with respect to the relative positions of the cyclopropane ring and the functional groups at the 3-C atom located on the opposite side across the cyclohexane ring. Under the conditions of reactions involving electrophilic addition to β-3,4-epoxycarane, the comparative "activities" of the nucleophilic species attacking the electron-deficient 3-C atom in the intermediate 'onium compound and of the $C_{(1)}$–$C_{(7)}$ bond in the cyclopropane ring, behaving as an intramolecular nucleophile in the 1,3-transannular shift, are no less important:



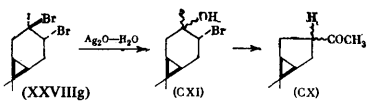
It follows from an examination of the literature data that electrophiles can be arranged in the following sequence in terms of the degree of rearrangement in the reactions of β-3,4-epoxycarane: $Ac_2O > H_2O/H^+ > AcOH/AcONa$.[80,85,86,90]

In the reactions of β-3,4-epoxycarane (VIII) with AcBr in acetic anhydride[92], rearrangements with a 1,3-transannular shift are not observed at all.

3. REARRANGEMENTS WITH CONTRACTION OF THE SIX-MEMBERED RING

In the last decade studies on the reactions of carane derivatives with substituents at the vicinal secondary and tertiary carbon atoms revealed rearrangements with contraction of the six-membered ring of the Wagner–Meerwein type of rearrangement.

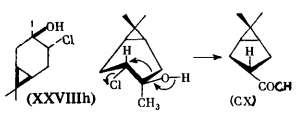
The first data on this rearrangement were obtained by Kuczynski and coworkers[82,83], who showed that, when 3β,4α-dibromocarane (XXVIIIg) is treated with an aqueous suspension of Ag_2O, the main product is 3-acetyl-6,6-dimethylbicyclo[3,1,0]hexane (CX); the configuration at the 3-C atom was not elucidated. The formation of the ketone (CX) from the carane derivative under the conditions of the nucleophilic substitution reaction was explained by the authors on the assumption that there is an intermediate stage involving the conversion of the carane derivative into 4-bromo-3-hydroxycarane (CXI) as an intermediate:



(XXVIIIg) (CXI) (CX)

The elimination of HBr from the intermediate is accompanied by a 1,2-shift of the $C_{(2)}$–$C_{(3)}$ bond in the six-membered ring.

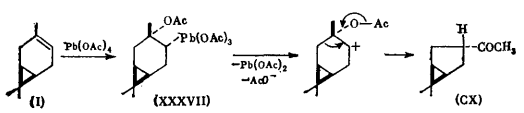
The probability of the involvement of 4-bromo-3-hydroxycarane (CXI) in the conversion of 3β,4α-dibromocarane (XXVIIIg) into the ketone (CX) was confirmed by data obtained in a study of the structures of the stereoisomeric 4-chloro-3-hydroxycarane (XXVIIIh) and 4-bromo-3-hydroxycarane (XXVIIIc). Under these conditions, 4-hydroxy-3-halogenocaranes give a high yield of the ketone (CX):[24,95]



(XXVIIIh) (CX)

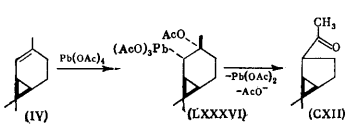
On treatment with silver acetate in acetic acid, 4α-chloro-3ρ-ethoxycarane forms the ketone (CX) with elimination of a molecule of C_2H_5Cl. 3ρ,4α-Dichlorocarane (XXVIIIb) is also partly converted into the ketone (CX).[47]

The ketone (CX) has been found in the products of the reaction of 3-carene with $Pb(OAc)_4$.[41,45] It was noted that this reaction may lead to the formation of a *cis*-adduct of the olefin with $Pb(OAc)_4$, the decomposition of which can also involve the contraction of the six-membered ring:



(I) (XXXVII) (CX)

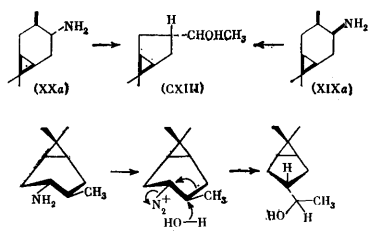
The bicyclic ketone (CXII) is apparently formed similarly in the reaction of 2-carene with $Pb(OAc)_4$:[62]



(IV) (LXXXVI) (CXII)

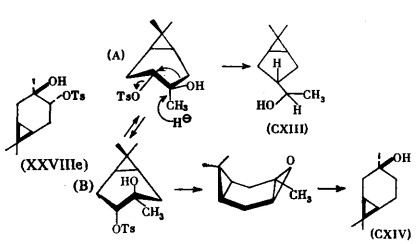
The rearrangement with contraction of the six-membered ring as a result of the 1,2-shift of the $C_{(3)}$–$C_{(4)}$ bond to the electron-deficient 2-C atom on decomposition of the adduct (LXXXVI) competes with the homoallyl rearrangement in which the cyclopropane ring is involved.

Cocker and coworkers[60] showed that the deamination of the amino-derivatives of *cis*-carane (XIXa) and (XXa), epimeric with respect to the 4-C atom, leads to the formation of appreciable amounts (up to 14% of the mixture of the reaction products) of *trans*-3-(α-hydroxyethyl)-6,6-dimethylbicyclo[3,1,0]hexane (CXIII). The rearrangement can also occur in the diozonium ion as in the case of the 4α-isomer (XXa) and in the carbonium ion with *trans*-attack by the nucleophile relative to the cyclopropane ring:



(XXa) (CXIII) (XIXa)

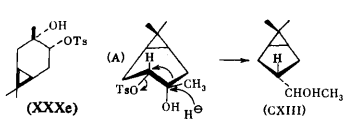
The rearrangement with a 1,2-shift of the $C_{(2)}$–$C_{(3)}$ bond via a concerted mechanism has been clearly observed in the hydrogenolysis of the monotosylates of carane-3,4-diols. The steric structures of the stereoisomeric carane-3,4-diols (XXVIIIa), (XXXa), and (XXXIa) and possibly of their monoethers consist of equilibrium mixtures of the conformers (A) and (B) with the six-membered ring in the half-chair form[22]. The hydrogenolysis of the monotosylate (XXVIIIe) leads to a 2:3 mixture of the two alcohols (CXIII) and (CXIV):



(XXVIIIe) (CXIII) (CXIV)

The formation of the former is due to the reaction of the monotosylate (XXVIIIe) in the di-*e*-form (A), since the stereoelectronic requirement imposed on the geometry of the transition state in the rearrangement with ring contraction, namely the anticoplanar disposition of the corresponding bonds, is met in this case. The behaviour of 4α-bromo-3ρ-hydroxycarane (XXVIIIc) under the same conditions is similar[24].

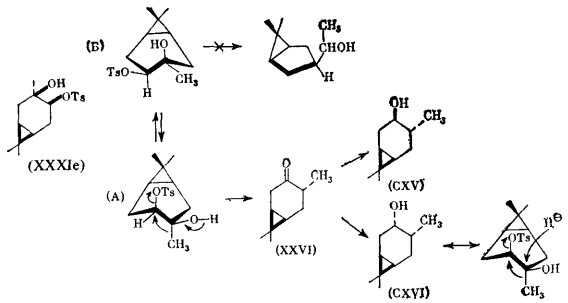
The hydrogenolysis of the monotosylate (XXXe) proceeds unambiguously with formation of the rearranged alcohol (CXIII); consequently the monotosylate (XXXe) likewise reacts in the preferred conformation (A) having the equatorial $C_{(4)}$–O linkage:



(XXXe) (CXIII)

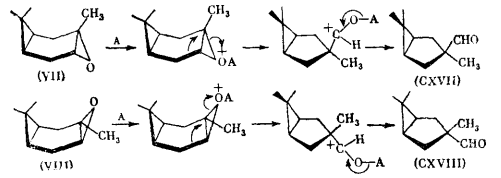
For the monotosylate (XXXIe), conformation (A) with the axial $C_{(4)}$–O bond is preferred. The rearrangement with contraction of the six-membered ring does not occur here: the processes occurring in the hydrogenolysis by $LiAlH_4$ involve a rearrangement with a 1,2-shift of the 10-CH_3 group, the stereoelectronic requirement of which (an

anticoplanar disposition of the $C_{(4)}-O$ and $C_{(3)}-C_{(10)}$ bonds)[91] is fulfilled in conformer (A):

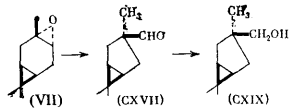


The formation of a 2:1 mixture of the epimeric alcohols (CV) and (CVI) as the hydrogenolysis products can be explained if it is assumed that the *E*2 elimination reaction yielding the *trans*-4-caranone (XXVI) takes place under the influence of $LiAlH_4$ together with the hydrogenolysis proper of the monotosylate (XXXIe), leading to *trans*-caran-*trans*-4-ol (CXVI); the stereoselective reduction of the *trans*-4-caranone by $LiAlH_4$ leads preferentially to the alcohol (CXV) with a *cis*-orientation of the OH group relative to the three-membered ring.

It is interesting to note that, among the 3,4-disubstituted carane derivatives, a rearrangement with a different type of contraction of the six-membered ring is characteristic of the stereoisomeric 3,4-epoxycaranes (VII) and (VIII). It involves a 1,2-shift of the $C_{(4)}-C_{(5)}$ bond. In 1967, three groups of investigators[97-99] published the results of studies on the isomerisation of 3,4-epoxycaranes under the influence of Lewis acids. The stereoisomeric aldehydes (CXVII) and (CXVIII), the formation of which has been explained by the rearrangement of the carbonium ion intermediates with a 1,2-shift of the ring $C_{(4)}-C_{(5)}$ bond, were found among the carbonyl reaction products:



The aldehydes (CXVII) and (CXVIII) are formed from the corresponding stereoisomeric 3,4-epoxycaranes also in the reaction with acetic anhydride[44,86]. According to Teisseire et al.[98], the conversion of 3,4-epoxycaranes into aldehydes is observed under the conditions of gas-liquid chromatography. Silica gel, acting as an electron-accepting agent, also promotes the rearrangement of α,3,4-epoxycarane into the aldehyde (CXVII).[52] On treatment with Al_2O_3, α-3,4-epoxycarane (VII) is partly converted into the alcohol (CXIC), corresponding to the product of the Cannizzaro reaction of the aldehyde (CXVII) formed initially[100]:



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The studies by S. S. Nametkin on terpenes made a most valuable contribution not only to the investigation of this class of natural products but also to organic chemistry as a whole. His brilliant research on camphor homologues enabled him to discover the camphene rearrangement of the second kind or the Nametkin rearrangement (given this name to distinguish it from the camphene rearrangement of the first kind or the Wagner rearrangement). One should mention particularly that Nametkin considered the stereochemical aspect of the complex rearrangements in the reactions investigated, which is a characteristic feature of modern organic chemistry.

REFERENCES

1. Z. Chabudziński, Wiad. Chem., 14, 501 (1960).
2. J. Verghese, Perfumery Essent. Oil Record, 56, 438 (1965).
3. J. Amer. Chem. Soc., 82, 5565 (1960) [There is no author for this reference as it refers to IUPAC nomenclative rules (Ed. of Translation)].
4. K. Gollnick and G. O. Schenk, Pure Appl. Chem., 9, 507 (1964).
5. K. Gollnick, S. Schroeter, G. Ohloff, G. Schade, and G. O. Schenk, Annalen, 687, 14 (1965).
6. V. A. Naumov and V. M. Bezzubov, Dokl. Akad. Nauk SSSR, 171, 634 (1966).
7. S. P. Acharya, Tetrahedron Letters, 4117 (1966).
8. P. J. Kropp, J. Amer. Chem. Soc., 88, 4926 (1966).
9. A. N. Vereshchagin and S. G. Vul'fson, Zhur. Strukt. Khim., 9, 1090 (1968).
10. S. P. Acharya and H. C. Brown, J. Amer. Chem. Soc., 89, 1925 (1967).
11. P. J. Kropp, D. C. Heckert, and T. J. Flautt, Tetrahedron, 24, 1385 (1968).
12. B. A. Arbuzov, A. R. Vil'chinskaya, Yu. Yu. Samitov, S. G. Vul'fson, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 2163 (1969).
13. B. A. Arbuzov, V. A. Naumov, and D. F. Shatrukov, Dokl. Akad. Nauk SSSR, 163, 355 (1965).
14. H. C. Brown and A. Suzuki, J. Amer. Chem. Soc., 89, 1933 (1967).
15. B. A. Arbuzov, A. N. Vereshchagin, S. G. Vul'fson, and Z. G. Isaeva, Izv. Akad. Nauk, Ser. Khim., 1966 (1968).
16. B. A. Arbuzov, Yu. Yu. Samitov, A. V. Aganov, and Yu. L. Kleiman, Dokl. Akad. Nauk SSSR, 184, 341 (1969).
17. B. A. Arbuzov, Yu. Yu. Samitov, and Sh. S. Bikeev, Dokl. Akad. Nauk SSSR, 216, 547 (1974).
18. W. Cocker, P. V. R. Shannon, and P. A. Staniland, J. Chem. Soc. (C), 946 (1966).
19. W. Cocker, A. C. Pratt, and P. V. R. Shannon, J. Chem. Soc. (C), 484 (1968).
20. M. S. Carson, W. Cocker, D. H. Grayson, A. C. Pratt, and P. V. R. Shannon, J. Chem. Soc. (B), 1136 (1968).
21. B. A. Arbusov, S. G. Vul'fson, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 306 (1971).
22. B. A. Arbuzov, V. A. Naumov, Z. G. Isaeva, and R. R. D'yakonova, Dokl. Akad. Nauk SSSR, 197, 333 (1971).
23. B. A. Arbuzov, V. A. Naumov, V. M. Bezzubov, Z. G. Isaeva, and G. Sh. Bikbulatova, Dokl. Akad. Nauk SSSR, 207, 596 (1972).
24. B. A. Arbuzov, Z. G. Isaeva, I. B. Nemirovskaya, and V. A. Naumov, 197, 1322 (1971).

25. B. A. Arbuzov, A. N. Vereshchagin, and S. G. Vul'fson, Izv. Akad. Nauk SSSR, Ser. Khim., 1969 (1968).
26. B. A. Arbuzov, A. N. Vereshchagin, S. G. Vul'fson, and G. Sh. Bikbulatova, Izv. Akad. Nauk SSSR, Ser. Khim., 1492 (1970).
27. I. P. Povodyreva, Z. G. Isaeva, R. R. Shagidullin, R. R. D'yakonova, and G. A. Bakaleinik, Dokl. Akad. Nauk SSSR, 207, 908 (1972).
28. R. R. Shagidullin, Z. G. Isaeva, I. P. Povodyreva, and R. R. D'yakonova, Dokl. Akad. Nauk SSSR, 202, 1349 (1972).
29. H. Kuczynski and K. Piatkowski, Roczniki Chem., 31, 59 (1957).
30. H. Kuczynski and Z. Chabudzinski, Roczniki Chem., 34, 177 (1960).
31. B. A. Arbuzov and A. R. Vil'chinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 954 (1967).
32. K. Gollnick and G. Schade, Tetrahedron Letters, 2335 (1966).
33. Z. Chabudzinski and D. Sedzik, Roczniki Chem., 40, 1889 (1966).
34. B. A. Arbuzov, Z. G. Isaeva, N. D. Ibragimova, S. G. Vul'fson, and A. N. Vereshchagin, Dokl. Akad. Nauk SSSR, 203, 581 (1972).
35. B. A. Arbuzov, V. V. Ratner, Z. G. Isaeva, and N. Kh. Abaeva, Izv. Akad. Nauk SSSR, Ser. Khim., 2762 (1974).
36. V. V. Ratner, Candidate's Thesis, Kazan University, 1963.
37. Z. G. Isaeva, B. A. Arbuzov, V. V. Ratner, and I. P. Povodyreva, Izv. Akad. Nauk SSSR, Ser. Khim., 466 (1965).
38. B. A. Arbuzov, Z. G. Isaeva, and V. V. Ratner, Izv. Akad. Nauk SSSR, Ser. Khim., 475 (1965).
39. B. A. Arbuzov, Z. G. Isaeva, and V. V. Ratner, Zhur. Org. Khim., 2, 1401 (1966).
40. J. Alkonyi, Chem. Ber., 96, 1873 (1963).
41. V. V. Ratner, Z. G. Isaeva, and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 2766 (1969).
42. B. A. Arbuzov, V. V. Ratner, and Z. G. Isaeva, Izv. Akad. Nauk SSSR, Ser. Khim., 45 (1973).
43. G. H. Whitham, J. Chem. Soc., 2232 (1961).
44. B. A. Arbuzov, Z. G. Isaeva, and I. P. Povodyreva, Izv. Akad. Nauk SSSR, 159, 827 (1964).
45. Z. G. Isaeva, Doctoral Thesis, Kazan University, 1967.
46. Z. G. Isaeva, I. B. Nemirovskaya, and B. A. Arbuzov, Dokl. Akad. Nauk SSSR, 171, 349 (1966).
47. B. A. Arbuzov, Z. G. Isaeva, and G. Sh. Bikbulatova, Izv. Akad. Nauk SSSR, Ser. Khim., 388 (1972).
48. H. Kuczynski and K. Marks, Roczniki Chem., 43, 943 (1969).
49. B. A. Arbuzov, Z. G. Isaeva, and I. S. Andreeva, Izv. Akad. Nauk SSSR, Ser. Khim., 838 (1965).
50. K. Gollnick, G. Schade, and S. Schroeter, Tetrahedron, 22, 139 (1966).
51. D. A. Baines and W. Cocker, J. Chem. Soc. (C), 2232 (1975).
52. V. S. Joshi, N. P. Damodaran, and S. Dev, Tetrahedron, 27, 475 (1971).
53. F. W. Semmler, Chem. Ber., 33, 1463 (1900); 35, 2047 (1902).
54. O. Wallach, Annalen, 360, 98 (1908).
55. M. I. Goryaev and G. A. Tolstikov, Dokl. Akad. Nauk SSSR, 141, 855 (1961).
56. G. A. Tolstikov, L. N. Lishtvanova, and M. I. Goryaev, Zhur. Obshch. Khim., 33, 683 (1963).
57. M. I. Goryaev and G. A. Tolstikov, Zhur. Obshch. Khim., 33, 1031 (1963).
58. W. Cocker, P. V. R. Shannon, and P. A. Staniland, J. Chem. Soc. (C), 915 (1967).
59. W. Cocker, D. P. Hanna, and P. V. R. Shannon, J. Chem. Soc. (C), 489 (1968).
60. W. Cocker, D. P. Hanna, and P. V. R. Shannon, J. Chem. Soc. (C), 1302 (1969).
61. G. Ohloff and W. Giersch, Helv. Chim. Acta, 51, 1328 (1968).
62. B. A. Arbuzov, V. V. Ratner, Z. G. Isaeva, and M. G. Belyaeva, Dokl. Akad. Nauk SSSR, 204, 1115 (1972).
63. Z. Chabudzinski and D. Sedzik, Roczniki Chem., 40, 1889 (1966).
64. B. A. Arbuzov, Z. G. Isaeva, A. R. Vil'chinskaya, and M. G. Belyaeva, Dokl. Akad. Nauk SSSR, 199, 1304 (1971).
65. B. A. Arbuzov, V. V. Ratner, Z. G. Isaeva, E. Kh. Kazakova, and M. G. Belyaeva, Izv. Akad. Nauk SSSR, Ser. Khim., 2752 (1971).
66. B. A. Arbuzov, Z. G. Isaeva, and V. V. Ratner, Dokl. Akad. Nauk SSSR, 164, 1289 (1965).
67. P. Pesnele and G. Ourisson, J. Org. Chem., 30, 1744 (1965).
68. M. Palmade, P. Pesnelle, J. Streith, and G. Ourisson, Bull. Soc. chim. France, 1950 (1963).
69. J. Streith and G. Ourisson, Bull. Soc. chim. France, 1960 (1963).
70. B. A. Arbuzov, Z. G. Isaeva, and V. V. Ratner, Dokl. Akad. Nauk SSSR, 134, 70 (1960).
71. B. A. Arbuzov, Z. G. Isaeva, and N. D. Ibragimova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 649 (1962).
72. B. A. Arbuzov, Z. G. Isaeva, and M. G. Gubaidullin, Izv. Akad. Nauk SSSR, Ser. Khim., 678 (1965).
73. W. D. P. Burns, M. S. Carson, W. Cocker, and P. V. R. Shannon, J. Chem. Soc. (C), 3073 (1968).
74. M. S. Carson, W. Cocker, D. H. Grayson, and P. V. R. Shannon, J. Chem. Soc. (C), 2220 (1969).
75. P. H. Royle, W. Cocker, D. H. Grayson, and P. V. R. Shannon, J. Chem. Soc. (C), 1073 (1971).
76. T. Suga, T. Shishibori, and T. Matsuura, Bull. Chem. Soc. Japan, 45, 1873 (1972).
77. T. Norin, Tetrahedron Letters, 37 (1964).
78. D. Whittaker and D. V. Banthorpe, Chem. Rev., 72, 305 (1972).
79. P. J. Kropp, US P. 3510510 (1970); Chem. Abs., 73, 15 039 (1970).
80. Z. Chubudzinski and H. Kuczynski, Roczniki Chem., 36, 1173 (1962).
81. B. A. Arbuzov, V. A. Shaikhutdinov, and Z. G. Isaeva, Izv. Akad. Nauk SSSR, Ser. Khim., 2124 (1972).
82. H. Kuczynski, M. Walkowicz, C. Walkowicz, K. Nowak, and I. Siemion, Roczniki Chem., 38, 1625 (1964).
83. M. Walkowicz and H. Kuczynski, Roczniki Chem., 40, 1231 (1966).
84. E. Maslinski and E. Michalek, Roczniki Chem., 47, 285 (1973).
85. Z. G. Isaeva, V. A. Shaikhutdinov, and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 1154 (1968).
86. B. A. Arbuzov, Z. G. Isaeva, and V. A. Shaikhutdinov, Dokl. Akad. Nauk SSSR, 210, 837 (1973).
87. B. A. Arbuzov, Z. G. Isaeva, G. A. Bakaleinik, and A. A. Martynov, "Trudy II Vsesoyuznoi Konferentsii po Epoksidnym Monomeram i Epoksidnym Smolam, Dnepropetrovsk, 1974" (Transactions of the Second All-Union Conference on Epoxy-Monomers and Epoxy-Resins, Dnepropetrovsk, 1974), p. 126.

88. H. C. Brown and P. Geoghegan, Jr., J. Amer. Chem. Soc., 89, 1522 (1967).
89. B. A. Arbuzov, V. V. Ratner, Z. G. Isaeva, and E. Kh. Kazakova, Izv. Akad. Nauk SSSR, Ser. Khim., 385 (1972).
90. B. A. Arbuzov, Z. G. Isaeva, and E. Kh. Kazakova, Izv. Akad. Nauk SSSR, Ser. Khim., 2554 (1973).
91. B. A. Arbuzov, Z. G. Isaeva, R. R. D'yakonova, and G. A. Bakaleinik, Izv. Akad. Nauk SSSR, Ser. Khim., 2549 (1973).
92. B. A. Arbuzov, E. Kh. Kazakova, and Z. G. Isaeva, Izv. Akad. Nauk SSSR, Ser. Khim., 1681 (1972).
93. B. A. Arbuzov, Z. G. Isaeva, G. Sh. Bikbulatova, and V. A. Shaikhutdinov, Izv. Akad. Nauk SSSR, Ser. Khim., 969 (1975).
94. B. A. Arbuzov, Z. G. Isaeva, and R. R. D'yakonova, Izv. Akad. Nauk SSSR, Ser. Khim., 972 (1975).
95. B. A. Arbuzov, Z. G. Isaeva, and G. Sh. Bikbulatova, Dokl. Akad. Nauk SSSR, 195, 599 (1970).
96. B. A. Arbuzov, Z. G. Isaeva, and G. Sh. Bikbulatova, Dokl. Akad. Nauk SSSR, 195, 356 (1970).
97. Z. G. Isaeva and G. A. Bakaleinik, Dokl. Akad. Nauk SSSR, 176, 1310 (1967).
98. P. Teisseire, A. Galere, and M. Plattier, Bull. Soc. chim. France, 764 (1967).
99. R. L. Seittine and C. McDaniel, J. Org. Chem., 32, 2910 (1967).
100. V. S. Foshi, V. P. Damodaran, and S. Dev, Tetrahedron, 24, 5817 (1968).

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