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Some Rearrangements of Free Alkyl Radicals and Alkyl Cations in Solutions

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The results of studies of rearrangement reactions by the author and his co-workers during the last 20 years are described. A rearrangement of the n-propyl free radical in solutions as a result of the hydrogen 1,3-shift has been discovered and its characteristic features have been investigated (using carbon-14, deuterium, and tritium). The reaction involving the formation of organomercury compounds from mercury salts of carboxylic acids and peroxides has been studied and a mechanism has been proposed for it. New skeletal rearrangements in the thermal decomposition of cycloalkyl peroxides in benzene and bromoform have been discovered. It has been shown by the method of double ^{13}C NMR that some of the reactions involve the formation of species which manifest properties intermediate between those of free radicals and carbonium ions. The mechanism of the thermolysis of peroxides is considered.
The skeletal rearrangements and hydride shifts in the deamination and solvolysis of alicyclic compounds have been studied and a number of rearrangements with 1,2-migration of the halogen and in particular the isomerisation of acyloxybromopropanes in organic solvents, which takes place particularly readily, have been observed.
The bibliography includes 103 references.

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I. THE ISOMERISATION OF THE n-PROPYL RADICAL

A quarter of a century ago the available information about the feasibility of the isomerisation of free alkyl radicals under mild conditions in the liquid phase as a result of hydrogen shifts was contradictory. Thus Voevodskii and Mardaleishvili[1] suggested that free radicals (n-propyl, primary isobutyl, and cyclohexyl), formed from the corresponding olefins and atomic hydrogen in the presence of deuterium, isomerise in the gas phase (the hydrogen 1,3-shift) at room temperature. This hypothesis explained the high (up to 50%) degree of deuteriation of the radical recombination products.

On the other hand, Kharasch et al.[2] showed that isomerisation with a change in the skeleton does not occur on decomposition of acyl peroxides in carbon tetrachloride:

$$CH_3-CH_2-\dot{C}H_2 \rightleftarrows (CH_3)_2\dot{C}H \ .$$

Only n-propyl chloride is formed from butyryl peroxide, while only isopropyl chloride is formed from isobutyryl peroxide.

The possibility of the isomerisation of alkyl radicals in liquid-phase photochlorination has been studied[3]. Using deuterium-labelled isobutane, it was shown that the primary isobutyl radical does not isomerise to the tertiary radical:

$$CH_3-CD(CH_3)-\dot{C}H_2 \rightleftarrows CH_3\dot{C}(CH_3)-CH_2D \ .$$

Model reactions in which the hydrogen 1,3-shift in the free radical formed initially should be thermodynamically favourable, i.e. should lead to the formation of more stable radicals, have been investigated[4-7]. However, the n-hexyl as well as the δ- and γ-phenylalkyl radicals did not isomerise. Only the non-isomerised chlorides were formed in all cases:

$$(CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-COO)_2 \xrightarrow{CCl_4} \longrightarrow CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-Cl \ ;$$

$$(Ph-CH_2-CH_2-CH_2-CH_2-COO)_2 \xrightarrow{CCl_4} Ph-CH_2-CH_2-CH_2-CH_2-Cl \ ;$$

$$(Ph-CH_2-CH_2-C(CH_3)H-COO)_2 \xrightarrow{CCl_4} Ph-CH_2-CH_2-CHCl-CH_3 \ .$$

However, we believe it to be extremely improbable that the free alkyl radicals, if such are formed as kinetically independent species, for example, in the decomposition of acyl peroxides in solutions, should be altogether incapable of isomerisation. It is well known that free radicals are capable of abstracting a hydrogen atom from the solvent molecule in solutions:

$$R^{\cdot} + H:C\swarrow\searrow \longrightarrow R-H + {}^{\cdot}C\swarrow\searrow \ .$$

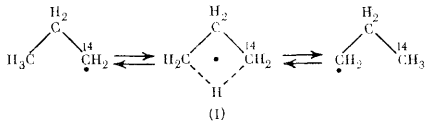
There are no grounds for the assumption that in the presence of suitable steric conditions they cannot abstract hydrogen from their C–H group with a corresponding shift of the free valence. The degree of isomerisation of the radical depends on the ratio of the rates of isomerisation and substitution. It is to be expected that at moderate temperatures the degree of isomerisation is low and isomerisation can be detected only by highly sensitive experimental techniques.

We investigated the decomposition of n-butyryl peroxide, labelled with ^{14}C in the α-position, in boiling carbon tetrachloride[8,9]:

$$(CH_3-CH_2-{}^{14}CH_2-COO)_2 + 2CCl_4 \rightarrow 2CH_3-CH_2-{}^{14}CH_2-Cl + 2CO_2 + CCl_3-CCl_3 \ .$$

Analysis of the distribution of the radioactive label in propyl chloride showed that, together with the normal product ($CH_3-CH_2-{}^{14}CH_2-Cl$), an appreciable amount (4.0 ± 0.5%) of propyl chloride containing the label in the 3-position ($^{14}CH_3-CH_2-CH_2-Cl$) is formed.

It is more likely that the isomerisation proceeds in a single stage via the four-membered cyclic transition state (I):



(I)

In the light of the results of the study of the isomerisation of the n-propyl radical in solution, it was of interest to consider the reason for the absence of isomerisation in the experiments of De Tar and co-workers[4-6] even when the hydrogen 1,3-shift could lead to a thermodynamically more stable radical of the benzyl type:

$$Ph-CH_2-CH_2-\dot{C}H-CH_3 \rightleftarrows Ph-\dot{C}H-CH_2-CH_2-CH_3 .$$

The author of this review can so far see no reasons, other than the high symmetry of the cyclic transition state in the case of the n-propyl radical, which may favour the 1,3-isomerisation.

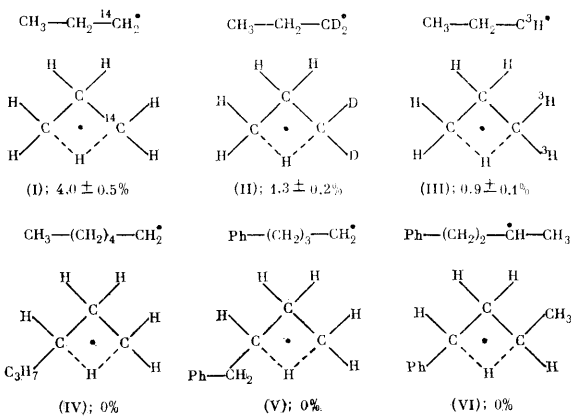
Even a slight decrease of the degree of symmetry in the transition stage (I) appreciably reduces the degree of 1,3-isomerisation. Thus the substitution of two hydrogen atoms even for deuterium {decomposition of [α-D_2]butyryl peroxide in carbon tetrachloride} reduces the extent of isomerisation from 4.0 ± 0.5% to 1.3 ± 0.1%:[10]

$$CH_3-CH_2-\dot{C}D_2 \rightleftarrows \dot{C}H_2-CH_2-CD_2H .$$

If tritium is employed instead of deuterium, the extent of isomerisation falls to 0.9 ± 0.1%.[11]

The proposed transition states for the β-isomerisation of the three free radicals (I)–(II) which we investigated and the free radicals (IV)–(VI) studied by De Tar and co-workers[4,5] are presented in Scheme 1.

Scheme 1



Since the free radical formed in solution can undergo two competing kinds of reactions—can abstract an atom from the solvent molecule or can isomerise—then naturally the faster the former process the lower the degree of isomerisation of the radical. It is known that the ease of abstraction of H, Cl, and Br atoms from the solvent molecule by the free radical increases in the sequence Cl < H < Br. Presumably, when CCl_4 is replaced by bromoform, the degree of isomerisation falls. This hypothesis has been confirmed in the study of the decomposition of [α-D_2]butyryl peroxide in bromoform. In chloroform the radical $CH_3-CH_2-\dot{C}D_2$ isomerised to the extent of 1.3 ± 0.1% and in bromoform only to the extent of 0.7 ± 0.1%.[12]

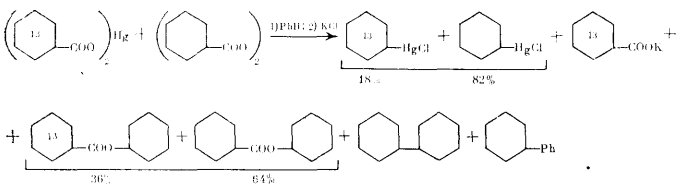
II. THE REACTIONS OF THE MERCURY SALTS OF CYCLOALKANECARBOXYLIC ACIDS WITH PEROXIDES

The reaction of the mercury salts of carboxylic acids with peroxides, leading to the formation of organomercury compounds, has been known for a long time[13]:

$$(R-COO)_2Hg \xrightarrow{(RCOO)_2} R-HgOCOR + CO_2 .$$

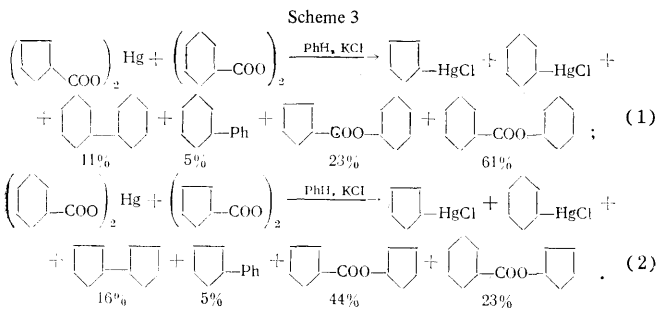
It was believed that the peroxide plays the role of a catalyst in this reaction. In reality the reaction mechanism proved to be more complex[14-16]. The study of the reaction between mercury cyclohexanoate labelled with ^{13}C in the ring and cyclohexanoyl peroxide established[14] that the peroxide is the source of the main product (Scheme 2):

Scheme 2



Since the results obtained were unexpected, we investigated additionally the[15] interactions of mercury cyclopentanoate with cyclohexanoyl peroxide [reaction (1)] and of mercury cyclohexanoate with cyclopentanoyl peroxide [reaction (2)]; both reactions were carried out in benzene at 80 °C under the conditions described by Shatkina et al.[14] The organomercury compounds obtained were converted into the corresponding bromides by the reaction with bromine in glacial acetic acid; the composition of the reaction products was determined by gas–liquid chromatography (GLC). The analytical data for the products formed in the reactions investigated are presented in Scheme 3 and in Table 1:

Scheme 3



(1)

(2)

It follows from Schemes 2 and 3 that hydrocarbons, namely bicycloalkyls and phenylcycloalkanes, are formed only from the alkyl groups in the corresponding peroxides: bicyclohexyl and phenylcyclohexane in reaction (1) and bicyclopentyl and phenylcyclopentane in reaction (2). The study of the mixture of esters showed that two esters are formed in each reaction, the alcohol component of which corresponds to the alkyl group of the peroxide employed while the acid component corresponds to the alkyl group of the peroxide or the mercury salt.

Table 1 shows that cyclohexylmercury chloride predominates in the mixture of organomercury compounds in reaction (1), which is consistent with the results obtained using mercury [^{13}C]cyclohexanoate.[14] However, cyclohexylmercury chloride also predominates in reaction (2), where the preferential formation of cyclopentylmercury chloride would have been expected by analogy.

Table 1. The composition in reactions (1) and (2) (%) (bromide fraction)*.

Reaction		
(1)	95	5
(2)	73	27

*Bromobenzene was detected in the mixture of bromide in both reactions.

Consideration of the results obtained by Shatkina et al.[14] suggests that two reactions predominate in the system investigated (mercury salts–peroxide): thermal decomposition of the peroxide leading to hydrocarbons and an ester and the reaction of the peroxide with the mercury salt. The latter probably begins with attack by the alkyl group of the peroxide on the mercury atom and the subsequent course of the reaction is determined by the ease of decomposition of the carboxylate radicals formed:



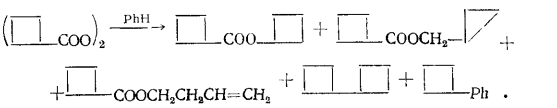
According to Ol'dekop et al.[16] and Hart and Wyman[17], cyclohexanoyl peroxide decomposes faster than cyclopentanoyl peroxide. This can in fact account for the preferential formation of cyclohexylmercury chloride in both reactions. Since there is an excess of cycloalkyl radicals derived from the peroxide in the reaction mixture, the carboxylate radicals formed recombine with them to produce two esters.

The absence from the products of both reactions of hydrocarbons containing the group derived from the mercury salt and also of esters containing the group derived from the mercury salt in the alcohol component suggests that the decarboxylation of the carboxylate radicals takes place in the complex of the mercury salt with the peroxide and is accompanied by a synchronous attack by the cycloalkyl radicals formed on the mercury atom.

III. THERMAL DECOMPOSITION OF ACYL PEROXIDES

The study of the reaction of mercury cyclobutanoate with cyclobutanoyl peroxide in boiling benzene established[18] the formation, together with other products, of esters whose alcohol component has been to a large extent rearranged as a result of the contraction or opening of the ring.

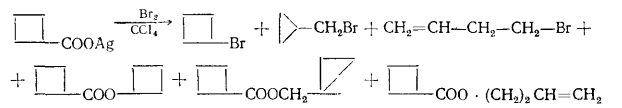
Subsequently a study was made[19] of the thermal decomposition of pure cyclobutanoyl peroxide in boiling benzene. The composition of the reaction products was determined by GLC. The esters were analysed by the chromatography of the reaction mixture and repeated chromatography of the alcohols obtained as a result of the alkaline hydrolysis of the ester fraction. This demonstrated the formation (apart from the cyclobutyl ester of cyclobutanecarboxylic acid) of rearranged esters, namely the cyclopropylmethyl and 3-butenyl esters of cyclobutanecarboxylic acid (the proportions of the products were 47 : 48 : 5). The hydrocarbons in the low-boiling fraction formed in the reaction were not investigated; the formation of bicyclobutyl and phenylcyclobutane was established:



Interesting results were obtained in the study of the thermal decomposition of cyclobutanoyl peroxide in bromoform[20].

In the literature there is a widely held view that the absence of the rearrangement is evidence for a free-radical mechanism and, conversely, that the presence of rearranged products indicates a carbonium ion mechanism. Thus a free-radical mechanism, based mainly on the absence of rearrangement products, has been proposed in studies[21,22] devoted to problems of the halogenodecarboxylation of acids by $Pb(OAc)_4$ and LiCl. In the catalytic decomposition of peroxides by copper complexes[23], the carbonium ion formed by the one-electron oxidation of the free radicals is believed to be responsible for the formation of the rearranged products.

However, we showed[24] that rearranged bromides, namely cyclopropylmethyl and allylmethyl bromides, are formed in the reaction of silver cyclobutanecarboxylate with bromine (the Borodin–Hunsdiecker reaction) in addition to cyclobutyl bromide and the rearranged esters of cyclobutanecarboxylic acid (known from literature data[25]):



It might have been hoped that the analogous rearrangement would be observed also in the thermal decomposition of cyclobutanoyl peroxide. Indeed cyclobutyl bromide and rearranged bromides, namely cyclopropylmethyl and allymethyl bromides, in proportions of 85 : 5 : 10 on average, as well as a mixture of esters, namely cyclobutyl, cyclopropylmethyl, and 3-butenyl esters of cyclobutanecarboxylic acid in proportions of 65 : 30 : 5, were isolated on decomposition of this peroxide in bromoform at 140 °C. Thus a rearrangement, which is fairly likely to have a free-radical mechanism, has been observed[20].

A study has also been made of the problem of the possible formation of rearranged esters in the thermal decomposition of cycloalkylacetyl peroxides. According to Hart and Wyman[26,27], ring expansion products are not formed in the decomposition of aliphatic cyclic acyl peroxides (ranging from C_3 to C_6) in CCl_4. Such compounds have not been detected either in the products of the reaction of cyclobutylmethyl iodide with benzoyl peroxide or di(t-butyl) peroxide or in the reaction of cyclobutylmethyl chloride with Ph_3SnH.[28] Products formed as a result of ring opening have been isolated in the former reaction (the formation of 5-iodopentene has been demonstrated).

We detected[29] rearranged esters in the thermal decomposition of cyclobutylacetyl and cyclopentylacetyl peroxides in benzene at 80 °C. The composition of the main reaction products (esters and high-boiling hydrocarbons) was determined by GLC; the hydrocarbons in the low-boiling fraction were not investigated. The formation of 1,2-dicyclobutyl- and 1,2-dicyclopentyl-ethanes, benzylcyclobutane, and benzylcyclopentane was established. The

esters were analysed by chromatographing the alcohols obtained by the alkaline hydrolysis of the ester fraction; the composition of the esters is presented in Table 2.

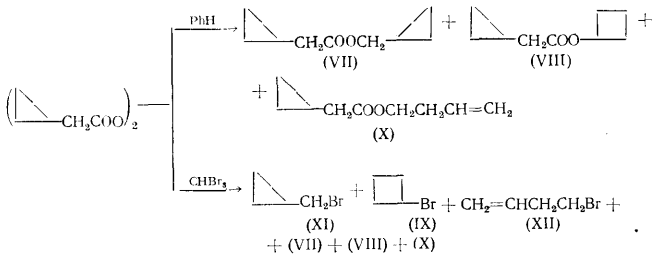
The data in Table 2 show that, apart from esters having the usual structure, esters whose alcohol component has rearranged as a result of ring expansion are formed in the thermolysis of cyclobutylacetyl and cyclopentylacetyl peroxides, the tendency towards ring expansion being more pronounced in the case of cyclobutylacetyl peroxide.

Table 2.

Initial peroxide	Composition of ester fraction	
$[(CH_2)_n CHCH_2COO]_2$	$(CH_2)_n CHCH_2COOCH_2 \cdot CH(CH_2)_n$	$(CH_2)_n CHCH_2 \cdot COOCH(CH_2)_{n+1}$
$n=3$	70	30
$n=4$	80	20

In the study of the thermal decomposition of bis(cyclopropylacetyl) peroxide[26,30], only the cyclopropylmethyl ester of cyclopropylacetic acid (VII) was found in the reaction products. After the decomposition of this peroxide in hexachloroacetone, cyclopropylmethyl chloride and the product of the homoallyl rearrangement of the cyclopropylmethyl radical, namely 3-butenyl chloride, were detected in addition to the ester (VII).[31]

In the study of the thermal decomposition of cyclopropylacetyl peroxide in $CHBr_3$ and in benzene at 65–70 °C [32] we observed for the first time the formation of the products of a rearrangement with ring expansion—cyclobutyl cyclopropylacetate (VIII) and cyclobutyl bromide (IX). Apart from compounds (VIII) and (X), cyclopropyl cyclopropylacetate, 3-butenyl cyclopropylacetate (X), cyclopropylmethyl bromide (XI), and 3-butenyl bromide (XII) are formed in $CHBr_3$; a mixture of the esters (VII) and (VIII) is produced in benzene. The bromides (IX), (XI), and (XII) are obtained in proportions of 7 : 84 : 9, while the esters (VII), (VIII), and (X) are formed in proportions of 80 : 19 : 1 in $CHBr_3$ and 70 : 13 : 17 in benzene:



The compositions and structures of the products were determined by GLC and ^1H NMR.

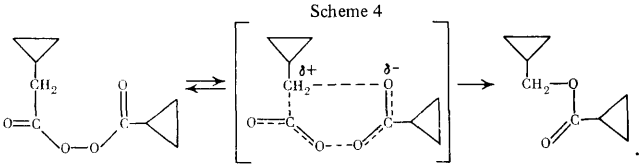
IV. THE MECHANISM OF THE THERMOLYSIS OF ALICYCLIC ACYL PEROXIDES

Analysis of the literature data shows that the thermal decomposition of acyl peroxides is a complex process; the products may be formed via both radical and non-radical (ionic or molecular) mechanisms. The contribution of each pathway depends on the structure of the peroxide and on the conditions of its decomposition.

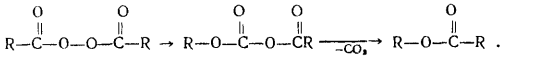
Whereas there is at present no doubt about the radical pathway for the formation of hydrocarbons and halogenoderivatives in the decomposition of acyl peroxide, the mechanism of the formation of esters cannot be decided unambiguously in most cases. The employment of various investigators of the tracer atom (^{18}O) method[30,33] and of the method of optically active peroxides[34], the study of the influence of solvents[35] and polar additives[36] on the decomposition of peroxides, and investigation of the thermolysis kinetics[26] do not as a rule justify a conclusion concerning the true mechanism of the formation of the esters.

In their study of the kinetics of the decomposition of alicyclic peroxides in CCl_4, Hart and Wyman[26] concluded, on the basis of the observed anomalously high rate of decomposition of cyclopropylacetyl peroxide, that the formation of the corresponding ester has a cyclic mechanism (Scheme 4):

Scheme 4



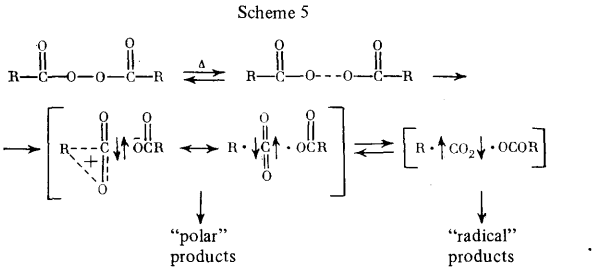
Oae et al.[30], who investigated the decomposition in CCl_4 of the same peroxide labelled with ^{18}O in the carbonyl group, found the complete distribution of the label with respect to both oxygen atoms in the ester and concluded that the ester is formed via a radical pathway. Some investigators[37,38] believe that the esters are the products of the decomposition of the carbonates formed initially:



An ionic mechanism of the decomposition of certain peroxides in polar solvents has been proposed in a number of studies: $RCOO^- {}^+OOCR$ (see, for example, Smid et al.[35]).

Another approach to the explanation of the mechanism of the thermolysis of acyl peroxides has been proposed by Walling[32]. According to Walling's mechanism (Scheme 5), the decomposition of acyl peroxides does not involve competing heterolytic and homolytic reactions, the "polar" and "radical" products being formed from a single intermediate radical-ion pair:

Scheme 5

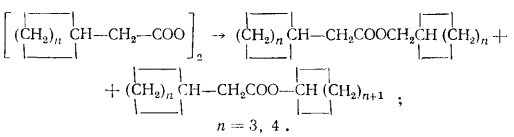


However, this scheme does not allow an objective solution of the problem of the pathway followed in the formation of particular products in these reactions. Thus Walling believes that there are "polar" products, while other investigators[40] who used Walling's mechanism, assigned them to "radical" products.

The method of chemically induced dynamic nuclear polarisation (CIDNP) now makes it possible to draw reliable inferences about the mechanism of the decomposition of acyl peroxides. The polarisation of esters is direct evidence for

the radical pathway leading to their formation on decomposition of acetyl, benzoyl, cyclopropanoyl, etc. peroxides[41]. In other cases the problem of the mechanism of the formation of esters can be solved only tentatively.

In the study of the thermal decomposition of alicyclic acyl peroxides, the formation of rearranged esters was demonstrated[42]. Thus the decomposition of cyclobutylacetyl and cyclopentylacetyl peroxides in benzene involves the formation, apart from esters having the normal structure (cyclobutylmethyl cyclobutylacetate and cyclopentylmethyl cyclopentylacetate respectively), of products rearranged as a result of ring expansion—cyclopentyl cyclobutylacetate and cyclohexyl cyclopentylacetate respectively:

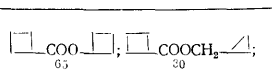
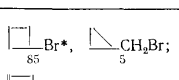
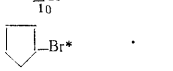
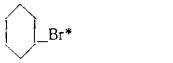
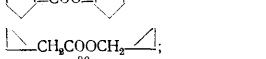
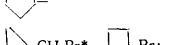
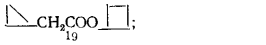
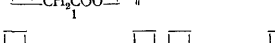


$n = 3, 4.$

The formation of products rearranged as a result of the contraction or opening of the ring, both esters and bromides, was also observed in a study of the thermal decomposition of cyclobutanoyl peroxide in benzene and bromoform[19].

Lippmaa et al.[43] investigated the CIDNP in the thermal decomposition of primary and secondary peroxides in benzene and in a benzene + bromoform mixture, namely cyclobutanoyl peroxide (XIII), cyclopentanoyl peroxide (XI), cyclohexanoyl peroxide (XV), cyclopropylacetyl peroxide (XVI), cyclobutylacetyl peroxide (XVII), and cyclopentylacetyl peroxide (XVIII). According to Kaptein[44], who studied the CIDNP of the decomposition products of the peroxides (XIII)–(XVIII) in hexachloroacetone, cyclo-olefins and cycloalkyl chlorides are polarised, while the esters formed are not polarised; he did not detect rearranged products on decomposition of the peroxides (XIII) and (XVI).

Table 3. Products of the thermolysis of alicyclic acyl peroxides in $CHBr_3$.

Peroxide	Reaction products, rel.%	
	esters	bromo-derivatives
(XIII)		
		
(XIV)		
(XV)		
(XVI)		
		
(XVII)		
(XVIII)		
		

*Polarised products.

Lippmaa et al.[43] were interested primarily in the possibility of detecting the CIDNP in the rearranged products. The peroxides were thermolysed at 60–75 °C in the thermostatted cavity of an NMR spectrometer. The authors used 10% solutions of the peroxides in benzene and the same solutions with added 10% $CHBr_3$. Table 3 presents the main products of the decomposition reactions of the peroxides in bromoform (the same mixtures of esters are formed in benzene). Our results[43] of the study of CIDNP in the decomposition reactions of the peroxides (XIII)–(XV) are generally identical with those of Kaptein[44]: only cyclo-olefins and the corresponding bromides with a normal structure are polarised. The rearranged bromides and esters formed on thermolysis of the peroxide (XIII), which we detected, are not polarised.

The thermolysis of the peroxides (XVI) and (XVII) is characterised by the formation of polarised unsaturated hydrocarbons (butene and pentene) and polarised bromides. The character of the polarisation of the hydrocarbons is consistent with the polarisation of the radical before ring opening. In the thermolysis of the peroxide (XVIII), an unsaturated hydrocarbon (hexene) is not formed, which is consistent with the greater thermodynamic stability of the five-membered ring. In the decomposition of the peroxide (XVI) in the benzene + bromoform mixture, 4-bromobutene—the product of the rearrangement of cyclopropylmethyl bromide—is polarised, while the esters formed are not polarised.

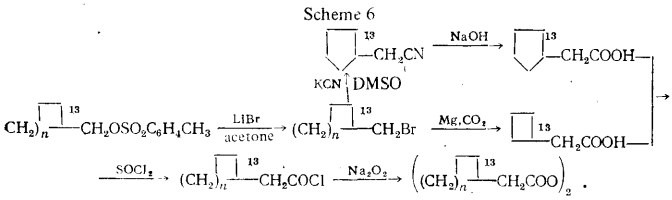
Our results and the literature data permit the conclusion that the CIDNP of esters is observed only in those cases where the decomposition of the peroxide results in the formation of comparatively long-lived radicals. In the remaining cases the absence of the polarisation of the esters can be explained by the fact that the latter are formed via a non-radical (polar) mechanism; or the decomposition of the peroxide proceeds via a radical pathway but there is no appreciable polarisation in the pairs of radicals RCOOR formed in view of the very short (less than 10^{-10} s) existence of the primary cage.

The lack of direct evidence for the free-radical pathway to the formation of esters (rearranged and non-rearranged) led us to test the possibility of the formation of the latter via a heterolytic mechanism[45]. It is known that skeletel rearrangements of alicyclic carbonium ions, formed in nucleophilic substitution reactions (deamination, solvolysis, transformation of alcohols into alkyl halides, etc.), which lead to ring expansion, are always accompanied by the migration of hydride ions in the ring[46–48]. If analogous carbonium ions are formed in the peroxide decomposition reactions which we investigated, one may expect isomerisation as a result of the migration of hydride ions in the expanded ester ring. The use of cycloalkylacetyl peroxides labelled with ^{13}C should show whether hydride shifts leading to the distribution of the ^{13}C atoms in the ring occur in the expanded ring†.

†The use of the ^{14}C label for the investigation of the mechanisms of organic reactions suffers from the significant disadvantage that the distribution of the label in the reaction products is determined by a very laborious degradation, which requires a long time (weeks and even months). Together with Lippmaa, the present author developed for the first time and used[72,73] a new method for the investigation of the rearrangements, consisting of the employment of the ^{13}C label and ^{13}C double nuclear magnetic resonance (DNMR). This method permits an enormous saving of time, since it does not require the degradation of the products; the distribution of the label in the final products is determined from the spectra in the course of several hours. At the present time this is the usual research technique generally accepted throughout the world.

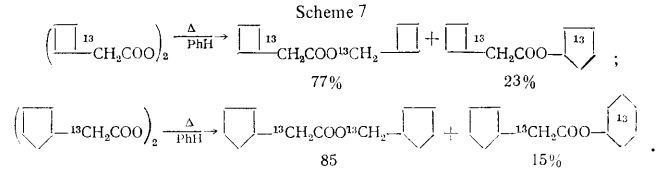
The initial cyclobutyl- and cyclopentyl-[^{13}C]acetyl peroxides were obtained in accordance with Scheme 6#:

Scheme 6



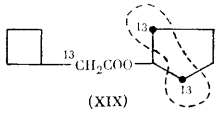
All the stages of the synthesis were tested to make sure that the position of the ^{13}C label is rigorously fixed. The peroxides were decomposed in benzene under the usual conditions[29]. The composition of the ester fraction was determined by GLC; the results of the analysis are presented in Scheme 7:

Scheme 7



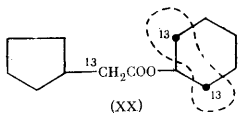
The position of the ^{13}C label in the esters was determined by the ^{13}C double nuclear magnetic resonance; the following distribution of the ^{13}C atoms was found from the spectra:

(a) in the decomposition of cyclobutyl[^{13}C]acetyl peroxide:



(XIX)

(b) in the decomposition of cyclopentyl[^{13}C]acetyl peroxide§:



(XX)

Evidently the alcohol components of both esters contain ^{13}C atoms (in equal amounts) only in the 2,5-positions in compound (XIX) and in the 2,6-positions in compound (XX), as should have been the case in the absence of ring isomerisation. In the cyclobutylmethyl and cyclopentylmethyl components of the corresponding esters, the entire ^{13}C is contained in the methylene group of the side chain.

Thus it has been established that *the esters formed in the thermolysis of cyclobutylacetyl and cyclopentylacetyl peroxides in benzene undergo a skeletal rearrangement leading to the expansion of the ring in the alcohol component of the molecule; there are no hydride shifts.*

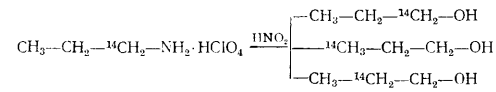
It is known that esters are not formed at all in the photolysis of cyclopentylacetyl peroxide where the most favourable conditions are generated for radical reactions[49]. Taking this fact into account and also our data showing the absence of chemically induced dynamic nuclear polarisation in the esters and the presence of rearranged esters in the thermolysis of the peroxides, one may conclude that the free-radical pathway to the formation of the esters is unlikely. On the other hand, the absence of hydride shifts in the ring in the alcohol components of the rearranged esters rules out the possibility of the formation of at least the usual carbonium ions during the reaction.

The results obtained suggest that the thermolysis of cycloalkylacetyl peroxides involves the formation in the transition state of a radical-ion pair in which species of the carbonium ion type undergo a skeletal rearrangement but do not possess sufficient energy and a sufficiently long lifetime for the occurrence of hydride shifts.

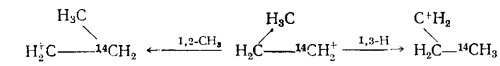
In other words, we encountered in these reactions species which are apparently intermediate between free radicals and carbonium ions.

V. THE ISOMERISATION OF CARBONIUM IONS IN DEAMINATION REACTIONS

In a series of studies[50-56] it was shown that the deamination of n-propylamine labelled with ^{14}C in the 1-position results in the formation of n-propyl alcohol containing ^{14}C (3–4% overall) not only in the 1-position but also in the 2- and 3-positions:



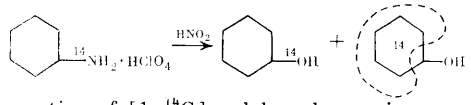
This result was explained either by the intermediate formation of an asymmetrically protonated cyclopropane or by the fact that two parallel reactions of the propyl cation take place: the 1,2-migration of the methyl group and the hydride 1,3-shift:[57]



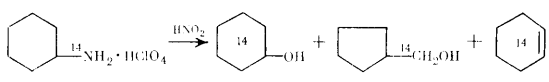
Neither of these explanations can be regarded at the present time as fully justified experimentally.

VI. THE HYDRIDE SHIFTS IN THE DEAMINATION REACTIONS OF ALICYCLIC AMINES

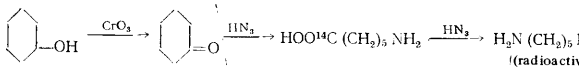
The study of the isomerisation of alkyl cations with migration of hydride ions[51,52,58] led to the hypothesis[51] that the hydroxy-group in the cyclohexanol molecules, formed on treatment of cyclohexylamine with nitrous acid, is not linked solely to the carbon atom to which the amino-group was attached in the initial cyclohexylamine molecule. This was confirmed in another investigation[59] with the aid of the radioactive ^{14}C label:



The interaction of [1-^{14}C]cyclohexylammonium perchlorate with nitrous acid leads to the formation of a mixture of cyclohexanol and cyclopentylmethanol:



In order to establish the position of the ^{14}C atom in the cyclohexanol molecule, the latter was subjected to degradation:



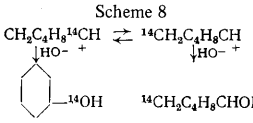
#The initial tosylates were obtained analogously[44].

§The same result was obtained when the ^{13}C DNMR spectra of the alcohols (cyclopentanol and cyclohexanol), isolated after the alkaline hydrolysis of the mixture of esters, were measured.

The pentamethylenediamine proved to be radioactive¶, its radioactivity amounting to 3.7 ± 0.3% of that of the cyclohexanone. This implies that the hydroxy-group in certain cyclohexanol molecules is not linked to the carbon atom to which the amino-group had been attached in the initial cyclohexylamine molecule.

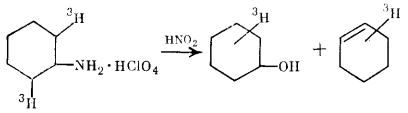
Thus the cyclohexyl cation isomerises in accordance with Scheme 8:

Scheme 8



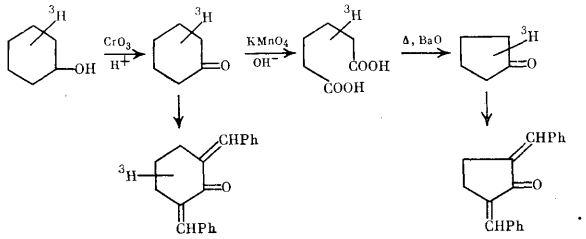
After the study of Reutov and Shatkina[59], it became clear that the mechanism of the Dem'yanov interconversion of alicyclic compounds is more complex than had been thought; *it is complicated by isomerisations involving a shift of hydride ions*.

The isomerisation of the cyclohexyl cation, formed on deamination, as a result of the hydride shift has been confirmed[61] using the tritium label. The products of the deamination of [2,6-$^3H_2$]cyclohexylamine are cyclohexene and cyclohexanol:



The degradation of [^{3}H]cyclohexanol was carried out in accordance with Scheme 9:

Scheme 9

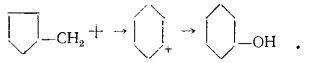


It was established that the extent of isomerisation of the cyclohexyl cation is 4.8 ± 0.3% and that the isomerisation is mainly due to the H^-1,2-shift (3.5%): the contribution of the H^-1,3-shift was 1.3% in this instance.

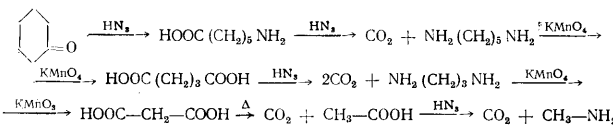
The hydride shift accompanying the expansion of the five-membered ring on deamination of [1-^{3}H]cyclopentylmethylamine have been investigated by the present author and his co-workers in Ref.62 and the isomerisation in the deamination of n-alkylamines has been studied in Refs.63–65.

The influence of anions with different nucleophilic properties on the degree of isomerisation of the [1-^{14}C]cyclohexyl cation formed on deamination of labelled cyclohexylamine has been investigated[66]. In the presence of the ClO_4^-, $H_2PO_4^-$, and CH_3COO^- anions, the degrees of isomerisation of this cation were 3.7 ± 0.3%, 5.0 ± 0.5%, and 3.7 ± 1.4% respectively. The absence of an appreciable influence of the change in the nucleophilic properties of the anions on the degree of isomerisation of the cation shows that the transition state is formed in all cases with participation of the molecules of the same substance derived from the solvent. This substance can apparently be only water. A change in the reaction temperature from 20° to 90 °C also does not affect the degree of isomerisation of the [1-^{14}C]cyclohexyl cation.

It is known that the reaction of aminomethylcycloalkanes with nitrous acid leads to cycloalkanols as a result of the rearrangement of cycloalkylmethyl cations to cycloalkyl cations. Thus, according to the data of Smith et al.[67], the reaction of aminomethylcyclopentane with nitrous acid leads to the formation, together with unsaturated hydrocarbons, of a mixture of alcohols whose main component is cyclohexanol:

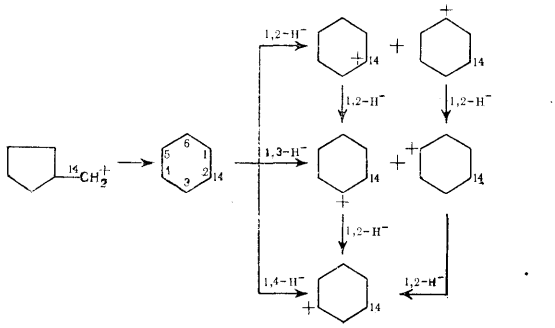


The question whether the cyclohexyl cation isomerises as a result of hydride shifts in the given reaction is of natural interest. In this connection a study was made of the reaction of aminomethylcyclopentane with nitrous acid using the ^{14}C isotope.[68] The reaction of aminomethyl[^{14}C]cyclopentane with nitrous acid was performed in an aqueous solution of sodium dihydrogen phosphate at 90 °C, as in the study of Smith et al.[67] The resulting mixture of alcohols was oxidised in order to isolate [^{14}C]cyclohexanone, which was subjected to degradation in accordance with the following scheme:



It follows from the radioactivities obtained that cyclohexanol contains ^{14}C not only in the 2-position but also in all the remaining positions, which indicates the isomerisation of the cyclohexyl cation. The cyclohexyl cation can isomerise as a result of hydride shifts from the 2,6-positions (the H^-1,2-shift), the 3,5-positions (the H^-1,3-shift), and the 4-position (the H^-1,4-shift) or as a result of consecutive shifts in accordance with Scheme 10:

Scheme 10



The distribution of the label among all the positions of the six-membered ring can be caused, generally speaking, both by independent H^-1,2-, 1,3-, and 1,4-shifts and by a combination of consecutive H^-1,2-shifts (and also H^-1,3–1,2-shifts). Shatkina et al.[68] left this question open believing that the isomerisation proceeds via independent H^-1,2-, 1,3-, and 1,4-shifts.

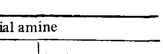
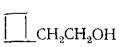
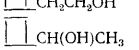
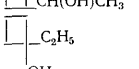
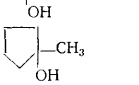
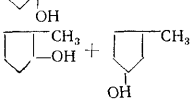
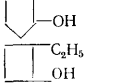
The difference between the relative radioactivities of cyclohexanone and pentamethylenediamine is 4.5%; according to Scheme 10, it corresponds to half the H^-1,2-shifts, whereas

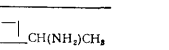
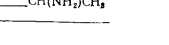
¶The low degree of rearrangement of the cyclohexyl cation may be explained by the fact that it reacts very rapidly with the solvent to form cyclohexanol. The fact that the reaction of *cis*-[2-D]cyclohexylammonium perchlorate with nitrous acid leads to the formation of at least 94% of *cis*-[2-D]cyclohexanol has been explained analogously[60].

the cyclohexyl cation isomerises to the extent of 9% as a result of H^-1,2-shifts. The radioactivity of methylamine (1.2%) is caused by half the H^-1,3-shifts, so that the cyclohexyl cation isomerises to the extent of 2.4% as a result of H^-1,3-shifts. The degree of isomerisation due to the H^-1,4-shifts is equal to the difference between the relative radioactivities of trimethylenediamine and half the sum of the percentage isomerisations due to the H^-1,2- and 1,3-shifts; this difference is 1.2%. Thus the [2-^{14}C]cyclohexyl cation formed as an intermediate in the reaction of aminomethyl[^{14}C]cyclopentane with nitrous acid isomerises to the extent of 12.6 ± 1.0% due to the hydride shifts.

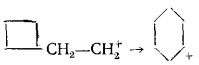
Interesting results were obtained in a study of the deamination of 1-cyclobutyl- and 2-cyclobutyl-ethylamines[69]†. The deamination was carried out in an aqueous solution of sodium dihydrogen phosphate at 90 °C; the results of the analysis of the reaction products are presented in Table 4.

Table 4. Deamination of 1-cyclobutyl- and 2-cyclobutyl-ethylamines.

Reaction products	Initial amine	
		
	37.4	4.4
	4.2	53.4
	17.4	6.9
	18.7	23.5
	14.3	7.6
	0.3	—
	17.4	6.9

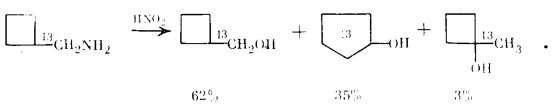
Inspection of the data in Table 4 shows that the deamination of 1-cyclobutyl- and 2-cyclobutyl-ethylamines entails the formation of a large amount of rearranged products. The set of alcohols isolated from the products of the first and second reactions is the same, but the degrees of rearrangement of the intermediate carbonium ions in the reactions investigated are different. The rearrangement accompanied by the expansion of the ring contributes 31–33% in both reactions. Apart from the skeletal rearrangement, the carbonium ions undergo a rearrangement as a result of the hydride ion shift. In the deamination of 2-cyclobutylethylamine the degree of rearrangement as a result of the migration of hydride ions, leading to products without ring expansion, is greater (39%) than in the case of 1-cyclobutylethylamine (20%). Evidently this was to be expected, since the primary carbonium ion () formed in the former case should rearrange to a much greater extent (to tertiary and secondary carbonium ions) than the more stable secondary carbonium ion () formed in the latter case.

The formation of large amounts of 1-, 2-, and 3-methylcyclopentanols in both reactions indicates a considerable tendency towards ring expansion in the intermediate cyclic carbonium ions. Ring expansion by two carbon atoms, leading to a cyclohexanol, takes place to a slight extent (0.3%) and only in the case of 2-cyclobutylethylamine. The absence of cyclohexanol from the deamination products of 1-cyclobutylethylamine indicates a one-stage rearrangement of the carbonium ion:



In the study of the deamination of aminomethylcyclobutane, we employed the ^{13}C DMNR method[71]. Dem'yanov and co-workers[74] showed that the deamination of aminomethylcyclobutane is accompanied by ring expansion and leads to the formation of cyclopentanol and the normal reaction products—cyclobutylmethanol; the yields and ratios of the products were not determined.

The earlier study of the deamination of aminomethyl[^{14}C]-cyclopentane and the demonstration of the rearrangement of the intermediate carbonium ion[68] made it of interest to study the deamination of aminomethyl[^{13}C]cyclobutane in order to observe the isomerisation of the carbonium ion leading to ring expansion. The deamination was carried out in an aqueous solution of sodium dihydrogen phosphate at 90 °C. The composition of the reaction products was determined by GLC and the distribution of the ^{13}C in the reaction products was found by the ^{13}C DNMR method[73]; the results of the analysis of the reaction products are presented below:



Inspection of the above data shows that the deamination of aminomethyl[^{13}C]cyclobutane results in the formation of a considerable amount of rearranged products. The contribution of the rearrangement accompanied by ring expansion is 35%. The formation of 1-methylcyclobutanol shows that, apart from the skeletal rearrangement, the carbonium ion isomerises due to the migration of the hydride ion, which leads to the formation of a tertiary cation.

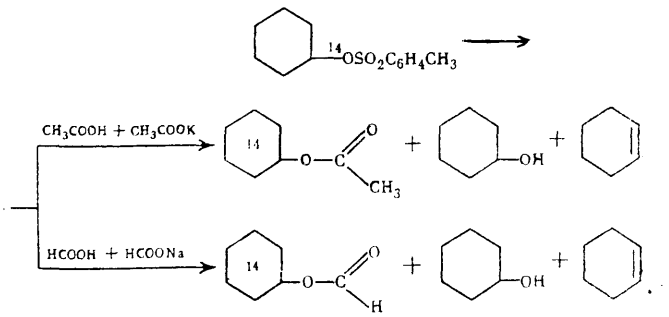
The distribution of the ^{13}C label in the cyclopentanol molecule was found from the ^{13}C DNMR spectrum. It was established that cyclopentanol contains ^{13}C not only in the 2-position but also in all the positions, which indicates the isomerisation of the intermediate carbonium ion owing to the migration of the hydride ion in the ring. In carrying out a comparison with data[68] for the isomerisation of the carbonium ion formed on deamination of aminomethyl[^{14}C]cyclopentane, one should note an appreciably greater degree of isomerisation due to hydride shifts (45% compared with 12.5%) of the carbonium ion formed from aminomethylcyclobutane and its smaller capacity for ring expansion (35% compared with 75%).

The stereochemistry of the Dem'yanov rearrangement and the influence of conformational factors on the latter have been studied in a number of investigations[75–77].

†The formation of rearranged products in the deamination of [1-^{14}C]-2-cyclopropylethylamine has been demonstrated[70].

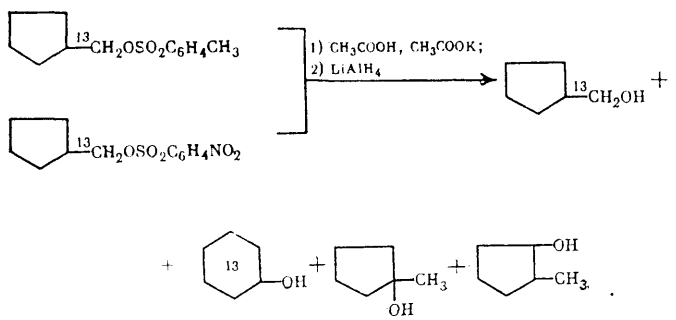
VII. THE ISOMERISATION OF CARBONIUM IONS IN SOLVOLYTIC REACTIONS

The isomerisation of the [1-^{14}C]cyclohexyl cation in acetolysis and formolysis has been studied[78]:



The solvolysis of [1-^{14}C]cyclohexyl toluene-*p*-sulphate was carried out by heating the latter with glacial acetic acid and potassium acetate at 50° and 100 °C or with anhydrous formic acid and sodium formate at 50 °C for 16 h. The cyclohexyl cation isomerises as a result of hydride shifts to the extent of 7% in acetolysis and 60% in formolysis. Analogous results were obtained in the study of the influence of the water content in the medium on the types of hydride shifts in the reaction of [2,6-D_2]cyclohexyl toluene-*p*-sulphonate.[79]

The acetolysis of cyclopentyl[^{13}C]methyl toluene-*p*-sulphonate and *p*-nitrobenzenesulphonate has also been studied[80]:



Analysis of the distribution of the label in the reaction products showed that the isomerisation due to hydride shifts takes place to the extent of 25% in the case of the toluene-*p*-sulphonate and 24% in the case of the *p*-nitrobenzenesulphonate.

The isomerisation of the cations formed as intermediates in the solvolysis of cyclopentylmethyl and cyclohexyl arenesulphonates labelled with ^{13}C or ^{14}C is significantly influenced by the ionising capacity of the medium and temperature; the influence of the leaving group is weak[81].

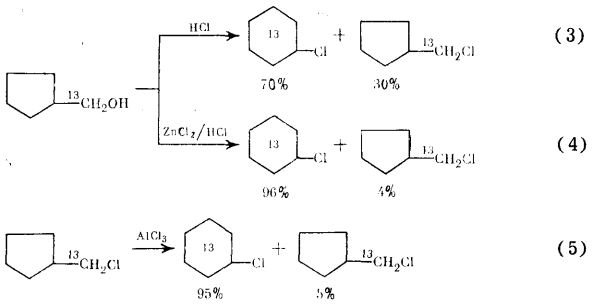
The following mixtures of products are formed in the acetolysis of cyclobutyl[^{13}C]methyl toluene-*p*-sulphonate and cyclobutyl[^{13}C]methyl *p*-nitrobenzenesulphonate:[82]

The distribution of ^{13}C in the cyclopentyl acetate molecule was determined by the ^{13}C DNMR method under the conditions of total uncoupling of the hydrogen nuclei[72]. The significant influence of the nature of the departing group on the rearrangement accompanied by ring expansion and conversely the absence of its influence on the isomerisation in the cyclopentane ring as a result of hydride shifts are noteworthy.

An analogous behaviour has been observed in the acetolysis of the corresponding 2-cyclobutylethyl arenesulphonates[83], as can be seen from the data in Table 5.

The hydride shifts were also investigated in the reactions of cyclic alcohols with the Lucas reagent ($ZnCl_2$/HCl).[84-88] Scheme 11 presents some of the reactions investigated, including the reaction with aluminium chloride[87]:

Scheme 11



(3)

(4)

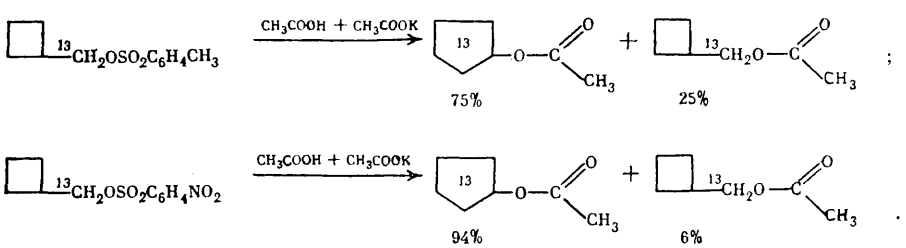
(5)

Table 5. The products of the acetolysis (rel.%) of 2-cyclobutylethyl toluene-*p*-sulphonate and *p*-nitrobenzenesulphonate.

Initial compound	OAc	OAc	OAc (*cis*-)	OAc (*trans*-)	OAc	Ring expansion, %
OTs	23.0	22.0	20.0	33.0	2.0	77
ONs	5.0	37.0	20.0	34.0	4.0	95

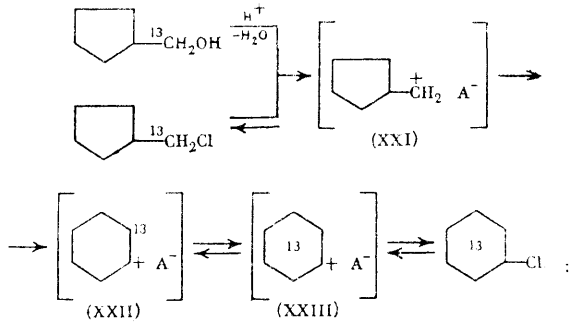
Note. Ns = *p*-nitrobenzenesulphonyl (Ed.of Translation).

The cyclohexyl chloride formed contains the label in all the positions in the cyclohexane ring and not only in the 2-position, as would have been the case in the absence of isomerisation. The virtually uniform distribution of the label in



the ring shows that the cyclohexyl cation undergoes the maximum possible isomerisation. One can imagine the following probable mechanism of the reactions: in the first stage the ion pair (XXI) is formed rapidly (as a result of the protonation of the carbinol with subsequent elimination of water or via the ionisation of cyclopentylmethyl chloride by the Lewis acids) and is in its turn irreversibly# converted into the ion pair (XXII) (Scheme 12):

Scheme 12



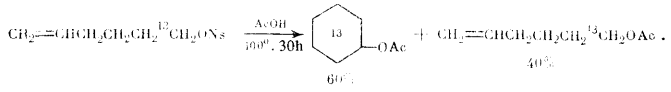
(XXII) (XXIII)

$A^- = AlCl_4^-$, $ZnCl_3^-$, HCl_2^- .

The cyclohexyl cation stabilised by the complex anion is fairly stable and isomerises as a result of hydride shifts. Ion pairs of type (XXII) are formed and subsequently give rise to the reaction products.

The isomerisation of the cyclohexyl cation on heating cyclohexanol with boric acid has been investigated. The expansion of the cyclopentane ring to the cyclohexane ring has been discovered in the demercuration of cyclopentylmethylmercury acetate[90].

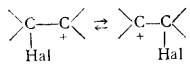
The acetolysis of [1-^{13}C]-5-hexenyl and cyclopentyl[^{13}C]methyl p-nitrobenzenesulphonates has also been investigated[91]. It has been found that the degree of cyclisation reaches 60% in the acetolysis of [1-^{13}C]-5-hexenyl *p*-nitrobenzenesulphonate after 30 h at 100 °C; the [^{13}C]cyclohexyl acetate formed has been fully isomerised, which has resulted in a uniform distribution of the label in the ring:



Analogous data have been obtained in the study of the acetolysis of cyclopentyl[^{13}C]methyl *p*-nitrobenzenesulphonate[80] under the same conditions in the absence of potassium acetate. A uniform distribution of the label was also obtained in the main reaction product, namely cyclohexyl acetate, which indicates the 100% isomerisation of the intermediate cation as a result of the migration of hydride ions. The equivalent results of these reactions suggest the formation of the same intermediate cation responsible for the isomerisation.

VIII. REARRANGEMENTS WITH THE 1,2-MIGRATION OF THE HALOGEN ATOM

Numerous rearrangements of carbonium ions due to the 1,2-migration of the halogen have been discovered in the study of a number of deamination and solvolytic reactions:

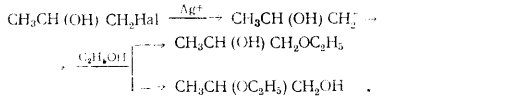


The simplest model reactions, namely the deamination of β-halogenoethylamines, have been studied using the ^{14}C label[92-96]:

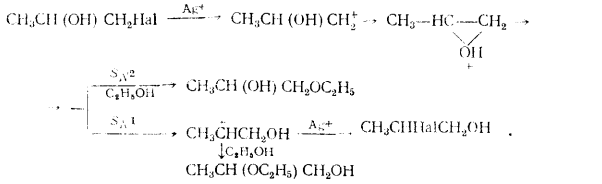


The degree of isomerisaton varies in the range 5–27% for chlorine and 30–50% for bromine. For a survey of the rearrangements and deamination reactions, see Reutov and Gudkova[97].

The alcoholysis of 1-halogeno-2-propanols and 2-halogeno-1-propanols in the presence of silver nitrate apparently proceeds with the nucleophilic 1,2-migration of the hydroxy-group[98]:



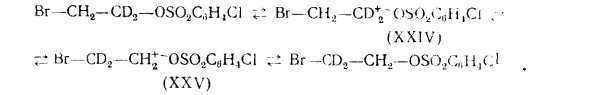
The authors quote the following hypothetical reaction mechanism:



In the solvolysis of the simplest model compounds, the degree of 1,2-migration of the halogen is as a rule higher than in the deamination reaction. Thus the degree of 1,2-migration of bromine reaches 50% in the course of the trifluoroacetolysis of [1-^{14}C]-2-bromoethyl arenesulphonates (Ar = Ph, *p*-ClC_6H_4, *p*-$CH_3C_6H_4$, or β-$C_{10}H_7$).[99] The acetolysis of 2-bromoethyl *p*-nitrobenzenesulphonate is accompanied by 40.8% 1,2-migration of the halogen[100]. As a rule, with the increase of the ionising power of the acid and with decrease of its nucleophilic properties, the degree of migration of the halogen increases[101,102]. Thus the degree of migration increases from 0 to ~4% for chlorine and from 33 to 56% for bromine in the solvolysis of [1-^{14}C]-2-halogenoethyl *p*-nitrobenzenesulphonates and *p*-bromobenzenesulphonates on passing from CH_3COOH to HCOOH and then to CF_3COOH.

In the acetolysis of halogenoethyl sulphonates in aprotic solvents, the degree of isomerisation increases with increasing polarity of the solvent. Thus the acetolysis of [1-^{14}C]-2-bromoethyl arenesulphonates in benzene is not accompanied by isomerisation at all, while in nitrobenzene the extent of the 1,2-migration of the halogen atom is 49%.

It is of interest to note that the isomerisation of the initial sulphonate, which had not reacted, was observed in the acetolysis of the [2,2-D_2]-2-bromoethyl *p*-chlorobenzenesulphonate. This isomerisation apparently takes place in the ion pairs (XXIV) and (XXV) with their reconversion into the covalent substrate:



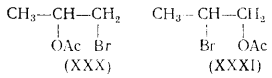
(XXIV) (XXV)

#The reversibility of this stage has been demonstrated by special experiments.

IX. THE ISOMERISATION OF ACYLOXYBROMOPROPANES

In the study of the products of the solvolysis of 1(2)-halogeno-2(1)-propyl tosylates $CH_3CH(OTs)CH_2Cl$ (XXVI), $CH_3CH(OTs)CH_2Br$ (XXVII), $CH_3CHClCH_2OTs$ (XXVIII), and $CH_3CHBrCH_2OTs$ (XXIX) in acetic acid, it was observed that the reaction products consist in each case of two halogenoalkyl acetates—unisomerised and isomerised as a result of the 1,2-migration of the halogen.

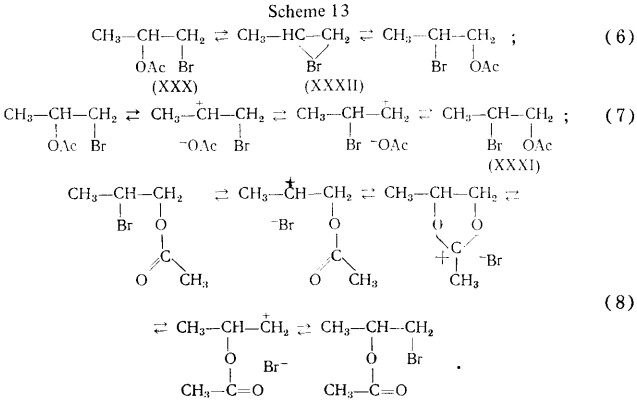
When these reactions are studied in the presence of sodium acetate, the picture becomes more complex[102]. For example, in the solvolysis of compounds (XXVII) and (XXIX), the products of secondary processes (1,2-dibromo- and 1,2-diacetoxypropanes) appear in addition to $CH_3CH(OAc)CH_2Br$ (XXX) and $CH_3CHBrCH_2OAc$ (XXXI), but the ratio of compounds (XXX) and (XXXI) remains the same as in the absence of added sodium acetate (70 : 30). These results led to the hypothesis that the acetoxybromopropanes formed undergo a reversible isomerisation owing to the 1,2-migration of bromine already in the acetolysis of the initial bromotosylates:



(XXX) (XXXI)

Indeed it has been shown[101] that, when pure compounds (XXX) and (XXXI) are heated in glacial acetic acid (for 30 h at 100 °C), the same equilibrium mixture, containing 70% of 1-bromo-2-propyl acetate and 30% of 2-bromo-1-propyl acetate, is formed. Three possible reaction mechanisms [(6), (7), and (8) in Scheme 13] were examined:

Scheme 13

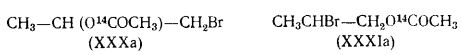


(6)

(7)

(8)

In order to discover which is the true mechanism of the isomerisation, the tracer atom method was employed[102]. The isomeric acetoxybromopropanes (XXXa) and (XXXIa) labelled with ^{14}C in the acetoxy-group were synthesised:



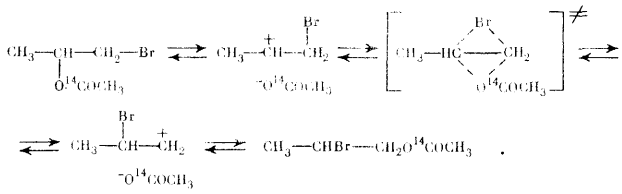
(XXXa) (XXXIa)

Each radioactive isomer was heated in glacial acetic acid for 30 h at 100 °C, i.e. until the attainment of equilibrium between the isomeric acetoxybromopropanes, after which the loss of radioactivity was compared with the degree of isomerisation. In both cases the isomerisation terminated with partial retention of the radioactive label in acetoxybromopropanes [16% for compound (XXXa) and 10% for compound (XXXIa)].

If the acetoxonium mechanism (7) operated, the complete retention of the radioactivity would have been observed, and in addition 1,2-diacetoxypropanes should have appeared in the reaction mixtures. The result of the isomerisation of the labelled compounds combined with the complete absence of 1,2-diacetoxypropane makes it possible to exclude the acetoxonium mechanism from consideration. If the reactions of compound (XXXa) and (XXXIa) with acetic acid proceeded via the S_N2 mechanism, the products would have been non-radioactive and non-isomerised acetoxybromopropanes. If the reaction proceeded exclusively via the formation of carbonium ions, an equilibrium mixture of acetoxybromopropanes with complete loss of radioactivity would have been formed.

Some retention of radioactivity can apparently be explained by the fact that the isomerisation proceeds at least partly in the stage involving the formation of contact or solvate-separated ion pairs. The isomerisation proceeds in this case via a synchronous mechanism as a consequence of the simultaneous migration of the bromine atom and the labelled acetoxy-group (Scheme 14):

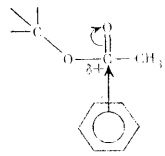
Scheme 14



The role of the main driving force leading to the formation of ion pairs in the given reaction is apparently assumed by the hydrogen bonds between the solvent molecules and the acetoxy-group in compounds (XXX) and (XXXI), although one cannot exclude *a priori* also the possibility that the dipole–dipole interaction between the molecules of acetic acid and the C–OAc bond plays a role.

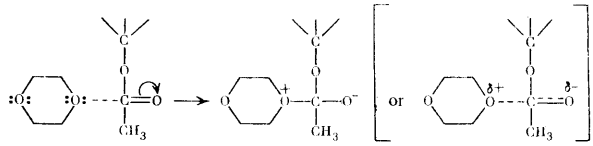
It is of interest that the isomerisation proceeds not only in acetic acid but also in benzene, toluene, and dioxane[101,102]. The isomerisation was carried out for 30 h at 100 °C and it was established that it proceeds only in those cases where the solvent molecules contain π or p electrons; the isomerisation does not occur in n-octane where such electrons are absent.

The isomerisation mechanism is apparently different from that in glacial acetic acid. Presumably in the case of aromatic solvents the main driving force of the reaction involves the interaction of the π-electron system of the benzene ring with the carboxyl carbon carrying a partial positive charge (the formation of a kind of π-complex):

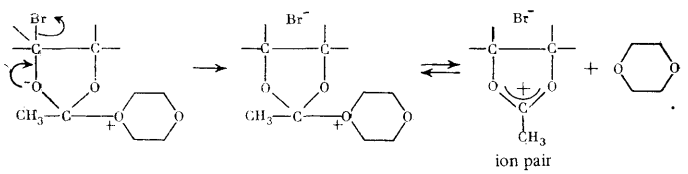


If this hypothesis is adopted, one may expect that this kind of interaction can also occur in solvents of the type of dioxane containing atoms with free p electrons and can be more intense than the interaction due to π-electron systems. The above interaction creates favourable conditions for the operation of the oxolonium mechanism (Scheme 15):

Scheme 15

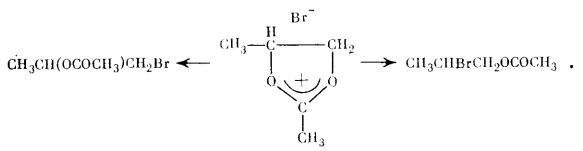


The carbonyl group activated in this way can probably play the role of an "internal" nucleophile in relation to the C–Br bond present in the molecule of the acetoxybromo-derivative:



ion pair

Next the ion pair can be stabilised by being converted into the isomeric acetoxybromopropanes:



The corresponding trifluoroacetoxybromopropanes do not isomerise. This is apparently due to the impossibility of the interaction of solvent molecules with the carboxyl carbon atom, examined above, owing to the steric hindrance generated by the three fluorine atoms. On the other hand, the corresponding trimethylacetoxybromopropanes (for which the steric hindrance is still greater) isomerise faster than acetoxybromopropanes and the reaction proceeds even in n-heptane. The stabilising influence of the t-butyl group on the acetoxonium cation formed apparently plays a decisive role in this case; the necessity for the activation of the carbonyl group by solvent molecules does not then arise.

* * *

We may note in conclusion that the development of the chemistry of alkyl radicals and alkyl cations can serve as a good illustration of the familiar postulate that science develops in jumps depending on the appearance of new research techniques. Thus qualitatively new results in the chemistry of carbonium ions are associated with the employment of superacid media, NMR, the tracer atom method, and in particular the ^{13}C double NMR. An equally great importance of the development and application of new research methods can be traced also in the chemistry of aromatic carbonium ions[103].

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