REARRANGEMENTS OF FREE ALKYL RADICALS AND ALKYL CATIONS IN SOLUTION

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INTRODUCTION

The extent and diversity of the problems embraced by the title preclude any comprehensive treatment of them in a single lecture. I shall, therefore, confine myself mainly to a discussion of the rearrangements of radicals and cations due to hydrogen shifts. In the case of radicals this concerns migration of the neutral atoms and in the case of cations—of hydride ions. A considerable portion of the lecture will be devoted to a description of the work done in this field by the author and his co-workers chiefly in the Moscow University and the Institute for Elementary-organic Compounds of the Academy of Sciences of the U.S.S.R.
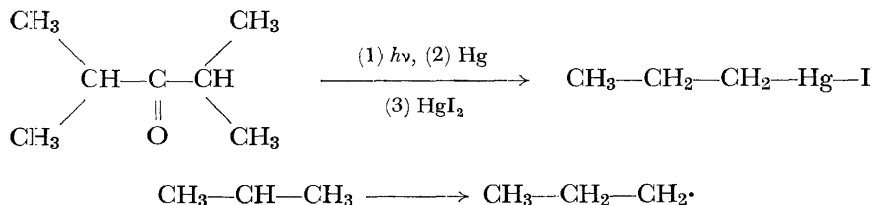
ISOMERIZATION OF ALKYL RADICALS

No one doubts at present that free radicals, both in the gaseous and liquid phases, are capable of isomerization.

From their very beginning, and until the present time, gaseous-phase and liquid-phase studies of free particles proceeded along relatively independent lines. The gaseous-phase studies have centred almost entirely about the reaction kinetics of the simpler radicals (methyl, ethyl, *etc.*). Liquid-phase work has involved a wide range of radicals, from the simplest to the most complex, and includes investigations into methods for their production, into their reactivities and into their utilization, in particular, for synthetic purposes.

Despite these differences, workers engaged in both gaseous- and liquid-phase studies arrived almost simultaneously at the conclusion that free radicals are capable of isomerization.

That the isopropyl radical isomerizes to normal propyl was inferred by Glazebrooke and Pearson[1] from the fact that reaction of the photolytic products of diisopropyl ketone with metallic mercury, and subsequent treatment with mercuric iodide, afforded n-propylmercuric iodide.

$$
\begin{array}{c}
CH_3 \qquad\qquad CH_3 \\
\diagdown \qquad\quad \diagup \\
CH-C-CH \qquad \xrightarrow{\begin{array}{c}(1)\ h\nu,\ (2)\ Hg\\ \hline (3)\ HgI_2\end{array}} \qquad CH_3-CH_2-CH_2-Hg-I \\
\diagup \quad \| \quad \diagdown \\
CH_3 \quad O \quad CH_3
\end{array}
$$

$$
CH_3-CH-CH_3 \xrightarrow{\qquad} CH_3-CH_2-CH_2\cdot
$$

Semenov and co-workers[2] had to assume isomerization of free radicals in order to explain certain phenomena in the liquid-phase oxidation of hydrocarbons.

Thus, studying the mercury-sensitized photochemical oxidation of hydrocarbons at temperatures above $100°$, they[3] came to the conclusion that intermediate isomerization of the peroxide radicals takes place, as, for example:

$$CH_3—O—O· \longrightarrow ·CH_2—O—O—H$$
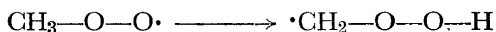
The inference that free alkyl radicals in the gaseous phase apparently can isomerize even at room temperature follows from the studies of Voevodskii and Mardaleishvili[4] on deuterium exchange of free n-propyl, primary isobutyl and cyclohexyl radicals. The isomerization (β-isomerization) was suggested as an explanation of the strong (up to 50 per cent) deuteration of the recombination products.
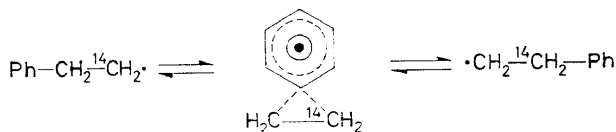
ISOMERIZATION OF FREE RADICALS IN SOLUTION

Considerable material has now accumulated concerning the isomerization of free radicals in solution, accompanied by rearrangement of the carbon skeleton or migration of a halogen atom.

The first to observe skeletal rearrangement of free radicals were Urry and Kharasch[5], while studying the reaction between phenylmagnesium bromide and neophyl chloride in the presence of cobalt chloride.

$$Ph—C(CH_3)_2CH_2· \xrightarrow{\text{Rearrangement}} \overset{·}{C}(CH_3)_2—CH_2—Ph$$
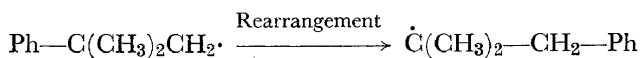
Later, other skeletal rearrangements were revealed in cobalt chloride catalysed reactions between organomagnesium compounds and halogen derivatives[6, 7], in particular, rearrangement with 1,2 migration of the aryl group[7].
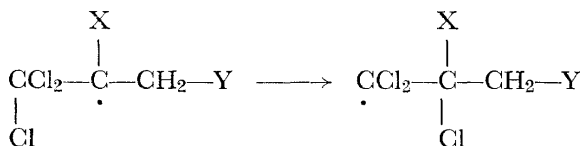

Similar free radical rearrangements were discovered in the t-butyl peroxide decarbonylation of aldehydes[8-14]. The following example is from the work of Winstein and Seubold[8].
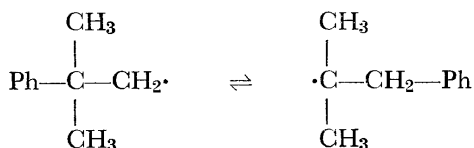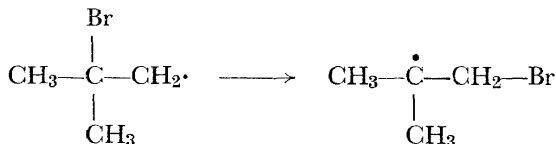
Nesmeyanov, Freidlina and co-workers[15−20] discovered the isomerization in solution of the special halogenated radicals, resulting in a 1,2 migration of a halogen atom.

$$
\underset{\underset{Cl}{|}}{\overset{\overset{X}{|}}{CCl_2}}\!\!-\!\!\overset{\bullet}{C}\!\!-\!\!CH_2\!\!-\!\!Y \longrightarrow \underset{\overset{\bullet}{}}{CCl_2}\!\!-\!\!\underset{\underset{Cl}{|}}{\overset{\overset{X}{|}}{C}}\!\!-\!\!CH_2\!\!-\!\!Y
$$

(X and Y = H and Cl, H and Br, CH₃ and Cl, Cl and Br,
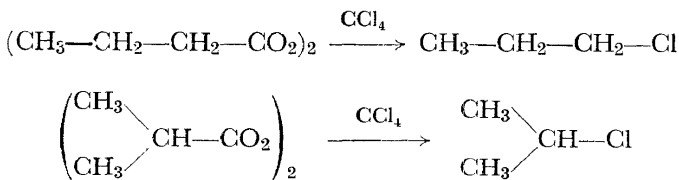H and CCl₃, CH₃ and Br, Cl and Cl, Br and Br)

Recently Skell, Allen and Gilmour described the rearrangement of the bromine-substituted isobutyl radical in the photochemical chlorination of t-butyl bromide. Here also the isomerization is due to a 1,2 shift of the halogen[21].

$$
\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{CH_3}}\!\!-\!\!C\!\!-\!\!CH_2\!\bullet \longrightarrow CH_3\!\!-\!\!\underset{\underset{CH_3}{|}}{\overset{\bullet}{C}}\!\!-\!\!CH_2\!\!-\!\!Br
$$

ISOMERIZATION OF ALKYL RADICALS

It was not known until very recently whether simple alkyl radicals are capable of undergoing isomerization in solution under mild conditions.

All attempts made hitherto to observe this phenomenon had yielded only negative results. Thus, for instance, Kharasch[22], studying the decomposition of n-butyryl and isobutyryl peroxides in carbon tetrachloride could not detect even traces of isopropyl chloride in the former or propyl chloride in the latter reaction.

$$(CH_3\!\!-\!\!CH_2\!\!-\!\!CH_2\!\!-\!\!CO_2)_2 \xrightarrow{\ CCl_4\ } CH_3\!\!-\!\!CH_2\!\!-\!\!CH_2\!\!-\!\!Cl$$

$$\left(\underset{CH_3}{\overset{CH_3}{{>}}}CH\!\!-\!\!CO_2\right)_2 \xrightarrow{\ CCl_4\ } \underset{CH_3}{\overset{CH_3}{{>}}}CH\!\!-\!\!Cl$$

He concluded on this basis that the n-propyl and isopropyl radicals do not isomerize into one another.

$$CH_3\!\!-\!\!CH_2\!\!-\!\!CH_2\bullet \;\rightleftarrows\!\!\!\!/\!\!\!\!\rightleftarrows\; CH_3\!\!-\!\!\underset{\bullet}{CH}\!\!-\!\!CH_3$$
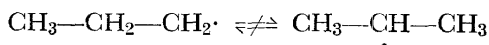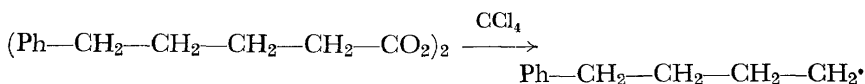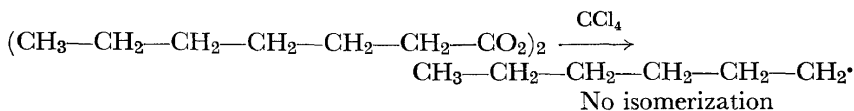
This then threw doubt on the validity of the results of Glazebrook and Pearson[1] mentioned earlier.

Brown and Russell[23] investigated the possibility of isomerization of alkyl radicals in liquid-phase photochlorination. Using labelled isobutane the

authors showed that no isomerization of primary to the secondary isobutyl radical takes place.

$$CH_3—CD—CH_2 \cdot \quad \rightleftarrows \quad CH_3—\overset{\bullet}{C}—CH_2D$$
$$\underset{CH_3}{\big|} \qquad\qquad\qquad \underset{CH_3}{\big|}$$

Investigating the decomposition of heptanoyl and δ-phenylvaleryl peroxide in carbon tetrachloride[24, 25]. DeTar also arrived at the conclusion that free radicals in solutions† under mild conditions do not undergo isomerization.

$$(CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CO_2)_2 \xrightarrow{CCl_4}$$
$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2 \cdot$$
$$\text{No isomerization}$$

$$(Ph—CH_2—CH_2—CH_2—CH_2—CO_2)_2 \xrightarrow{CCl_4}$$
$$Ph—CH_2—CH_2—CH_2—CH_2 \cdot$$

The nature of all the end products carefully isolated and analysed by De Tar clearly showed that the n-hexyl radical and phenyl-n-butyl radical did not isomerize. Thus, no reliable proofs had been presented hitherto that isomerization of alkyl radicals occurs in solution under mild conditions†. At the same time, if free alkyl radicals formed, for instance, in the decomposition of diacyl peroxides in solution do exist as independent kinetic entities, they should be capable of isomerization.

As is well known, free alkyl radicals can remove a hydrogen atom from a molecule of solvent:
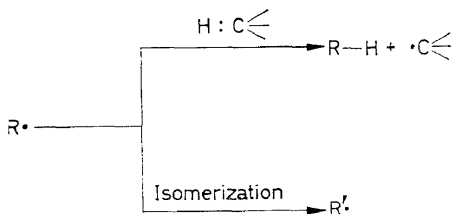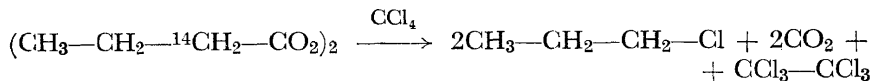

There is, therefore, no reason to suppose that under favourable steric conditions these radicals could not also remove hydrogen atoms from themselves with accompanying valency shifts. The extent of isomerization will depend upon the relative isomerization and substitution rates. At moderate peroxide decomposition temperatures isomerization of the free radicals could be so small as to be detectable only by very refined techniques. Bearing this in mind, the author (together with Shatkina)[27, 28] studied

† The suggestion by Grob and Kammuler[26] that in the thermal degradation of phenylhexanoic acid peroxide the isomerization $Ph—CH_2—(CH_2)_3—CH_2 \cdot \rightarrow Ph—\overset{\cdot}{C}H(CH_2)_3—CH_3$ can possibly take place is apparently correct although it requires confirmation on analogous systems.
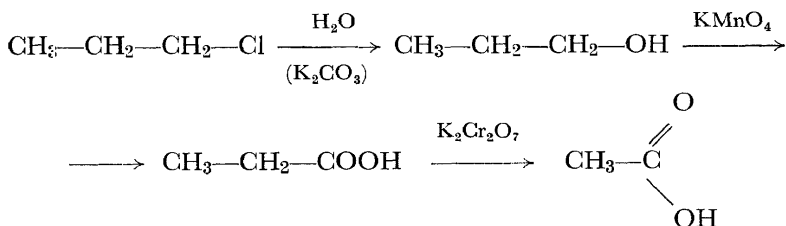
the decomposition in boiling carbon tetrachloride of n-butyryl peroxide labelled in the α-position with radioactive ^{14}C†.

$$(CH_3\!-\!CH_2\!-\!^{14}CH_2\!-\!CO_2)_2 \xrightarrow{\ CCl_4\ } 2CH_3\!-\!CH_2\!-\!CH_2\!-\!Cl + 2CO_2 + \\ + CCl_3\!-\!CCl_3$$

Not only n-propyl-1-^{14}C but also propyl-3-^{14}C chloride was found:

$$CH_3\!-\!CH_2\!-\!^{14}CH_2\!-\!Cl \ and \ \ ^{14}CH_3\!-\!CH_2\!-\!CH_2\!-\!Cl$$
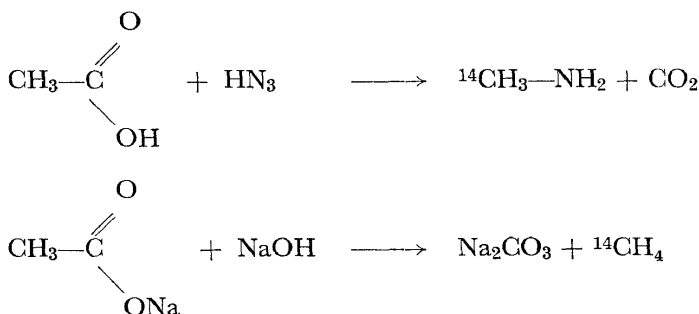
A short proof is given for the formation of n-propyl-3-^{14}C chloride. In order to locate the ^{14}C atom in the propyl chloride molecule, it was converted by hydrolysis and oxidation to n-propionic acid which was further oxidized to acetic acid:

$$CH_3\!-\!CH_2\!-\!CH_2\!-\!Cl \xrightarrow[\ (K_2CO_3)\ ]{\ H_2O\ } CH_3\!-\!CH_2\!-\!CH_2\!-\!OH \xrightarrow{\ KMnO_4\ }$$

$$\xrightarrow{\ } CH_3\!-\!CH_2\!-\!COOH \xrightarrow{\ K_2Cr_2O_7\ } CH_3\!-\!\overset{\displaystyle O}{\underset{\displaystyle OH}{C}}$$
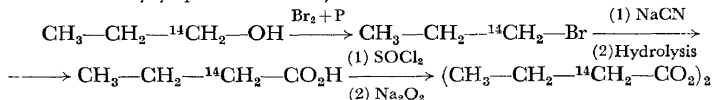
It was shown by special experiments that the initial butyryl peroxide contained the label only in the α-position and that under the reaction conditions employed no rearrangement occurred at any stage of the conversion of n-propyl chloride to acetic acid.

The acetic acid was found to be radioactive (ca. 4 per cent of the total propionic acid activity), from which it follows that the n-propyl radicals underwent partial isomerization. In order to establish the position of the label in the acetic acid, the latter was subjected to Schmidt cleavage on the one hand, and its sodium salt was fused with alkali on the other:
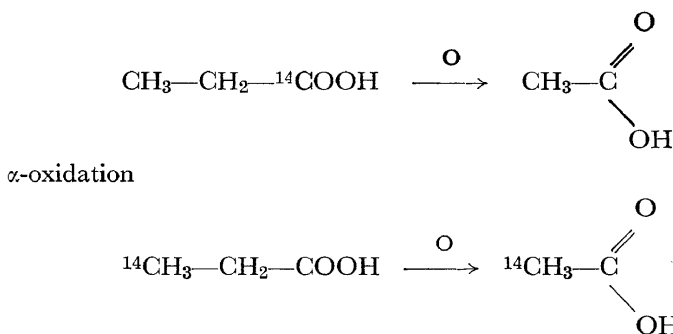
$$CH_3\!-\!\overset{\displaystyle O}{\underset{\displaystyle OH}{C}} + HN_3 \longrightarrow \ ^{14}CH_3\!-\!NH_2 + CO_2$$

$$CH_3\!-\!\overset{\displaystyle O}{\underset{\displaystyle ONa}{C}} + NaOH \longrightarrow Na_2CO_3 + \ ^{14}CH_4$$

† ^{14}C-labelled n-butyryl peroxide was synthesized as follows:

$$CH_3\!-\!CH_2\!-\!^{14}CH_2\!-\!OH \xrightarrow[\ \ ]{\ Br_2+P\ } CH_3\!-\!CH_2\!-\!^{14}CH_2\!-\!Br \xrightarrow[\ (2)Hydrolysis\ ]{\ (1)\ NaCN\ }$$

$$\xrightarrow{\ } CH_3\!-\!CH_2\!-\!^{14}CH_2\!-\!CO_2H \xrightarrow[\ (2)\ Na_2O_2\ ]{\ (1)\ SOCl_2\ } (CH_3\!-\!CH_2\!-\!^{14}CH_2\!-\!CO_2)_2$$
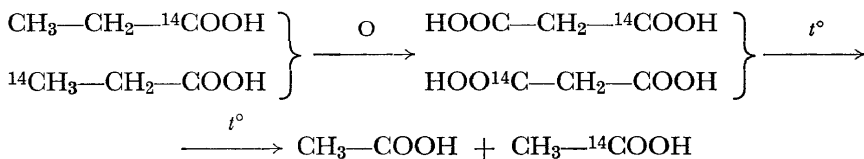
The carbonate resulting from the alkali fusion was found to be inactive, whereas in the other reaction the activity of the acid passed over entirely to the methylamine.

Formation of completely inactive carbon dioxide showed that in the potassium dichromate oxidation of propionic acid only the α-position is affected:

$$CH_3-CH_2-{}^{14}COOH \quad \xrightarrow{O} \quad CH_3-C\overset{\displaystyle O}{\underset{\displaystyle OH}{\big<}}$$

α-oxidation

$$^{14}CH_3-CH_2-COOH \quad \xrightarrow{O} \quad {}^{14}CH_3-C\overset{\displaystyle O}{\underset{\displaystyle OH}{\big<}}$$

which therefore gives acetic acid with no activity in the carboxyl group. If β-oxidation had occurred together with the α-reaction, viz.

$$\left.\begin{array}{c} CH_3-CH_2-{}^{14}COOH \\[4pt] {}^{14}CH_3-CH_2-COOH \end{array}\right\} \xrightarrow{O} \left.\begin{array}{c} HOOC-CH_2-{}^{14}COOH \\[4pt] HOO^{14}C-CH_2-COOH \end{array}\right\} \xrightarrow{t^\circ}$$

$$\xrightarrow{t^\circ} CH_3-COOH + CH_3-{}^{14}COOH$$

the acetic acid would have possessed some of the label in the carboxyl group, and this in turn would have given rise to radioactive carbon dioxide on reaction with hydrazoic acid:

$$CH_3-{}^{14}COOH + HN_3 \longrightarrow CH_3-NH_2 + {}^{14}CO_2$$
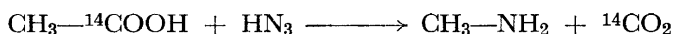
Actually, however, the CO_2 proved to be inactive†.

It is thus clear that the free propyl radical formed in the thermal decomposition of n-butyryl peroxide in solution:
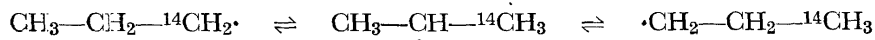
$$(CH_3-CH_2-CH_2-COO)_2 \longrightarrow 2CH_3-CH_2-CH_2\cdot + 2CO_2$$
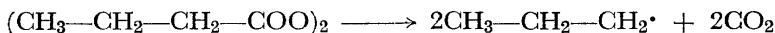
undergoes isomerization of the type

$$CH_3-CH_2-{}^{14}CH_2\cdot \quad \rightleftharpoons \quad \cdot CH_2-CH_2-{}^{14}CH_3$$

† According to Lorber and Cook[29], potassium dichromate oxidation of propionic-2-^{13}C, 3-^{14}C acid gives not only ^{12}C, but also some ^{13}C and ^{14}C labelled carbon dioxide (evidently propionic acid is oxidized further than to acetic acid). These data in no way affected our results, however, because we determined the activity of acetic acid, rather than of CO_2.

The mean activity values of acetic acid and methylamine obtained in three experiments showed that under the conditions mentioned earlier the n-propyl radical isomerizes to the extent of 4 ± 0.5 per cent.

Considering the probable mechanism of n-propyl radical isomerization, one can first of all reject two-stage hydrogen migration from the α-position.

$$CH_3—CH_2—{}^{14}CH_2 \cdot \ \rightleftharpoons \ CH_3—\underset{\cdot}{CH}—{}^{14}CH_3 \ \rightleftharpoons \ \cdot CH_2—CH_2—{}^{14}CH_3$$

Against such a mechanism are not only steric factors but also the experiments of Kharasch, who could not detect even traces of isopropyl chloride on the decomposition of n-butyryl peroxide in carbon tetrachloride. The assumption that the non-classic radical
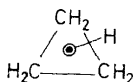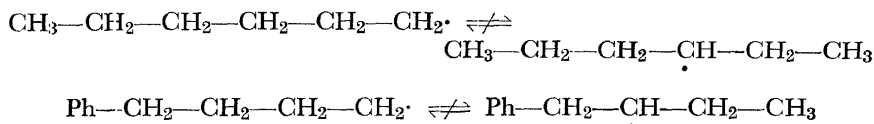

is formed, which can be regarded as a kind of cyclopropane–hydrogen atom complex, also does not agree with the experimental data. The equal probability of rupture at each of the three C—C cyclopropane bonds (in the reaction with CCl_4) would have led to equidistribution of the label among all three positions of the propyl radical. Actually, however ^{14}C was found only at positions 1 and 3.

The most probable isomerization mechanism is the one-step, 1,3-hydrogen shift *via* the four-membered transition state (A):

(A)
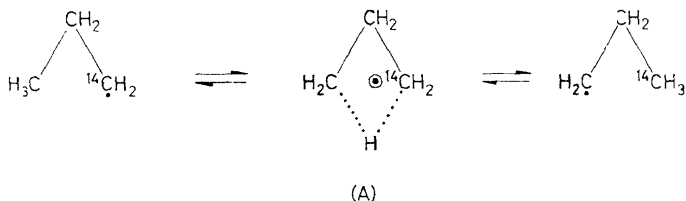
In view of the results obtained in the isomerization of the n-propyl radical in solution, it would be of interest to know why DeTar found no isomerization of n-hexyl and phenylbutyl radicals

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2 \cdot \ \rightleftharpoons\!\!\!/$$
$$CH_3—CH_2—CH_2—\underset{\cdot}{CH}—CH_2—CH_3$$

$$Ph—CH_2—CH_2—CH_2—CH_2 \cdot \ \rightleftharpoons\!\!\!/ \ Ph—CH_2—\underset{\cdot}{CH}—CH_2—CH_3$$
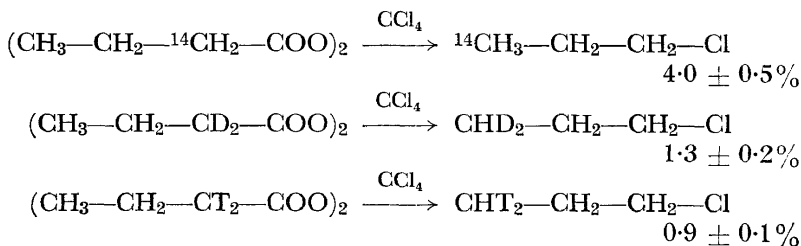
although in both cases a 1,3-hydrogen shift is formally possible (not to mention the 1,4 shift with formation of a stabilized radical of the benzyl type that could occur in the second case).

Since the lifetime of both radicals in boiling carbon tetrachloride should not differ greatly from that of the propyl radical, one must search for another cause to account for the different behaviour of these three species.

A possible key to this problem is suggested by the results of the author's

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study (together with Ostapchuk, Bundel and Remova) on the isomerization of deuterium- and tritium-substituted n-propyl radicals. In this study of the behaviour of radicals, approaching as closely as possible, although differing somewhat from n-propyl, it was found that the percentage of isomerized propyl chloride diminishes on passing from n-butyryl-α-^{14}C peroxide to n-butyryl-α-D_2 peroxide and further to n-butyryl-α-T_2 peroxide†.

$$(CH_3—CH_2—^{14}CH_2—COO)_2 \xrightarrow{CCl_4} {}^{14}CH_3—CH_2—CH_2—Cl$$
$$4\cdot 0 \pm 0\cdot 5\%$$

$$(CH_3—CH_2—CD_2—COO)_2 \xrightarrow{CCl_4} CHD_2—CH_2—CH_2—Cl$$
$$1\cdot 3 \pm 0\cdot 2\%$$

$$(CH_3—CH_2—CT_2—COO)_2 \xrightarrow{CCl_4} CHT_2—CH_2—CH_2—Cl$$
$$0\cdot 9 \pm 0\cdot 1\%$$

In *Figure 1* are represented the proposed transition states for β-isomerization of three radicals investigated by the author and of two radicals investigated by DeTar.
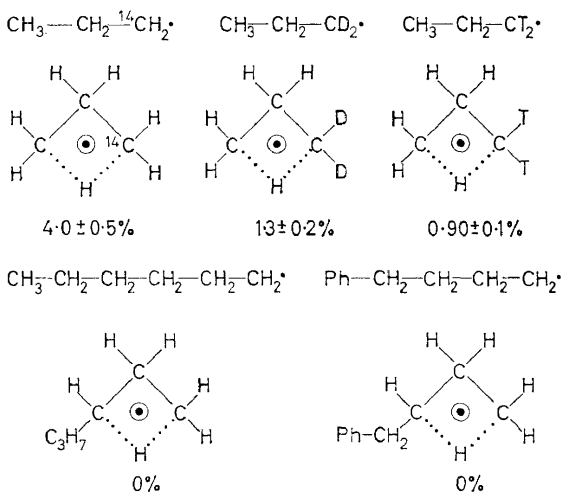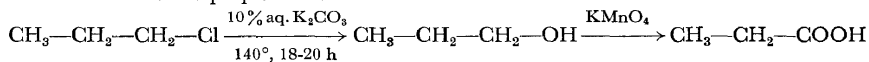

Figure 1

The causes of the different behaviour of all these radicals cannot lie in the energy relations of bond rupture and formation in the course of the isomerization. Thus, the energy of the methylene C—H bond which is

† The amount of deuterium and of tritium in position 3 of n-propyl chloride was determined in identical ways. Propyl chloride was hydrolysed to ethyl alcohol and the latter was then oxidized to propionic acid.

$$CH_3—CH_2—CH_2—Cl \xrightarrow[140°,\ 18\text{-}20\ h]{10\%\ aq.\ K_2CO_3} CH_3—CH_2—CH_2—OH \xrightarrow{KMnO_4} CH_3—CH_2—COOH$$

After careful purification the percentage of deuterium (or tritium) in the propionic acid was determined by ordinary methods.

The absence of hydrogen shifts during hydrolysis of propyl chloride and oxidation of propyl alcohol was established by special experiments.

broken during isomerization of the radicals CH_3—CH_2—CH_2—CH_2—CH_2—$CH_2\cdot$ and Ph—CH_2—CH_2—CH_2—$CH_2\cdot$ is less than that of the resultant methyl C—H bond. There are also no grounds for the view that the five radicals shown in *Figure 1* possess considerably different lifetimes. The possible causes for the greater tendency of the n-propyl than of the other free radicals to isomerize by means of a 1,3-shift may lie both in the favourable conformational factors and in the relatively high symmetry, of the transition state:


$$R=R'=R''=R'''=H$$
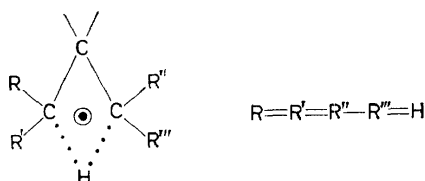
The percentage decrease of rearrangement on passing from the n-propyl to the dideuteriumpropyl and then to the ditritiumpropyl radical may also be due to a certain difference in electron density at the first unsaturated carbon atom of the three species, in addition to the diminishing symmetry of the transition state.

One might mention, in concluding this part of the lecture, that, as would be expected, the percentage isomerization of the n-propyl radical decreases on changing from carbon tetrachloride to bromoform.

Thus, in the decomposition of n-butyryl-D_2 peroxide in bromoform at $145°$ the amount of propyl-3-D_2 bromide formed by β-isomerization of the n-propyl radical is only $0\cdot6 \pm 0\cdot2$ per cent,

$$(CH_3—CH_2—CD_2—COO)_2 \xrightarrow[\sim145°]{CHBr_3} \underset{0\cdot6 \,\pm\, 0\cdot2\%}{CHD_2—CH_2—CH_2—Br}$$
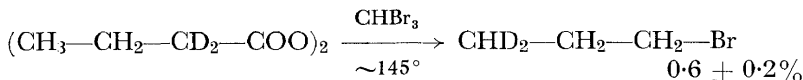
i.e. appreciably less than the amount ($1\cdot3 \pm 0\cdot2$ per cent) of the corresponding propyl chloride, formed in the β-isomerization of the n-propyl radical at the boiling point of carbon tetrachloride. This is probably due to the more favourable conditions for the competing reaction of halogen removal by the propyl radical in bromoform, bromine being more readily removed than chlorine.
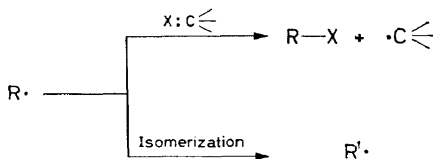

Reactivity of X—C bond with
respect to X : Cl<H<Br

ISOMERIZATION OF ALKYL CATIONS

I now turn to some problems of alkyl cation isomerization in solution. When it had been established that n-propyl radical isomerization is the

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result of a 1,3 hydrogen shift, it was quite natural to compare the behaviour of the n-propyl radical with that of the n-propyl cation in solution. The literature[30] contains a description of the interesting skeletal rearrangement of the n-propyl cation, assumed to proceed *via* formation of the simplest possible non-classical carbonium ion (B).

$$CH_3$$

$$H_2C \cdots\!\!\!^{14}CH_2$$

(B)

$$CH_3-CH_2-^{14}CH_2^+ \qquad\qquad ^+CH_2-^{14}CH_2-CH_3$$
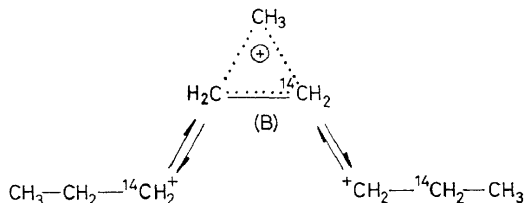
Some doubts were entertained as to the adequacy of the proof of this rearrangement, differing fundamentally from the one found by the author for the free n-propyl radical.

Since this work had served as the basis for far-reaching theoretical conclusions as to the nature of rearrangements of the pinacol type, and of the simple non-classical carbonium ion, it was decided to repeat the experiments[31, 32].

As is known, the possibility of the intermediate formation of non-classical carbonium ions is at present no longer questioned†. The first to suggest the importance of the non-classical carbonium ion as an intermediate in many reactions was Dewar[33].

Reactions of cyclic (particularly polycyclic) compounds proved to be fruitful ground for the growth of non-classical ion concepts. Illustrated in *Figure 2* are non-classical cations which undoubtedly play an important part in many reactions.
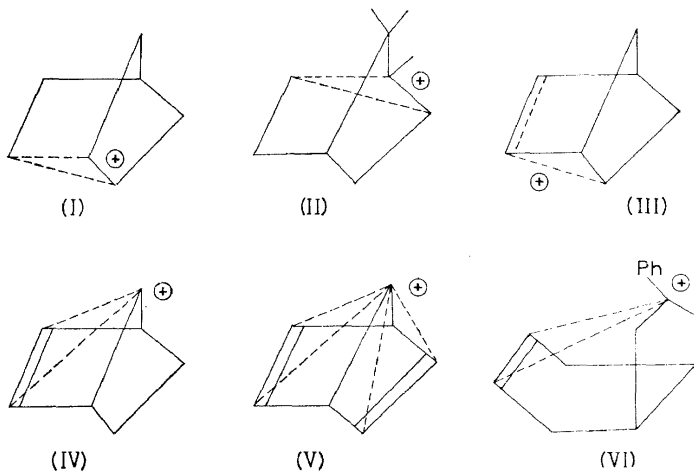

Figure 2

† See, however, ref. 32a.

The bridged cation (I) is to be found in reactions of exo-norbornyl compounds[34]. Cation (II) appears in the solvolysis of camphene hydrochloride or of isobornyl derivatives, while homoallylic cation (III) stems from norbornenyl systems[35]. The recently discovered non-classical cations (IV), (V) and (VI) possess unusually high stability[36].

It has been established mainly by Roberts and co-workers[37] that the carbonium ion (VII), which probably owes its existence in large part to electron delocalization, is formed in some reactions of cyclopropylmethyl derivatives (*Figure 3*).
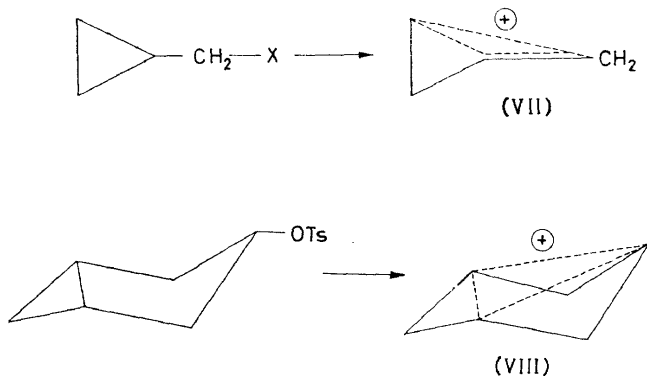


(VII)

(VIII)

Figure 3

Recently, Winstein and co-workers[38] described an interesting example of a non-classical carbonium ion (VIII), formed in the solvolysis of *cis*-3-bicyclo(3,1,0) hexyltosylate.

The relative stability of intermediate non-classical carbonium ions in the acyclic series is still a problem open to discussion, although there is no doubt as to their participation in reactions of compounds of this series.

Reactions proceeding with formation of carbonium ions are often accompanied by skeletal rearrangement. In a generalized form these can be represented as follows:
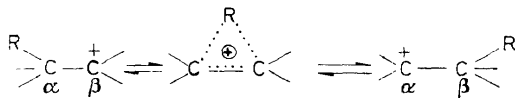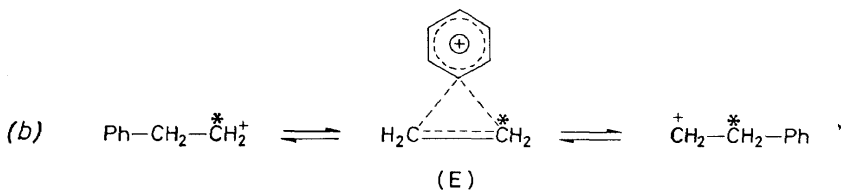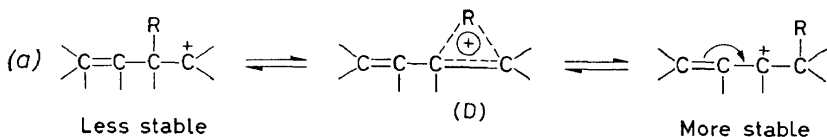

The simplest conceivable case of such isomerization is rearrangement of n-propyl cation:

(C)
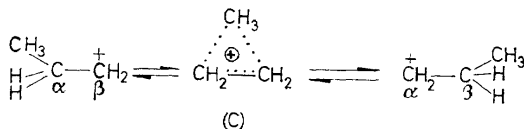
This should proceed *via* the simplest non-classical carbonium ion (C).

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The driving force of rearrangements in which carbonium ion formation plays an essential part may be either (a) the greater stability of the final carbonium cation or (b) synartetic (anchimeric) acceleration, for example:

(a) Less stable   (D)   More stable

(b) $Ph-CH_2-\overset{*}{C}H_2^+$ ⇌ $H_2\overset{}{C}\text{------}\overset{*}{C}H_2$ ⇌ $\overset{+}{C}H_2-\overset{*}{C}H_2-Ph$
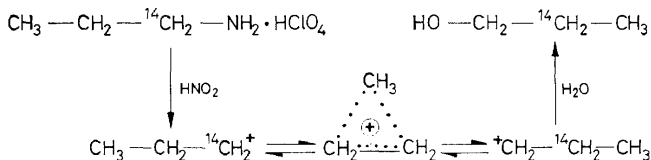
(E)

Synartetic (anchimeric) acceleration

In the latter case the non-classical carbonium ion (E) is stabilized by delocalization of the positive charge through interaction with the π-electrons of the benzene ring.

Alkyl groups are apparently also capable of stabilizing the three-membered non-classical cation (X) due to their positive inductive effect. Of course stabilization should be less than that due to the aromatic ring.

(IX)   (X)   (XI)

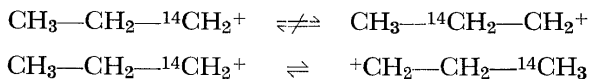Most stable   Less stable   Least stable
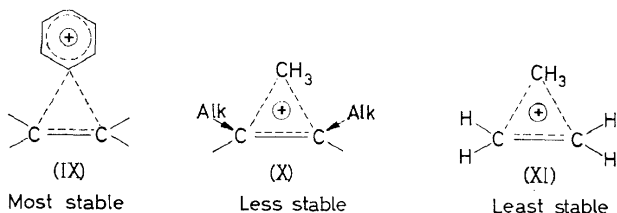
The least stable of the possible ions should be the simplest non-classical ion (XI), owing to the least possibility of positive charge delocalization. It was assumed, however, that such an ion forms in the course of the reaction between n-propylamine and nitrous acid[30].


$CH_3-CH_2-{}^{14}CH_2-NH_2 \cdot HClO_4$ $HO-CH_2-{}^{14}CH_2-CH_3$

|HNO_2 |H_2O

$CH_3-CH_2-{}^{14}CH_2^+$ ⇌ $CH_2\text{------}CH_2$ ⇌ ${}^+CH_2-{}^{14}CH_2-CH_3$

It has already been mentioned that the reaction of n-propylamine-1-^{14}C perchlorate with nitrous acid was repeated and it was found that in reality the n-propyl cation in this reaction undergoes isomerization similar to that

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discovered by us for the propyl radical[31, 32] rather than skeletal rearrangement (*via* formation of the non-classical carbonium ion):

$$CH_3—CH_2—^{14}CH_2^+ \rightleftharpoons\!\!\!\!/\!\!\!\!\rightleftharpoons CH_3—^{14}CH_2—CH_2^+$$

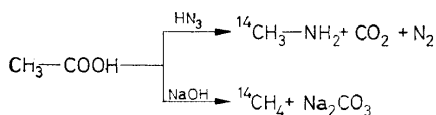$$CH_3—CH_2—^{14}CH_2^+ \rightleftharpoons ^+CH_2—CH_2—^{14}CH_3$$

A short proof of this conclusion is now given. Reaction of n-propylamine perchlorate with nitrous acid led to the formation of n-propyl and isopropyl alcohols:

$$CH_3—CH_2—^{14}CH_2—NH_2·HClO_4 \xrightarrow{HNO_2} CH_3—CH_2—CH_2OH +$$
$$+ CH_3—CH—CH_3†$$
$$|$$
$$OH$$
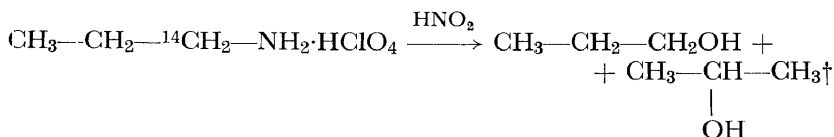
Permanganate oxidation of n-propyl alcohol afforded propionic acid, which was further oxidized by potassium dichromate to acetic acid and carbon dioxide
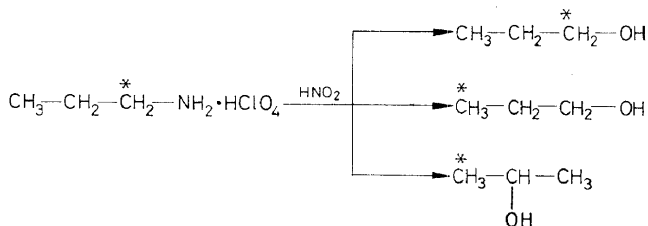
$$CH_3—CH_2—CH_2—OH \xrightarrow{KMnO_4} CH_3—CH_2—COOH \xrightarrow{K_2Cr_2O_7}$$
$$\xrightarrow{\qquad} CH_3—COOH + CO_2$$
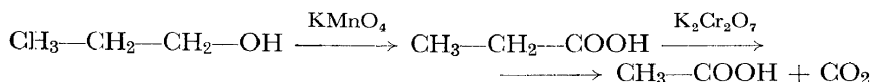
Acetic acid was subjected to (*a*) Schmidt degradation and (*b*) alkali fusion. In the first case the label was entirely in the methylamine, in the second, in the methane

$$CH_3—COOH \begin{cases} \xrightarrow{HN_3} {}^{14}CH_3—NH_2^+ CO_2 + N_2 \\ \xrightarrow{NaOH} {}^{14}CH_4 + Na_2CO_3 \end{cases}$$

Obviously, the n-propyl alcohol formed in the reaction of n-propylamine-1-^{14}C with nitrous acid contained radioactive ^{14}C only in positions 1 and 3. Similarly, it was shown that isopropyl alcohol contains ^{14}C only in position 1 (but not in position 2).
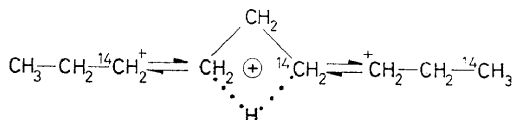
The positions of the labels can be seen in the following diagram:

$$CH_3—CH_2—\overset{*}{C}H_2—NH_2·HClO_4 \xrightarrow{HNO_2} \begin{cases} CH_3—CH_2—\overset{*}{C}H_2—OH \\ \overset{*}{C}H_3—CH_2—CH_2—OH \\ \overset{*}{C}H_3—CH—CH_3 \\ \phantom{\overset{*}{C}H_3—CH}| \\ \phantom{\overset{*}{C}H_3—CH}OH \end{cases}$$
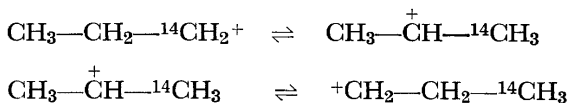
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† Isomerization of n-propyl cation to isopropyl cation in the reaction of n-propylamine with nitrous acid was reported long ago[39], considerable quantities of isopropyl alcohol having been found among the reaction products (yield of n-propyl alcohol 7 per cent, and isopropyl alcohol 32 per cent).

Rearrangement of n-propyl-1-^{14}C cation to n-propyl-3-^{14}C cation occurs to the extent of 8 ± 0.8 per cent. What then is the mechanism of rearrangement of the n-propyl cation?

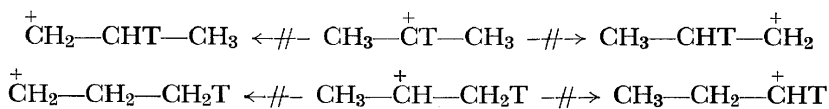The isomerization we observed of the n-propyl cation could be either a one-stage migration of hydrogen anion from the β-position:

or a two-stage migration of hydrogen anion from the α-position:

$$CH_3—CH_2—^{14}CH_2{}^+ \;\rightleftharpoons\; CH_3—\overset{+}{C}H—^{14}CH_3$$

$$CH_3—\overset{+}{C}H—^{14}CH_3 \;\rightleftharpoons\; {}^+CH_2—CH_2—^{14}CH_3$$

We showed that the isomerization proceeds in accordance with the first mechanism, in a single stage. The proof was based on a study of the products of the reaction between nitrous acid and tritium-containing propylamine (n-propylamine-2-T$_1$):
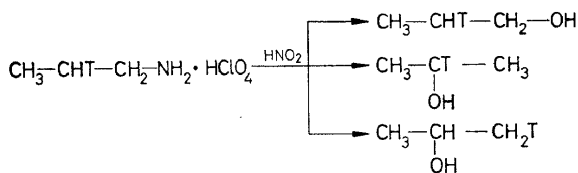
The normal alcohol formed by this reaction contained tritium only in position 2. This shows unambiguously that under the experimental conditions isopropyl cation is not converted into n-propyl cation.

$$\overset{+}{C}H_2—CHT—CH_3 \;\xleftarrow{\;/\!/\;}\; CH_3—\overset{+}{C}T—CH_3 \;\xrightarrow{\;/\!/\;}\; CH_3—CHT—\overset{+}{C}H_2$$

$$\overset{+}{C}H_2—CH_2—CH_2T \;\xleftarrow{\;/\!/\;}\; CH_3—\overset{+}{C}H—CH_2T \;\xrightarrow{\;/\!/\;}\; CH_3—CH_2—\overset{+}{C}HT$$

It has thus been demonstrated that the isomerization of n-propyl cation which was discovered proceeds by a one-stage mechanism, evidently *via* the 4-membered, cyclic transition state of type (F).


(F)
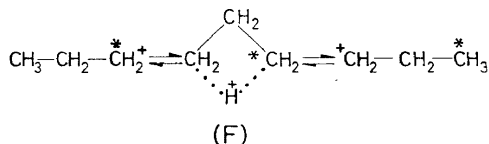
It may be mentioned that Karabatsos[40] also arrived at this conclusion in a study of the same isomerization by another method, using tetradeuterated n-propylamine:

$$CH_3—CD_2—CD_2—NH_2 \cdot HClO_4 \xrightarrow{HNO_2} \quad CH_3—CD_2—CD_2—OH$$
$$+$$
$$CD_2H—CD_2—CH_2—OH$$
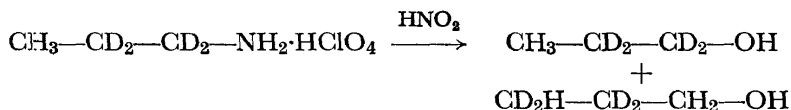
He obtained a mixture of alcohols that did not contain hydrogen (protium) in position 2.

Finally, Skell and co-workers investigating the reactions of carbonium ions formed in the deoxideation of alcohols[41] recently observed 1,3-shift of hydride ions[42], including 1,3 rearrangement, of n-propyl cation[43]:
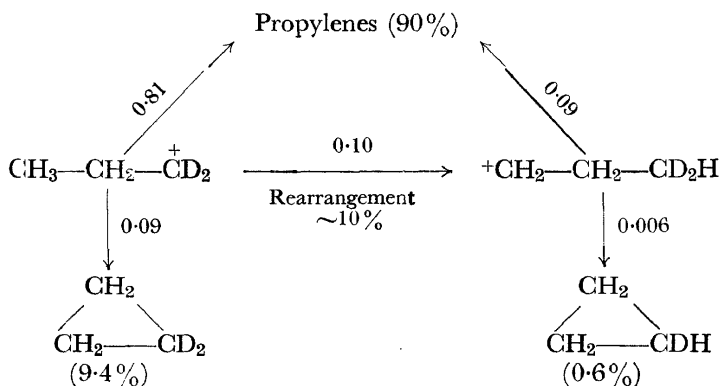

As can be seen, the percentage of 1,3-rearrangement of the propyl cations formed under irreversible reaction conditions of n-propylamine deamination and n-propanol deoxideation is of about the same magnitude (*ca.* 10 per cent).

The isomerization of n-propyl cation was studied under reversible conditions, using n-propyl chloride. Whereas n-propyl-1-^{14}C chloride in contact with aluminium chloride forms isopropyl chloride very rapidly:

$$CH_3—CH_2—^{14}CH_2—Cl \xrightarrow[\text{Fast}]{AlCl_3} \quad CH_3—CH—^{14}CH_3$$
$$|$$
$$Cl$$
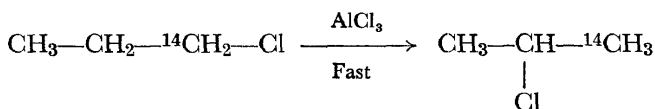
only traces of isopropyl chloride are formed on prolonged contact of propyl chloride with zinc chloride in concentrated hydrochloric acid by room temperature. At the same time, rearrangement takes place, n-propyl-1-^{14}C chloride being converted into n-propyl-3-^{14}C chloride[44]:

$$CH_3—CH_2—^{14}CH_2—Cl \underset{ZnCl_2, HCl}{\rightleftharpoons} \quad ^{14}CH_3—CH_2—CH_2—Cl$$
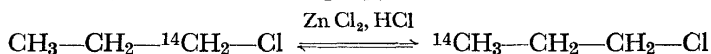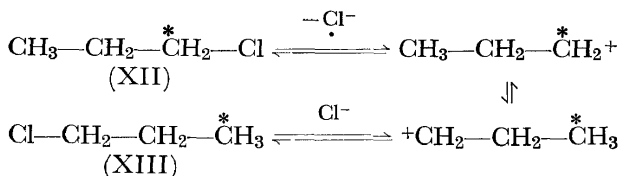
The different behaviour of n-propyl chloride in the presence of aluminium chloride on the one hand and of zinc chloride and hydrochloric acid on the other clearly points to different degrees of freedom in the n-propyl cations formed in these two cases. If completely free alkyl cations had formed in both cases their behaviour should have been the same.

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Apparently both the 1,2 and 1,3 hydrogen shifts occur in a complex with a polarized carbon–chlorine bond of the type

$$CH_3—CH_2—\overset{\delta+}{CH_2}\cdots\cdots Cl\cdots\cdots\overset{\delta-}{M}Cl_n$$
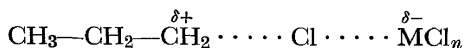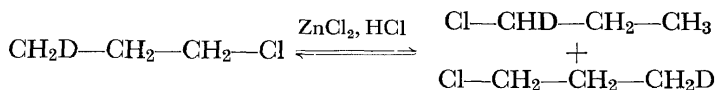
rather than in the free n-propyl cation. Evidently the C—Cl bond is more polarized in the presence of aluminium chloride than zinc chloride.

In contrast to the above-described deamination and deoxideation reactions, isomerization of n-propyl cation in this case proceeds under reversible conditions, since compounds (XII) and (XIII) at both ends of the reaction are the same n-propyl chloride.

$$CH_3—CH_2—\overset{*}{CH_2}—Cl \xrightleftharpoons{\overset{-Cl^-}{\overset{\bullet}{}}} CH_3—CH_2—\overset{*}{CH_2}{}^+$$

(XII) $\Updownarrow$

$$Cl—CH_2—CH_2—\overset{*}{CH_3} \xrightleftharpoons{Cl^-} {}^+CH_2—CH_2—\overset{*}{CH_3}$$

(XIII)

The extent of rearrangement therefore depends upon the contact time of propyl chloride with zinc chloride and hydrochloric acid and upon the reaction temperature. Thus, when n-propyl-1-^{14}C chloride is reacted with a two-fold molar excess of zinc chloride and hydrochloric acid for 20 hours at 50° the rearrangement proceeds to the extent of 2·5 per cent, whereas at 50° for 100 hours it amounts to 7 per cent, and at 20° for 1,500 hours to 16 per cent. If the reaction components are heated for a sufficient length of time, equilibrium may be reached. Quite similar results were obtained (in collaboration with Bundel and Susan) in the reaction between zinc chloride plus hydrochloric acid and n-propyl-3-D_1 chloride.

$$CH_2D—CH_2—CH_2—Cl \xrightleftharpoons{ZnCl_2,\,HCl} \begin{array}{c} Cl—CHD—CH_2—CH_3 \\ + \\ Cl—CH_2—CH_2—CH_2D \end{array}$$

It is interesting that isopropyl chloride on contact with zinc chloride and deuterium chloride undergoes deuteroexchange of the type†:

$$\underset{\underset{Cl}{|}}{CH_3—CH—CH_3} \xrightleftharpoons{ZnCl_2,\,DCl} \underset{\underset{Cl}{|}}{CH_2D—CH—CH_3}$$
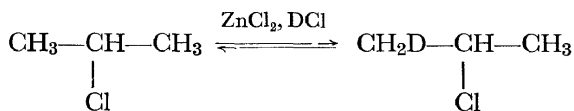
n-Propyl chloride does not participate in deuteroexchange under these conditions. These facts can evidently serve as evidence of the greater polarization of the carbon–chlorine bond in the alkyl halide complex with zinc chloride in the case of isopropyl chloride and, therefore, of the closer relation of this complex to the pure carbonium ion.

† Concerning the mobility of hydrogen atoms in tertiary and secondary alkyl halides in the presence of Lewis acids see the paper by Kursanov et al.[44a].

It should be mentioned that this result differs from the results obtained by Doering[45] who detected no deuterium in isopropyl chloride arising from the action of aluminium chloride and deuterium chloride on n-propyl chloride.

$$CH_3\text{---}CH_2\text{---}CH_2\text{---}Cl \xrightarrow{\quad AlCl_3,\ DCl \quad} CH_3\text{---}CH\text{---}CH_3$$
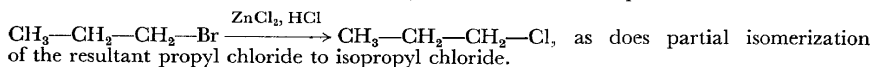$$\underset{Cl}{|}$$
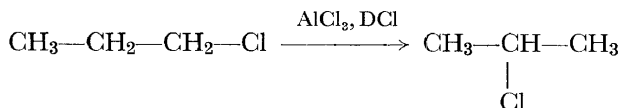
The cause of this difference possibly lies in the different degrees of freedom of the n-propyl cation under Doering and the author's reaction conditions. Doering carried out the reaction in the absence of solvent and with excess alkyl halide. The author *et al.* performed it in concentrated hydrochloric acid, a medium promoting carbonium ion formation to a greater extent than the not very polar alkyl halide. Moreover, the contact time of propyl chloride with aluminium chloride and deuterium chloride by Doering was only 5 minutes.

There is, however, no basis for the assumption that under our reaction conditions n-propyl chloride isomerization proceeds *via* free carbonium ion formation. Moreover, we obtained evidence that in the course of isomerization the alkyl–halogen bond is not completely ruptured. Thus, n-propyl-3-D_1 bromide rearranges in the presence of excess zinc chloride and hydrochloric acid to n-propyl-1-D_1 bromide. If during this process the carbon–bromine bond had ruptured then, as the zinc chloride and hydrochloric acid are present in excess, the n-propyl-3-D bromide should have been converted completely into the n-propyl-1-D chloride†.

Hence the rearrangement proceeds through formation of the polarized

(Ac= Lewis acid, ZnX_2 or H^+)

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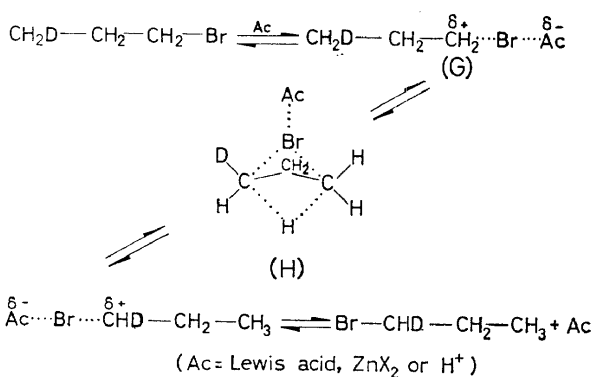
†Obviously substitution of bromine by chlorine also takes place at the same time:
$$CH_3\text{---}CH_2\text{---}CH_2\text{---}Br \xrightarrow{\quad ZnCl_2,\ HCl \quad} CH_3\text{---}CH_2\text{---}CH_2\text{---}Cl,$$ as does partial isomerization of the resultant propyl chloride to isopropyl chloride.

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complex (G) and a transition state of the type (H) rather than *via* the free carbonium ion†.

What is the mechanism of n-propyl-1-^{14}C chloride isomerization to n-propyl-3-^{14}C chloride?

Of the two possible ways for the isomerization of n-propyl cation, the one-stage (1,3-hydrogen shift) and the two-stage, the former holds here also.

A small amount of isopropyl chloride does form on prolonged contact of n-propyl chloride with zinc chloride and hydrochloric acid, but it was found by special experiments that, under the conditions employed, isopropyl chloride cannot for all practical purposes isomerize into n-propyl chloride:

$$CH_3—CH—CH_3 \xrightarrow[\quad]{ZnCl_2, HCl} \;\not\!\!/\!\!\longrightarrow CH_3—CH_2—CH_2—Cl$$
$$\;\;\;\;\;\;\;|$$
$$\;\;\;\;\;\;Cl$$

Apparently 1,3-hydrogen shifts are not so rare as had previously been supposed[46].

If one compares 1,3 and 1,2 hydrogen shifts then, providing all other

† In the 1,2 and 1,3 hydride ion shifts an important part could probably be played by the following five-membered (I) (or six-membered (J)) cyclic transition states (*cf.* ref. 45a).

However rearrangement of n-propyl bromide (due to 1,3-hydrogen shift) in the presence of excess zinc chloride and hydrochloric acid can take place only through the transition state (H) in which the bromine atom passes from C_1 to C_3.

conditions are equal (energy relations of the initial and final carbonium ions, reaction conditions, *etc.*) the former shift appears to be the one preferred. Apparently the transition state of type (K) is more advantageous than that of type (L).
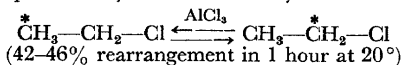

(K)   (L)
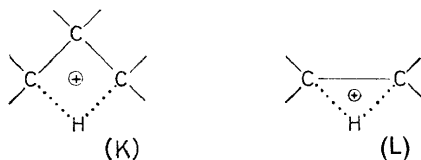
Evidence in favour of this is to be found in the author's results on the 1,3 hydrogen shift of n-propyl chloride under the influence of zinc chloride and hydrochloric acid (1,2 shift with the formation of isopropyl chloride occurs only to an insignificant extent†, as well as in the relative percentages of 1,3 hydrogen shift in n-propyl cation[30] and 1,2 hydrogen shift in ethyl cation[47] which are formed in the reaction of the corresponding amines with nitrous acid.

8 ± 0·8 % rearrangement

1·5 ± 0·1 % rearrangement
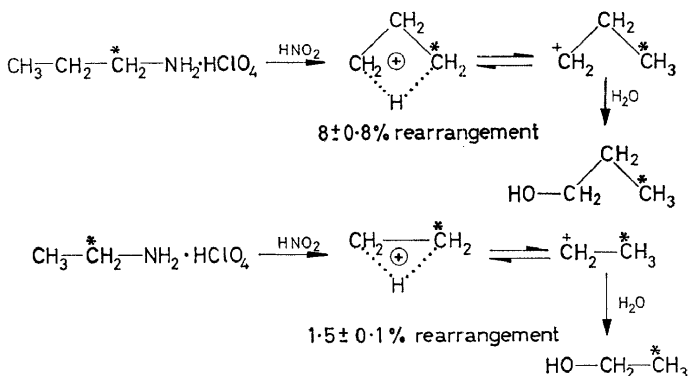
n-Propyl chloride isomerization, in which n-propyl cation forms under reversible conditions, was considered to be an appropriate reaction for revealing skeletal isomerization:
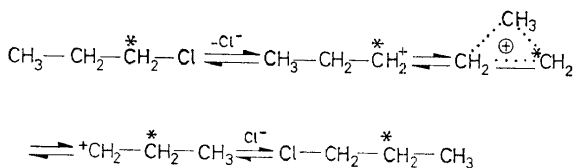

† Ethyl-2-^{14}C chloride quite readily isomerizes to ethyl-1-^{14}C in the presence of aluminium chloride[43]

$$\overset{*}{C}H_3 - CH_2 - Cl \underset{}{\overset{AlCl_3}{\rightleftharpoons}} CH_3 - \overset{*}{C}H_2 - Cl$$

(42–46% rearrangement in 1 hour at 20°)

Regrettably, the rate of this rearrangement cannot be compared with that of the 1,3 hydrogen shift of n-propyl chloride under the same conditions because in the presence of aluminium chloride, propyl chloride irreversibly undergoes practically instantaneous isomerization to isopropyl chloride.

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even though it proceeds much more slowly than isomerization by 1,3 shift. But it was not possible to detect n-propyl-2-^{14}C chloride in any of the experiments. However, there are no theoretical objections against the possibility of formation of the simplest non-classical carbonium ion. In the light of this the communication of Beeck, Otvos, Stevenson and Wagner[49], who studied the action of aluminium bromide on propane-1-^{13}C at room temperature in the presence of traces of moisture, is of considerable interest. According to these authors, on contact of propane-1-^{13}C with aluminium bromide for over 1000 hours about 33 per cent of propane-2-^{13}C appeared in the mixture:

$$\text{CH}_3\text{---CH}_2\text{---}\overset{*}{\text{CH}}_3 \xrightarrow[\quad]{\text{AlBr}_3} \text{CH}_3\text{---}\overset{*}{\text{CH}}_2\text{---CH}_3$$
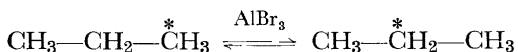
It is highly probable that this in fact is a case of skeletal isomerization proceeding through formation of the simplest non-classical carbonium ion.

HYDROGEN SHIFTS IN ALICYCLIC CARBONIUM IONS

In conclusion, hydrogen shifts in alicyclic carbonium ions will be discussed very briefly.

Quite obviously such shifts should be observed not only with alicyclic carbonium ions, but also with cyclic cations. They should manifest themselves in the form of non-classical, so to say, substitution or elimination reactions.

Indeed, 1,3-, 1,4-, 1,5- and 1,6-hydrogen shifts have been observed in reactions of 8–11-membered ring compounds[50–51]. Thus, Urech and Prelog[51] in a study of the solvolytic cleavage of cyclodecanol-1,2-[14]C₂ tosylate to cis- and trans-cyclodecenes† inferred, on the basis of the label distribution, that an important contribution is made by 1,5 and 1,6 hydrogen shifts.
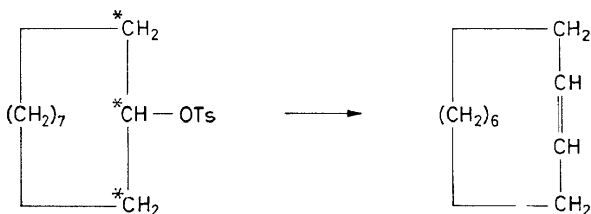

Deamination of cyclohexylamine-1-^{14}C was studied[32], a reaction in which 1,5 and 1,6 hydrogen shifts cannot occur. But in this case substitution of the amino group by hydroxyl also takes place partially according to the non-classical mechanism, since in the resultant cyclohexanol molecules are present with the hydroxyl not bound to the radioactive carbon.

The reaction between cyclohexylamine perchlorate with a ^{14}C-bonded

† Regarding the isotopic effect of solvolysis see ref 51.

amino group† and nitrous acid leads to the formation of a mixture of cyclohexanol and cyclopentylcarbinol:
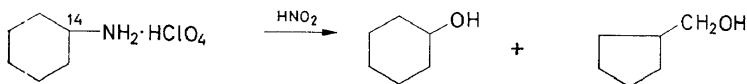
In order to establish the position of the label in the cyclohexanol it is subjected to the following degradation:


$$H_2N - (CH_2)_5 - NH_2 \quad + \quad {}^{14}CO_2$$
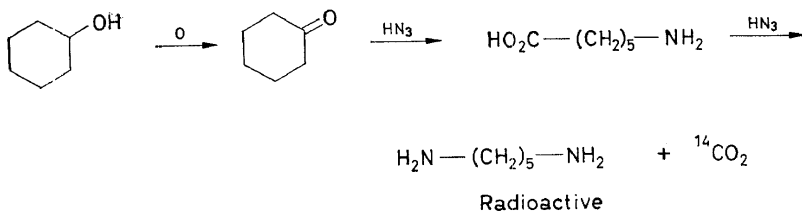
Radioactive

Pentamethylenediamine was found to be radioactive $(3\cdot7 \pm 0\cdot3$ per cent of the cyclohexanone activity)‡, showing that in some of the cyclohexanol molecules the hydroxyl was bound to carbon atoms other than that at which the amino group had been originally attached in the cyclohexylamine molecule.

† This compound was synthesized as follows:
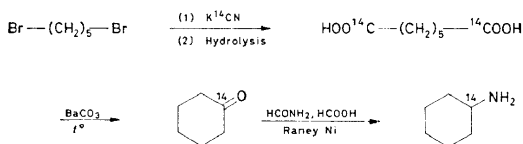
In order to be sure that the cyclohexylamine label was only at the carbon bonded to nitrogen, the following degradation was carried out: oxidation to cyclohexanone, reaction with hydrazoic acid to give 6-amino-hexanoic acid and then pentamethylene diamine, which proved to be inactive


Not radioactive
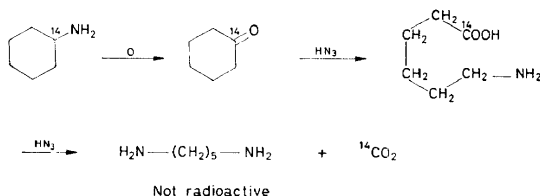
‡ The low percentage of cyclohexyl cation rearrangement can possibly be due to its rapid reaction with the solvent to give cyclohexanol. A similar explanation has been advanced by Streitwieser and Coverdall[53] to account for the fact that not less than 94 per cent *cis*-cyclohexanol-2-D is formed in the reaction of *cis*-cyclohexylamine-2-D with nitrous acid.

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Hence cyclohexylamine cation undergoes isomerization due to hydrogen shifts†.
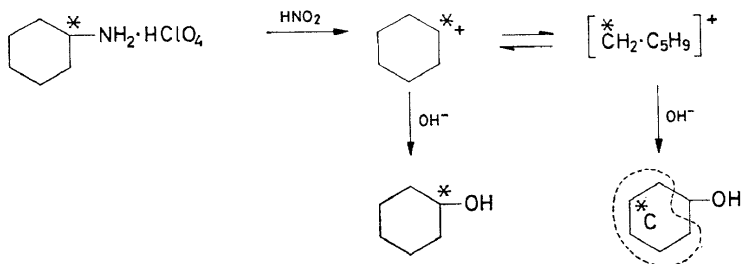
Hydrogen shifts also occur in the cyclohexyl cation formed in other reactions. Thus, the author (together with Sokolov) found that, in the phosphoric acid dehydration of cyclohexanoll-1-D cyclohexene is formed which contains deuterium not only in the ethylenic, but also in other, for instance, allyl, positions.
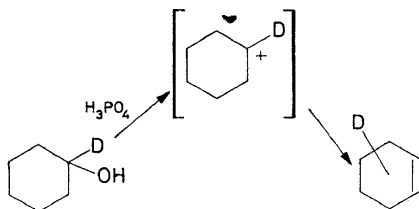
† It can readily be seen that migration of the label along the cyclohexyl ring cannot be due to a sequence of reversible ring enlargement-contraction reactions of the type
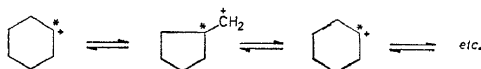

In all these skeletal rearrangements the label in the cyclohexyl cation remains on the positively charged carbon atom of the six-membered ring. However, the label can undergo shifts in other cases, e.g. Figure 4[54].
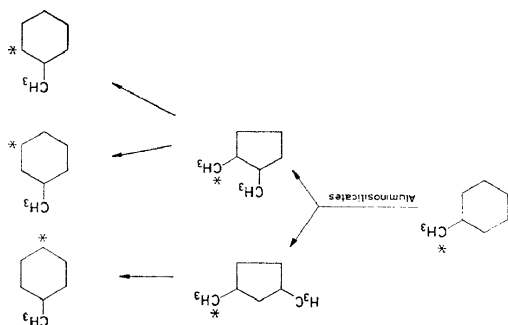
In a study of the solvolysis of deuterocyclohexanol tosylate the author (with Bundel and Savin) found on the basis of the label distribution that the isomerization of cyclohexyl cation is due mainly to 1,3-hydrogen shifts.
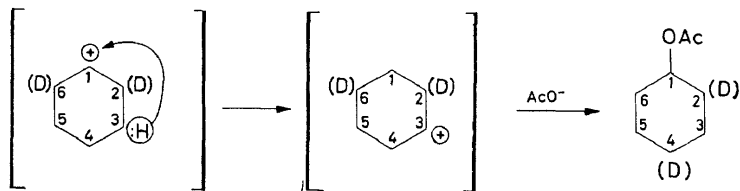
The synthesis and solvolysis of deuterocyclohexanol tosylate were carried out as follows:
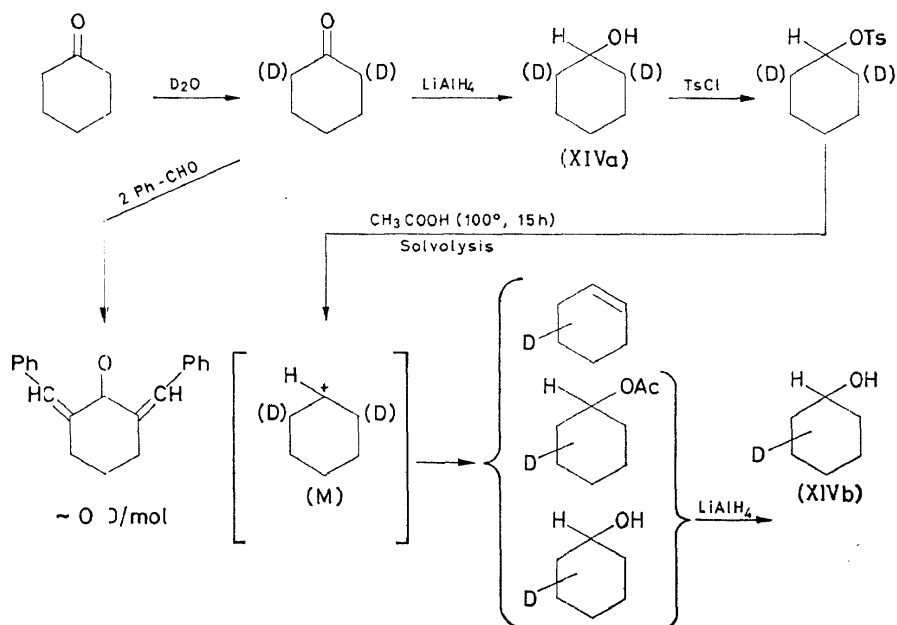
In order to establish the label distribution in cyclohexanol it was subjected to the following degradation:

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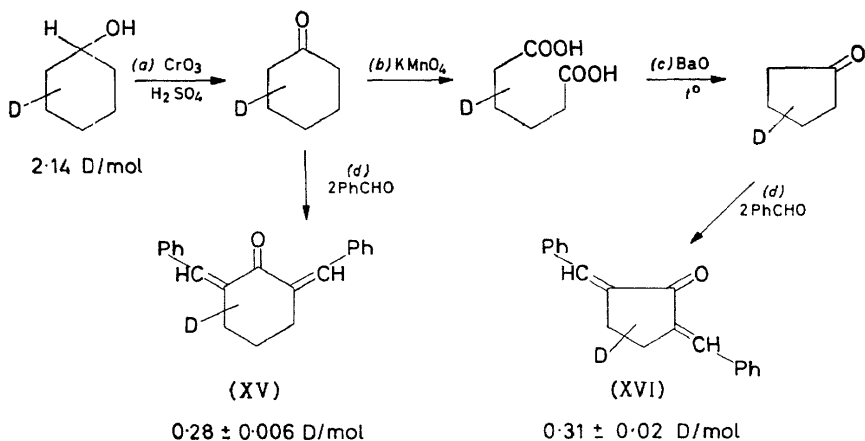
The similarity in deuterium content in (XV) and (XVI) shows that the isomerization of cyclohexyl-cation is due to 1,3-hydrogen shifts[†]:

In all these experiments the solvolysis was carried out in the presence of traces of moisture. Rearrangement of cyclohexyl-cation during the solvolysis of cyclohexanol tosylate occurs under these conditions approximately to the extent of 26 per cent.

If solvolysis was carried out in the absence of traces of moisture the percentage of the isomerization was increased to ~50 per cent. In these cases, apart from 1,3 shifts, 1,2 and 1,4 hydrogen shifts also play important rôles.

This phenomenon may be explained by different lifetimes of cyclohexyl-cations under different conditions (in the presence of reagents of different nucleophilicity: CH_3COOH and $CH_3COOH + H_2O$)

All these results show that substitution or elimination reactions as well as the Demyanov rearrangement, are much more involved than is usually thought, their mechanism being complicated by hydride ions shifts.

References

[1] H. H. Glazebrook and T. G. Pearson. *J. Chem. Soc.* **1936**, 177.
[2] N. N. Semenov. *Usp. Khim.* **20**, 673 (1951).
[3] N. V. Fok and A. B. Nalbandyan. *Dokl. Akad. Nauk SSSR* **86**, 589 (1952); **89**, 125 (1953).
[4] V. V. Voevodskii and R. E. Mardaleishvili. In *Problems of Chemical Kinetics, Catalysis and Reactivity (Voprosy Khimicheskoi Kinetiki, Kataliza i reaktsionnoi sposobnosti)* p. 40, Izd. Akad. Nauk SSSR (1955).
[5] W. H. Urry and M. S. Kharasch. *J. Am. Chem. Soc.* **66**, 1438 (1944).
[6] W. Urry and N. Nicolaides. *J. Am. Chem. Soc.* **74**, 5163 (1952).
[7] W. B. Smith and J. D. Anderson. *J. Am. Chem. Soc.* **82**, 656 (1960).
[8] S. Winstein and F. H. Seubold. *J. Am. Chem. Soc.* **69**, 2919 (1947).
[9] F. H. Seubold. *J. Am. Chem. Soc.* **75**, 2532 (1953).
[10] D. J. Curtin and M. G. Hurwitz. *J. Am. Chem. Soc.* **74**, 5381 (1952).
[11] D. J. Curtin and G. S. Caner. *J. Org. Chem.* **25**, 880 (1960).
[12] L. H. Slaugh. *J. Am. Chem. Soc.* **81**, 2262 (1959).
[13] J. W. Wilt and H. Philip. *J. Org. Chem.* **24**, 441 (1959).
[14] J. W. Wilt and H. Philip. *J. Org. Chem.* **25**, 891 (1960).
[15] A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin. *Dokl. Akad. Nauk SSSR* **81**, 199 (1951).
[16] V. N. Kost, T. T. Sidorova, and R. Kh. Freidlina. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 199 (1951);
A. N. Nesmeyanov. *Dokl. Akad. Nauk.* **132**, 606 (1960).
[17] A. N. Nesmeyanov, R. Kh. Freidlina, and A. B. Belyavskii. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1028 (1959).
[18] R. Kh. Freidlina, V. N. Kost, M. Ya. Khorlina, and A. N. Nesmeyanov. *Dokl. Akad. Nauk. SSSR* **128**, 316 (1959).
[19] R. Kh. Freidlina, M. Ya. Khorlina, and A. N. Nesmeyanov. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 659 (1960).
[20] R. Kh. Freidlina, V. N. Kost, M. Ya. Khorlina, and A. N. Nesmeyanov. *Dokl. Akad. Nauk SSSR* **137**, 341 (1961).
[21] P. S. Skell, R. G. Allen, and N. D. Gilmour. *J. Am. Chem. Soc.* **83**, 504 (1961).

† By means of special experiments it was established that no rearrangement takes place at stages (*a*), (*b*), (*c*) and (*d*).

[22] M. S. Kharasch, S. S. Kane, and H. C. Brown. *J. Am. Chem. Soc.* **63**, 526 (1941).
[23] H. C. Brown and C. Russell. *J. Am. Chem. Soc.* **74**, 3995 (1952).
[24] DeLos F. de Tar, and C. Weis. *J. Am. Chem. Soc.* **78**, 4296 (1956).
[25] DeLos F. de Tar. *J. Am. Chem. Soc.* **79**, 3041 (1957).
[26] C. Grob and H. Kammuler. *Helv. Chem. Acta* **340**, 2139 (1957).
[27] O. A. Reutov and T. N. Shatkina. *Dokl. Akad. Nauk SSSR* **133**, 381 (1960); *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2032 (1961).
[28] O. A. Reutov and T. N. Shatkina. *Tetrahedron* **18**, 305 (1962).
[29] V. L. Lorber and M. Cook. *J. Am. Chem. Soc.* **72**, 3041 (1957).
[30] J. D. Roberts and M. Halmann. *J. Am. Chem. Soc.* **75**, 5759 (1953).
[31] O. A. Reutov and T. N. Shatkina. *Dokl. Akad. Nauk SSSR* **133**, 381 (1960); *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 2040 (1961).
[32] O. A. Reutov and T. N. Shatkina. *Tetrahedron* **18**, 237 (1962).
[32a] H. C. Brown. "Strained transition states," *Spec. Publ.* No. 16, The Chemical Society, London (1962).
[33] M. J. S. Dewar. *The Electronic Theory of Organic Chemistry*, Oxford University Press, London (1949).
[34] J. D. Roberts, W. Bennett, and R. Armstrong. *J. Am. Chem. Soc.* **72**, 3329 (1950);
S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall. *J. Am. Chem. Soc.* **74**, 1127 (1952);
S. Winstein and D. Trifan. *J. Am. Chem. Soc.* **74**, 1147, 1154 (1952);
S. Winstein and K. C. Schreiber. *J. Am. Chem. Soc.* **74**, 2156 (1952);
J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr. *J. Am. Chem. Soc.* **76**, 4501 (1954);
J. D. Roberts and W. Bennett. *J. Am. Chem. Soc.* **76**, 4623 (1954);
J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr. *J. Am. Chem. Soc.* **77**, 3034 (1955).
[35] J. D. Roberts, W. Bennett, and R. Armstrong. *J. Am. Chem. Soc.* **72**, 3329 (1950);
S. Winstein, H. M. Walborsky, and K. Schreiber. *J. Am. Chem. Soc.* **72**, 5795 (1950);
J. D. Roberts and W. Bennett. *J. Am. Chem. Soc.* **76**, 4623 (1954);
J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr. *J. Am. Chem. Soc.* **77**, 3034 (1955);
S. Winstein and M. Shatavsky. *Chem. Ind. (London)* **1956**, 56.
[36] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward. *J. Am. Chem. Soc.* **77**, 4183 (1955);
S. Winstein and M. Shatavsky. *J. Am. Chem. Soc.* **78**, 592 (1956);
W. G. Woods, R. A. Carboni, and J. D. Roberts. *J. Am. Chem. Soc.* **78**, 5653 (1956);
S. Winstein and C. Ordonneau. *J. Am. Chem. Soc.* **82**, 2084 (1960);
G. Leal and R. Pettit. *J. Am. Chem. Soc.* **81**, 3160 (1959).
[37] J. Roberts and R. H. Mazur. *J. Am. Chem. Soc.* **73**, 2509, 3542 (1951);
J. D. Roberts and V. C. Chambers. *J. Am. Chem. Soc.* **73**, 5034 (1951);
C. G. Bergstrom and S. Siegel. *J. Am. Chem. Soc.* **74**, 145, 254 (1952);
J. D. Roberts and W. Bennett. *J. Am. Chem. Soc.* **76**, 4623 (1954);
R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts. *J. Am. Chem. Soc.* **81**, 4390 (1959);
S. Winstein and E. M. Kosower. *J. Am. Chem. Soc.* **81**, 4399 (1959).
[38] S. Winstein, J. Sonnenberg, and L. De Vries. *J. Am. Chem. Soc.* **81**, 6523 (1959).
[39] M. Mayer and Fr. Forster. *Ber.* **9**, 535 (1876);
F. C. Whitmore and R. S. Thorpe. *J. Am. Chem. Soc.* **63**, 1118 (1941).
[40] G. Karabatsos and C. E. Orzech, Jr. *J. Am. Chem. Soc.* **84**, 2838 (1962).
[41] P. S. Skell and I. Starer. *J. Am. Chem. Soc.* **82**, 2971 (1960);
M. S. Silver. *J. Am. Chem. Soc.* **82**, 2971 (1960); **83**, 3482 (1961).
[42] P. S. Skell and R. J. Maxwell. *J. Am. Chem. Soc.* **84**, 3963 (1962).
[43] P. S. Skell and J. Staker. *J. Am. Chem. Soc.* **84**, 3962 (1962).
[44] O. A. Reutov and T. N. Shatkina. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 195 (1963).
[44a] D. N. Kursanov, V. N. Setkina *et al. Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 758 (1959); 2032 (1960); 664 (1961); 668 (1961); 1303 (1961); 2032 (1961).
[45] W. Doering. *J. Am. Chem. Soc.* **71**, 1516 (1949).
[45a] Ya. K. Syrkin. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 600 (1959).
[46] A. Streitwieser, Jr. *Chem. Rev.* **56**, 571 (1956).
[47] J. D. Roberts and J. A. Jancey. *J. Am. Chem. Soc.* **74**, 5943 (1952).
[48] R. M. Roberts, G. A. Ropp, and O. K. Nevill. *J. Am. Chem. Soc.* **77**, 1764 (1955).
[49] O. Beeck, J. W. Otvos, D. P. Stevenson, and C. D. Wagner. *J. Chem. Phys.* **16**, 255 (1948)
[50] V. Prelog, H. J. Urech, A. A. Bothner-By, and J. Würsch. *Helv. Chim. Acta* **38**, 1095 (1955).
[51] H. J. Urech and V. Prelog. *Helv. Chim. Acta* **40**, 477 (1957).
[52] O. A. Reutov and T. N. Shatkina. *Dokl. Akad. Nauk SSSR* **142**, 835 (1962).
[53] A. Streitwieser and C. E. Coverdall. *J. Am. Chem. Soc.* **81**, 4275 (1959).
[54] M. M. Sakharov. *Dissertation.* Institute of Physical Chemistry of the Academy of Sciences, USSR, Moscow (1955).

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