

Isomerization of the Propyl Cation

O. A. Reutov, T. N. Shatkina

1960

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196001.50362>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

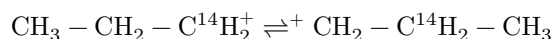
1960. Vol. 133, No. 3

CHEMISTRY

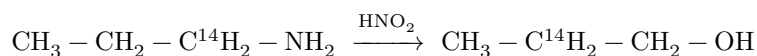
Corresponding Member of the Academy of Sciences of the USSR O. A. REUTOV
and T. N. SHATKINA

ISOMERIZATION OF THE PROPYL CATION

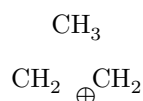
Roberts and Halmann ⁽¹⁾ described a rearrangement of the propyl cation



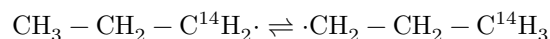
in the reaction of *n*-propylamine labeled with *C*¹⁴ with nitrous acid:



Naturally, this interesting rearrangement attracted the attention of chemists, since it represents the simplest case of a rearrangement of the pinacol type. The indicated rearrangement has already entered the newest textbooks of organic chemistry; on the basis of this rearrangement, the concept has been advanced of the simplest nonclassical cation

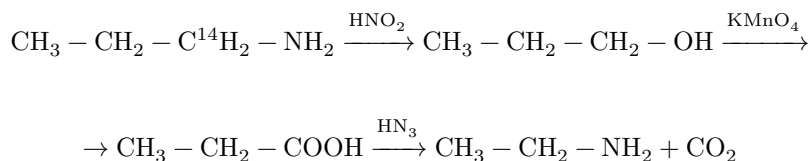


Recently we showed ⁽²⁾ that the free propyl radical in a solution of carbon tetrachloride does not undergo skeletal rearrangement. Instead, isomerization is observed with migration of a hydrogen atom from the β -position



In view of the rather frequently observed analogy in the behavior of radicals and cations, we analyzed the above-cited work of Roberts and Halmann ⁽¹⁾ and found that their conclusion concerning the nature of the rearrangement of the propyl cation is not the only possible one.

The authors decided that carbon *C*¹⁴ is located in the 2-position of the molecule of the *n*-propyl alcohol formed ($\text{CH}_3 - \text{C}^{14}\text{H}_2 - \text{CH}_2 - \text{OH}$) on the basis of the activity of ethylamine formed as a result of the following reactions:



active

That radioactive carbon C^{14} is bound precisely to nitrogen in the ethylamine molecule was an assumption of the authors, not proved experimentally.

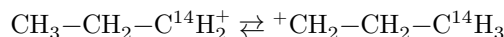
If, however, C^{14} is in fact located in the methyl group of the ethylamine molecule, then in this case the propyl cation did not undergo a rearrangement of the pinacol type, but was isomerized through migration of a hydride ion.*

We repeated the work of Roberts and Halmann and established that the indicated authors were mistaken.**

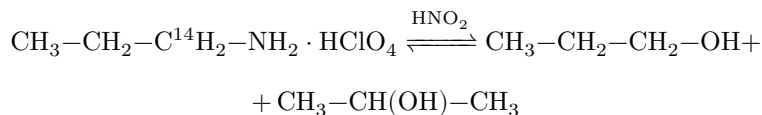
* It should be noted that the isomerization of the *n*-propyl cation into the iso-propyl cation in the reaction of *n*-propylamine with nitrous acid is stated as already known⁽³⁾; among the products of the indicated reaction, a considerable amount of isopropyl alcohol was found (yield of *n*-propyl alcohol 7%, isopropyl alcohol 32%).

** It should be noted that in work with other amines (3-aryl-1-propylamines-1- C^{14}) Roberts et al.⁽⁴⁾ impeccably proved skeletal rearrangements in the reaction with nitrous acid.

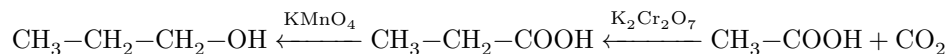
In reality, under the conditions considered, the propyl cation undergoes an isomerization analogous to the isomerization of the propyl radical discovered by us, namely:



The interaction of perchloric-acid *n*-propylamine (activity $1.54 \mu\text{Cu}/\text{mmol}$) with nitrous acid led to the formation of *n*-propyl and isopropyl alcohols.

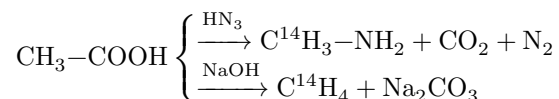


On oxidation of *n*-propyl alcohol with potassium permanganate, propionic acid was obtained (activity $0.57 \mu\text{Cu}/\text{mmol}$), which was further oxidized with potassium dichromate to acetic acid (activity $0.045 \mu\text{Cu}/\text{mmol}$) and carbon dioxide.



Acetic acid was: a) degraded by the Schmidt reaction and b) fused with alkali in the form of the sodium salt.

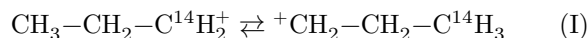
In the first case all the activity from the acetic acid passed into methylamine, and in the second, into methane:



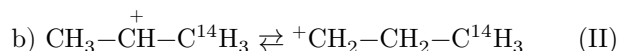
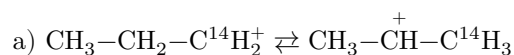
Thus it is clear that the *n*-propyl alcohol formed in the reaction of *n*-propylamine-1- C^{14} with nitrous acid contains radioactive carbon C^{14} only in positions 1 and 3.

By an analogous route we proved that isopropyl alcohol also contains C^{14} in positions 1 and 3 (but not in position 2).

The isomerization of the *n*-propyl cation found by us is either a one-stage process of migration of a hydrogen anion from the β -position,



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



In favor of the second mechanism is both the fact of formation of isopropyl alcohol in the reaction studied and the results of studies of hydrogen exchange of paraffins (for example, ⁵). On the other hand, in the literature (⁶) only the formation of isopropyl alcohol (without admixture of *n*-propyl alcohol) under the action of nitrous acid on isopropylamine has been described.*

Thus, the question of whether the isomerization found by us takes place in one stage or in two stages remains open for the present.

The capacity for isomerization with migration of hydrogen anions is undoubtedly, to some extent, a general property of alkyl cations. Roberts

* The results of this work require verification. Since, for the formation of *n*-propyl alcohol, isomerization of the more stable isopropyl cation into the less

stable *n*-propyl cation is necessary ($\text{CH}_3-\overset{+}{\text{CH}}-\text{CH}_3 \rightarrow \text{}^+\text{CH}_2-\text{CH}_2-\text{CH}_3$), it is evident that, if this isomerization does occur, then only to a small extent, and the reaction mixture can contain only a few percent of *n*-propyl alcohol.

with co-workers (7), for example, observed such isomerization for the ethyl cation in the reaction of ethylamine with nitrous acid. It is quite probable that such isomerization also occurs in the mutual transformations of alicycles by the Demyanov reaction.

From this assumption, for example, it follows that in molecules of cyclohexanol formed by the action of nitrous acid on cyclohexylamine, the hydroxyl group is attached not only to the carbon atom to which the amino group was attached in the starting cyclohexylamine molecule.

Finally, it should be noted that the absence of skeletal rearrangement of the propyl cation in the reaction we studied is by no means evidence that the indicated rearrangement cannot occur under other conditions.

Moscow State University
named after M. V. Lomonosov

Academy of Medical Sciences of the USSR

Received
1 IV 1960

REFERENCES

1. J. Roberts, M. Halman, *J. Am. Chem. Soc.*, **75**, 5759 (1953).
2. O. A. Reutov, T. N. Shatkina, *DAN*, **133** No. 2 (1960).
3. V. Mayer, Fr. Forster, *Ber.*, **9**, 535 (1876); F. C. Whitmore, R. S. Thorpe, *J. Am. Chem. Soc.*, **63**, 1418 (1941).
4. A. Fort, J. Roberts, *J. Am. Chem. Soc.*, **78**, 584 (1956).
5. V. N. Setkina, D. N. Kursanov, E. V. Bochkova, *Problems of Kinetics and Catalysis*, **9**, 234 (1957).
6. V. Mayer, Fr. Forster, *Ber.*, **9**, 535 (1876).
7. J. Roberts, J. Jancey, *J. Am. Chem. Soc.*, **74**, 5943 (1952).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.