

PRIMARY DOCUMENTS

ON THE QUESTION OF THE MUTUAL INFLUENCE OF ATOMS IN CHEMICAL COMPOUNDS

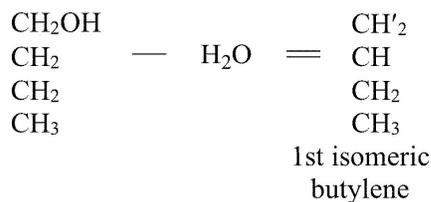
V. Morkovnikov (1)

Zhurnal Russkago Fiziko-Khimicheskago Obshchestva, 1869, 1, 242-247

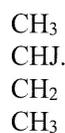
Translated by David E. Lewis

I. The Conversion of Isobutyl Alcohol into Tertiary Pseudobutyl (2) Alcohol.

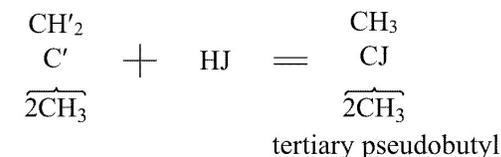
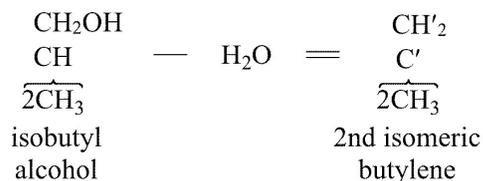
Much attention has already been paid to how the mutual influence of atoms is manifested in the elimination of hydrohalic acids from halides (3), in particular. I have formulated the general law that is seen in these reactions, as follows: *If an alcohol or a halide loses water or the hydrohalic acid, in the form of water, or acid, along with hydroxyl (OH) or halogen, the hydrogen bonded to the carbon directly linked to the carbon atom to which the hydroxyl or halogen was bound is always lost* (4). On the other hand, I have also suggested that the reverse reactions, i.e., when water or hydrohalic acids are added to unsaturated hydrocarbons that are not symmetrically constructed, the former are distributed in such a way that *the hydroxyl or the halogen always bonds to the least hydrogenated carbon* (5). The direct consequence of these two provisions is that when *eliminating* water from a *normal* alcohol containing more than three carbon units, we cannot obtain a *normal* homologue of ethylene, $n\text{CH}_2$ (6), and that by sequentially eliminating water from a primary alcohol and then adding water (7), one must move to secondary or tertiary pseudoalcohols. Thus, normal butyl alcohol should give the normal isomer of butylene, 4CH_2 (8)



By attaching the hydrogen iodide to this butene also, we should get the iodide from the secondary pseudobutyl alcohol of de Luynes:

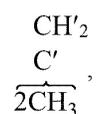


Similarly, isobutyl alcohol should go to the tertiary alcohol of Butlerov (9).



Due to the difficulty of obtaining a normal alcohol, I used isobutyl alcohol (fermentation alcohol) for the study in this specified area. For my study, the alcohol boiling at 105-110° after multiple fractional distillations was used. The iodide prepared from this alcohol was subjected, in turn, to fractional distillation into several separate fractions; the 1st was collected from 115° to 118° and the 2nd from 118° to 123°. The determination of iodine in the product boiling from 118° to 123° gave 67.7% iodine; the formula C_4H_9J requires 69.02%. Consequently, this fraction contains a small admixture with amyl iodide. But the transformation of the tertiary alcohol into the iodide showed that both distillates mainly consisted of C_4H_9J .

Since Butlerov has shown that the butene obtained from a tertiary alcohol,



on bonding with HJ, also gives the iodide of the tertiary alcohol, I prepared my butylene by heating isobutyl iodide with a strong alcoholic solution of potassium hydroxide. It was, without much preliminary examination, directly converted to the iodide by shaking with fuming hydriodic acid. In general, this immediately led to the formation of an oil; the formation of the compound is so easy that shaking just a few tens of times led to the complete absorption of the gas. The resulting iodide boiled almost without decomposition at 98°-100°, if isobutyl iodide boiling from 115°-118° was used in its preparation; the later fraction, which boiled from 118°-123°, also gave an iodide, boiling from 98°-101°. At the same time, a part of the iodide was treated separately with freshly prepared silver oxide in the presence of water. This immediately resulted in the formation AgJ and the liquid acquired a strong camphor smell peculiar to the tertiary alcohol. The alcohol was isolated from the aqueous solution by drying with fused potash. When distilled over metallic sodium, both portions gave almost the same boiling point 81°-82°, 82°-83°. The latter, which was obtained from the iodide boiling at 115°-118°, solidified at once to a crystalline mass; the other fraction of the tertiary alcohol I could not get in a crystalline form, which was probably due to minor impurities and extraneous matter.

The boiling points of the iodide and alcohol, as well as the characteristic smell of the latter and the ability to crystallize it with a little cooling, show beyond doubt that I was dealing with tertiary pseudobutyl alcohol.

The results reported fully confirm my above conclusions.

Kazan, October 1869.

References and Notes

- [The spelling of Markovnikov's name here would appear to be a misprint, but it is interesting to note that with the emphasis on the second syllable of the name, Markovnikov and Morkovnikov would sound alike when spoken aloud. The following explanation is provided by A. V. Zakharov (in *Kazan University: Chronology of the Formation and Development of the Chemical Laboratory and the Kazan School of Chemistry. Part I. 1806-1872*. Kazan University Press, Kazan, 2011; p 406, footnote 410); note that he cites verbatim from the biography of Zaitsev by Klyuchevich and Bykov: "Writing his family name using **o**—**Mo**rkovnikov—was almost universal in official documents and journal articles in the 1860s, although it also occurs much later [*emphasis added*]. Markovnikov himself explained that Butlerov kept writing the first syllable of his name using **o**, and that he was imitated by others. According to the original version by A. Klyuchevich and G. V. Bykov, 'on admission to the university, he was named just **Mo**rkovnikov on the passport. He later corrected it to "**Ma**rkovnikov,'" [but] Butlerov did not always remember about this." (A. S. Klyuchevich and G. V. Bykov, *Aleksandr Mikhailovich Zaitsev (1841-1910)*, Kazan University Press, Kazan, 1980, p 18). —DEL]
- [The prefix pseudo- is used to indicate branching of the main chain or its specific branching at the site of the functional group. Thus, both secondary alcohols and tertiary alcohols are referred to as pseudoalkyl alcohols. To distinguish the secondary from the tertiary alcohols, the tertiary alcohols are almost always referred to as tertiary pseudoalkyl alcohols. —DEL]
- [The Russian term is the compound noun *galoidoangidrid* (haloidoanhydride), either used because these compounds were generally made from alcohols and the acids, or used to represent the fact that the compound is formed by the hydrocarbon gaining a halogen and losing a hydrogen. The balanced equation shows the replacement of water (dehydration) by the hydrogen halide to give the alkyl halide. —DEL]
- [In modern terms, this would be specified as the β carbon. The major point that Markovnikov is making here is that the groups lost during an elimination reaction are lost from adjacent carbon atoms. —DEL]
- See: Materials on the mutual influence of atoms, etc., p 86. Scientific Notes of Kazan University, 1869.
- [This sentence is directed at the conventional wisdom of that time, held by a number of eminent chemists, that *n*-alkenes were chains of methylene groups with

the unsatisfied affinities at the terminal carbons, or what we would today call terminal carbenes. In fact, in his M. Khim. dissertation, and culminating in his Dr. Khim dissertation, Markovnikov had used addition reactions to prove that the unsatisfied affinities of alkenes are not on the terminal carbon atoms, but are, instead, on adjacent atoms (V. Markovnikov, Materials on the mutual influence of atoms in Chemical Compounds. Dr. Khim. Diss., Kazan, 1869; pp 30-31.) Markovnikov held what we would now call straight-chain 1-alkenes to be "normal" alkenes. The structure here for the first isomeric butylene is based

on his Dr. Khim. dissertation, and the condensed formula above it is simply relaying the fact that the molecular formula corresponds to a tetramer of methylene. —DEL]

7. [This is describing the dehydration–rehydration sequence beginning from an alcohol. —DEL]
8. [There is a typographical error here; the CH carbon should be designated CH'. —DEL]
9. [The product is not the alcohol (*tert*-butyl alcohol) itself, but rather its iodide. —DEL]

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Nominations are open for several posts within the Division of the History of Chemistry (HIST).

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- Secretary-Treasurer (2019-2020);
- Councilor (2020-2022 term);
- Alternate Councilor (2020-2022 term) NOTE: no incumbent is running.

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One must be a member of ACS AND of HIST to be eligible for any of these positions.

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Thank you for your interest and membership in HIST!

Vera Mainz, Sec/Treas HIST for CHAIR of the Nominations and Election Committee