

Studies from the chemical laboratory of Kazan,
communicated by *Alexander Saytzeff*.

(Received 12-Oct-1875.)

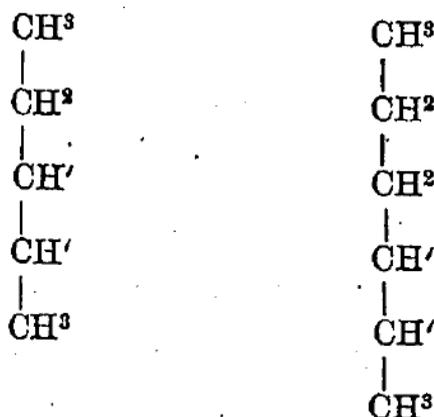
On the order of addition and elimination of hydrogen
iodide elements in organic compounds

By Alexander Saytzeff.

This paper is intended to show and explain the direction of some recent investigations in the chemical laboratory of the University of Kazan; therefore I touch on the question of the order of addition and elimination of elements of hydrogen iodide not in its whole extent, but only insofar as it is necessary for our purposes. In this paper I discuss only two points, namely the questions: a) the order of addition of hydrogen iodide elements to hydrocarbons of the series C^nH^{2n} and b) the order of elimination of elements of the Iodic anhydrides (aprotic) and on saturated monoalcohols.

On the first point the following law has now almost come to general application: *When unsymmetrical hydrocarbons of the series C^nH^{2n} are reacted by exposure to HI, the Iodine attaches to the least hydrogenated carbon atom.*

This law, as formulated by Markownikoff* determines the order of addition of HI only for asymmetrical C^nH^{2n} hydrocarbons whose free relationship, or to use another expression, whose double bond of the hydrocarbon is equally conceivable, in which the carbon atoms concerned have with the same number of hydrogen atoms. Example:



In what way will HI react with these hydrocarbons?

Looking through the literature we have come across some facts which indicate the order of addition of the elements of hydrogen iodide to the hydrocarbons of said structure. Nevertheless, it seemed of interest to carry out a thorough investigation in this direction.

From the stand point of the existing theory we could be allowed to assume that a corresponding amyl compound to the examples shown could be prepared from a diethyl

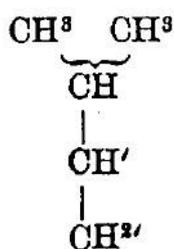
*) This journal **153**, 256.

alcohol start material. That is why we (G. Wagner and I), have made it our task to determine the structure of this hydrocarbon and on the same subject the reaction of the addition of the HI a detailed study. With the results of these investigations, as well as some facts that were known before our study which gave some measure of response to the question, the reader is given the following sets of knowledge: "About bromoamyls and amyglycols from diethyl alcohols" and "conversion to the diethyl alcohols and/or methylpropylalcohols" and in their assumed formation.

In the near future we intend to study other hydrocarbons analogous to our amyene structures which we hope will provide a sufficient quantity of data to expand our present knowledge of the synthesis of secondary alcohols.

Then I will go to the discussion of the second point raised by me the question, as to the order or pattern of elimination of iodine and hydrogen atoms from aprotic iodine-saturated monoalcohols. If one agrees with the well-known and factually supported view that only hydrocarbons of the series C^nH^{2n} are viable, then a free affinity will belong to two neighbouring carbon atoms, and one is entitled to draw from this inference that the hydrogen and iodine atoms will exit from the said aprotic iodine-saturated monoalcohols from two adjacent carbon atoms. If we now consider all possible structures of the said iodine-saturated alcohols we arrive at the view that the just drawn inference determines the pattern of elimination of the iodine and hydrogen atoms is only such that the product has a carbon atom attached to an iodine which is either connected directly to a carbon atom, or, or if multiple, only those that are of relative affinity on one carbon so that the same product is achieved by the hydrogen atom removing from one carbon atom and attaching to the other. Consequently (of course there is no rearrangement taking place during the reaction itself) this order of elimination of hydrogen and iodide atoms is hereby determined to occur only from the primary iodo groups and of such of secondary and tertiary alcohols that contain the same hydrocarbon radicals. However, this deduction may not also describe de-iodination of secondary and tertiary alcohols with unequal radicals, for those compounds containing two or three carbons linked to adjacent carbon atoms that hold an iodine, which are contained at uneven ratios through the compound (translator's note: asymmetrical!); either they are unequally hydrogenated, or they end up with the same number of hydrogen atoms, nevertheless the affinity for distribution of the more distant carbon atoms is not the same. These factors must all exert an influence over the order of elimination of HI from the compound.

All of these points have already been covered by Markownikoff (1869), however, at that time the known facts did not allow one to draw the correct conclusions in all cases. For example: Consider the identity of the amyene from amy hydrate and its HI start material which has been fermented from the equivalent amy alcohol, which at the time had the following structure attributed to it:



Is Markownikoff taking the viewpoint that the least hydrogenated carbon atom when in otherwise the same environment but with more hydrogens attached and was the least capable carbon of separating from those hydrogens. But it seemed to me that the iodine, in cases with multiple different hydrogenated reacting carbons that are in the same environment, will exit the compound taking the hydrogen with it from the least hydrogenated carbon atom. I have been led to such a view by the following clue and hints that exist in the literature: Linnemann has found that the simple brominated normal brombutyl with regard to the boiling point, is identical to bromoethylvinyl but differs from that of the butyl bromo compound made from methylethylalcohol. The analogy led him to draw the conclusion that the simple brominated normal brombutyl (as is the case with the corresponding propylcompound), must be identical to the butylbromo made from n-butyl alcohol. Diefs speaks for the likely difference of butylene from n-butyl alcohol and from Methylethylalcohol and consequently suggested that upon the occurrence of HI on the iodo reactant on methylethyl compounds the hydrogen departs from the least hydrogenated carbon atom.

Schorlemmer and Grimshaw's observations led to the same conclusion. These chemists found that the action of potassium acetate on a mixture of chloroanhydrides with primary and secondary heptyl alcohols, that two different heptylenes appeared to form; This could not take place if the ClH was escaping from the protochloride of secondary heptylalkohols, which makes the same conclusion as Markownikoff.

This is all still be reconciled with the facts to which Markownikoff based his view, which were shaken to the core by Flavitzky; his reported investigations point out that formation of normal amylene from fermentative alcohol takes this space during rearrangement.

A study in this direction appears hereafter of high interest. I have one in association with N. Grabowsky and the results of our research are assembled together in the communication: "On Brombutylene and butyl glycol from normal butyl alcohol."

While we were carrying out this investigation, Flavitzky has discovered in his laboratory that his Iodo-amylene compound underwent elimination in a manner that agrees with the views of Butlerov and Markownikoff, the properties of the heptylene from Pavlov have since become known. The fact observed by Flavitzky as well as the conclusions drawn by Butlerov and Markownikoff infer that new evidence towards the accuracy of my rule of the structure of the compounds produced in this way.

End of translation.