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A STUDY OF THE MECHANISM OF SOME REACTIONS BY THE METHOD OF HYDROGEN EXCHANGE

- USSR -

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A STUDY OF THE MECHANISM OF SOME REACTIONS BY THE METHOD OF HYDROGEN EXCHANGE

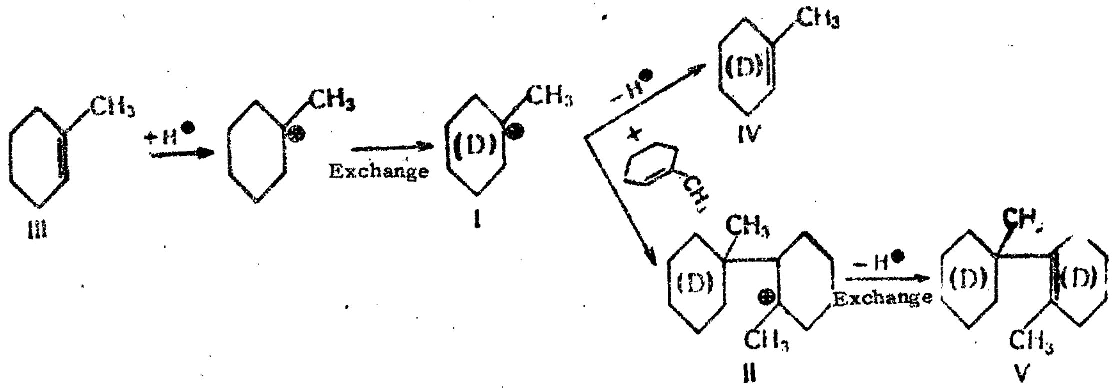
[This is a translation of an article by D. N. Kursanov, V. N. Setkina, et al, in Problemy Kinetiki i Kataliza, IX, Izotopy v Katalize (Problems in Kinetics and Catalysis, IX, Isotopes in Catalysis) Moscow, 1957, pages 242-244.]

The study of reactions of the hydrogen exchange of carbonium ions resulted in establishing a series of regulations [1].

We attempted to apply these regulations for the study of the mechanism of some heterolytic reactions.

1. We studied the reaction of dimerization of I-methylcyclohexane-I under the effect of deuterophosphorous acid. According to data obtained by Whitmore [2], dimerization of olefins under these conditions takes place with the formation of an intermediate ion of carbonium.

Considering that the characteristic feature of carbonium ions is their ability to exchange hydrogen, we would naturally expect that if the process of dimerization actually passed through the stage of formation of a carbonium ion, then in that case if the dimerization reaction is far from completion, the resulting dimer should have been deuteronized materially deeper than the monomer.

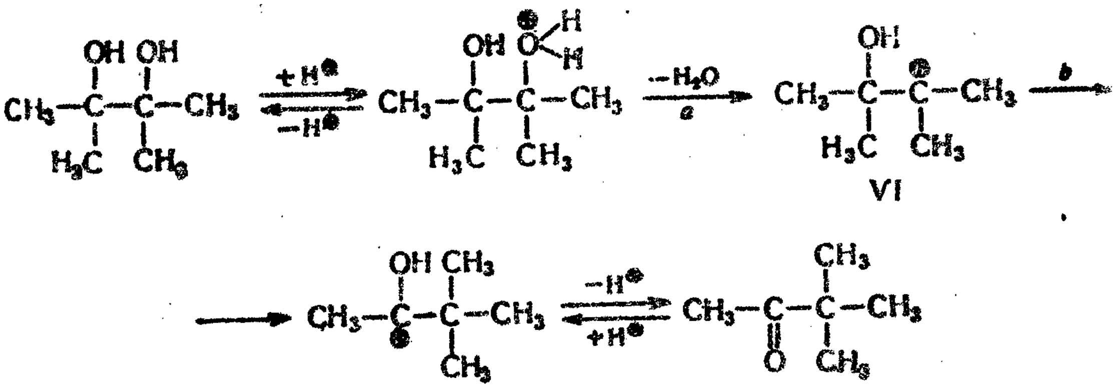


This is conditioned by reason of the fact that in the formation of dimer V, as shown on the enclosed diagram, it is imperative that the carbonium ions I and II should be present at a time when the monomer consists not only of exchanging molecules of olefin IV which therefore existed in a state of carbonium ions, but also of molecules of olefin III untouched by chemical conversions. Experience in matters of dimerization of I-methylcyclohexane-I fully substantiated this theory -- the resulting dimer was deuteronized markedly deeper than the olefin.

For instance, in the case when the formed dimer consisted of 20 percent of monomer introduced into the reaction, the excessive density of water as a result of combustion of the olefin would be 4240 γ /ml, dimers 36570 γ/ml.

Therefore, the obtained findings indicate that the dimerization of I-methylcyclohexane-I due to action of water-free D_3PO_4 indeed proceeds with the formation of intermediate ions of carbonium, and substantiates the earlier expressed theory concerning the mechanism of this reaction.

Further, we made an attempt to adapt hydrogen exchange for the study of the mechanism of the pinacolyl regrouping. It is possible to theorize that this heterolytic reaction is carried out by an ion mechanism according to this diagram:

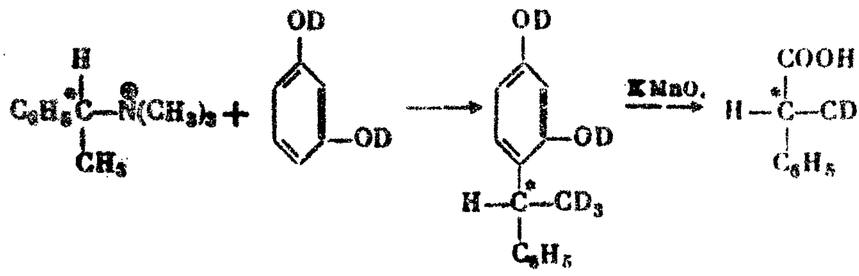


However, it is possible to expect that the stages a and b occur synchronously, without the formation of a free ion of carbonium VI. In particular, this is substantiated by the work of Bartlett [3], who found that during the pinacolyl regrouping, the migrating substitute enters from the side opposite to the side from which hydroxyl breaks away.

We regrouped pinacol into pinacolin by action of deutorosulfuric acid and established that the formed pinacolin contains three exchanged atoms of hydrogen, whereupon all three atoms were located at the carbon in the neighborhood of a ketone group. The exact location of the deuteron was determined by converting pinacolin (by oxidation with bromine alkali) into trimethylacetic acid which was burned in the form of a mercury salt, and the content of deuteron was determined in the water combustion. It was found that practically the entire deuteron was located in only a single methyl group of the pinacolin.

These findings attest to the fact that during the regrouping, carbonium ion VI does not form and that, practically, this reaction passes through a single stage (separation of an OH group and migration of an CH group occur simultaneously), and at the same time the reaction under the experimental condition is irreversible. The presence of deuterium in this case can be expected only in the methyl group, next to the carbonyl group, since under the reaction conditions the formed pinacon must exchange the three atoms of hydrogen belonging to it, connected with C_α. It is important to note the compliance of the results obtained by independent methods by Bartlett and ourselves. This at the present time can serve as a firm foundation for supporting the theory that pinacolin regrouping actually passes without formation of carbonium VI ion, and is accomplished in a single process, in a single act of disengagement of an OH group and migration of a CH group; that is, stages a and b of regrouping take place simultaneously.

Still another example is a study of the mechanism of the alkylation reaction of resorcitol with quaternary ammonium salt with optically active racidal d - α - phenethyl.



The reaction was conducted in a medium of a deuterium-donor, which appeared to be present in the excess deutoro-resorcitol. Apparently in that case, if the reaction proceeds through the stage of formation of a free ion of carbonium (methyl-phenyl-carbonium), then the formed alkylated resorcitol must be optically inactive (racemization in the stage of formation ion of carbonium) and contains deuterium. But in case the reaction passes through an activated complex, then the resulting product must have a reversed configuration and - as we assume - contains no deuterium.

Experience indicates that the reaction product appears to be racemic and actually contains deuterium (about ten percent of the value calculated for equilibrium exchange), and indicates formation of a carbonium ion. It is possible that the samll degree of deuterization is conditioned by the irreversibility of the reaction and the insufficient life duration of the methylphenylcarbonium, during which the equilibrium exchange -- in the conditions of the reaction -- is not able to stabilize.

The cited results give some foundation for hoping that the reaction of hydrogen exchange may be adapted for disclosure of intermediately-formed carbonium ions in the heterolytic reactions.

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