ISOMERIZATION OF CARBOCATION, FORMED IN THE ACETOLYSIS OF 5-HEXENYL-1-^{13}C AND CYCLOPENTYLCARBINYL-^{13}C p-NITROBENZENESULFONATE

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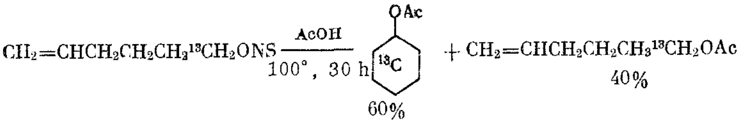
It is known that the acetolysis of 5-hexenyl p-nitrobenzenesulfonate in the presence of sodium acetate leads to the formation of 5-hexenyl acetate, and to the cyclization product, cyclohexyl acetate, in a ratio of 88: 12 [1]. The degree of cyclization increases up to 42% at 80.8°C in 52.3 h if the acetolysis is run without the sodium acetate [1].

We found that when the acetolysis of 5-hexenyl–1-^{13}C p-nitrobenzenesulfonate is run for 30 h at 100°C the cyclization reaches 60%, and the formed cyclohexyl-^{13}C acetate underwent complete isomerization, as a result of which the label was distributed uniformly along the ring of the cyclohexyl acetate molecule



The amount of ^{13}C in the cyclohexyl-^{13}C acetate was determined by nuclear magnetic double resonance under the conditions of a complete decoupling of the hydrogen nuclei [2].

Analogous data were obtained by us when the acetolysis of cyclopentylcarbinyl-^{13}C p-nitrobenzenesulfonate was run under the same conditions in the absence of potassium acetate. A uniform distribution of the label was also obtained in the principal reaction product, namely the cyclohexyl acetate, which testifies to a 100% isomerization of the intermediately formed cation due to the migration of the hydride ions. The equivalent results of these reactions make it possible to postulate the formation of the same intermediate cation, which is responsible for the isomerization.

LITERATURE CITED

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