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Yu. G. Bundel' , V. A. Savin, M. N. Ryabtsev,

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## Abstract

## Full Text

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## CHEMISTRY

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# ISOMERIZATION OF THE CYCLOHEXYL-2,6-$H_2^3$ CATION UNDER THE CONDITIONS OF THE DEAMINATION REACTION

Earlier we noted that the cyclohexyl cation formed under the conditions of the deamination reaction of cyclohexyl-2,6-$H_2^2$-amine under the action of nitrous acid undergoes isomerization caused by migration of the hydride ion ([1]).

In the present work, using as an example the deamination reaction of cyclohexyl-2,6-$H_2^2$-amine under the action of nitrous acid, the type of isomerization has been determined. For this purpose cyclohexylamine labeled with tritium in the $\alpha$-position was synthesized:

$$\text{cyclohexanone} \xrightarrow{T_2O} (T)-\text{cyclohexanone}-(T) \xrightarrow{NH_2OH} (T)-\text{cyclohexanone oxime}-(T) \xrightarrow{LiAlH_4} (T)-\text{cycloh}$$

The products of the deamination reaction of cyclohexyl-2,6-$H_2^3$-amine are cyclohexene and cyclohexanol.

$$(T)-\text{cyclohexylamine perchlorate}-(T) \xrightarrow{HNO_2} T-\text{cyclohexanol} + T-\text{cyclohexene}$$

Carrying out the degradation of cyclohexanol-$H^3$ according to the following scheme:

$$T-\text{cyclohexanol} \xrightarrow[H^+]{CrO_3} T-\text{cyclohexanone} \xrightarrow[OH^-]{KMnO_4} T-\text{dicarboxylic acid} \xrightarrow[BaO]{t^\circ} T-\text{cyclopentanone}$$

$$T-\text{cyclohexanone} \longrightarrow T-2,6\text{-bis(benzylidene)cyclohexanone}$$

$$T-\text{cyclopentanone} \longrightarrow T-2,5\text{-bis(benzylidene)cyclopentanone}$$

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1,2-hydride shift and 1,3-hydride shift diagrams

Figure 1: 1,2-hydride shift and 1,3-hydride shift diagrams

we established that the degree of isomerization of the cyclohexyl cation is $4.8 \pm 0.3\%$, and that the isomerization is mainly caused by a 1,2-hydride shift, amounting to 3.5%. The 1,3-hydride shift in this case amounted to 1.3%. The degree of isomerization caused by the 1,3-hydride shift ($d$) and by the 1,2-hydride shift ($e$) is found, respectively, from the following formulas:

$$d = 2\frac{(2b-a)}{c} \cdot 100\%; \qquad e = 2\left(\frac{a}{c} \cdot 100 - \frac{d}{2}\right)\%.$$

where $a$ is the activity of dibenzalcyclohexanone in imp/min · mm hydrogen, $b$ is the activity of dibenzalcyclopentanone in imp/min · mm hydrogen, and $c$ is the activity of the isomerized alcohol in imp/min · mm hydrogen. The transition state for each of the types of hydride shifts may be represented as follows:

1,2-hydride
shift

1,3-hydride
shift

Apparently, the small percentage of isomerization of the cyclohexyl cation is explained by its short lifetime. Indeed, from the literature it is known that the deamination of cis-2-$H_1^2$-cyclohexylamine proceeds with retention of configuration, i.e., the lifetime of the carbocation is less than the time required to establish conformational equilibrium ([2]).

**Table 1**

| Activity of cyclohexanol, imp/min · mm $H_2$ | Activity of cyclohexanol, imp/min · mm $H_2$ | Activity of $DB_5$, imp/min · mm $H_2$ | Activity of $DB_{c5}$, imp/min · mm $H_2$ | Activity of $DB_{c5}$, imp/min · mm $H_2$ |
|---|---|---|---|---|
| measured | reduced | | measured | reduced |
| 45 316 | 30 208 | 700 | 512 | 455 |
| 41 379 | 27 582 | 684 | 476 | 422 |

**Notes.** 1. $DB_5$ and $DB_{c5}$ are the activities of dibenzalcyclopentanone and dibenzalcyclohexanone, respectively.
2. The reduced activity is the activity recalculated for 18 hydrogen atoms.

The results of measuring the activity of the isomerization products are presented in Table 1.

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## CITED LITERATURE

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[2] A. Streitwieser, C. E. Coverdel, *J. Am. Chem. Soc.*, **81**, 4278 (1959).

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

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