REACTION OF 1-C^{13}-CYCLOHEXANOL WITH HYDROCHLORIC ACID AND THE LUCAS REAGENT

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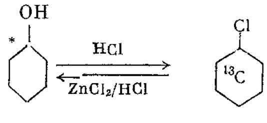
UDC 541.124:547.593.211:546.131

It has already been reported [1] that a completely isomerized cyclohexyl chloride is formed by the reactions of 1-C^{13}-cyclopentylcarbinol with hydrochloric acid and the Lucas reagent. In this study we have investigated the reactions of 1-C^{13}-cyclohexanol (I) (the C^{13}-labeled position is denoted by an asterisk) with hydrochloric acid saturated with HCl and the Lucas reagent under the conditions described for the corresponding reactions of cyclopentylcarbinol:

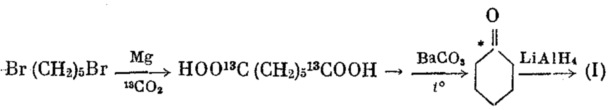


(I) (II)

Cyclohexyl chloride (II) is also formed as a result of the reaction; no ring contraction products were detected.

The formation of the same product (II) in the reactions of the carbinol and cyclohexanol and the establishment of the degree of its isomerization provide a possibility to compare the reactivity of the intermediately formed cations.

Compound (I) was synthesized via the scheme

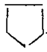


According to double NMR data, the C^{13} is found only in the 1-position in (I). The distribution of C^{13} in (II) was established by means of double NMR [2]. The results obtained are presented in Table 1. The data for the corresponding reactions of cyclopentylcarbinol are presented for comparison.

It is apparent from the data in Table 1 that isomerization of the cation proceeds more completely in the case of cyclopentylcarbinol: the distribution of the label is almost uniform, while in the case of cyclohexanol the percentage of C^{13} falls from C_1 to C_4. The total percent of isomerization is also higher in the case of cyclopentylcarbinol. This sort of difference was also observed previously. For example, in deamination reactions of the corresponding amines the degree of isomerization was higher in the case of cyclohexylamine (12.5 and 4%, respectively [3]).

The cations which are intermediately formed in the reactions of cyclopentylcarbinol and cyclohexanol are probably similar in structure, since the same product (II) is formed, but they are not identical, since the degree of their isomerization is different. The high degree of isomerization and the more complete reaction in the carbinol derivatives can apparently be explained by the higher stability of the intermediately formed cation. The gain in energy obtained on ring expansion, i.e., on transition from a primary cation to a secondary cation, promotes the longer lifetime of the carbonium ions and, consequently, the more complete transformations.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Institute of Cybernetics, Academy of Sciences of the Estonian SSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 618-619, March, 1972. Original article submitted March 24, 1971.

TABLE 1. —$^{13}CH_2OH$ (III)

Starting compound	Reagent	Isomerization, %	Distribution of ^{13}C in cyclohexyl chloride, %			
			C_1	C_2+C_6	C_3+C_5	C_4
I	HCl	78	11	10+10	6,5+6,5	6
III	HCl	79	8	9+9	7+7	8
I	$ZnCl_2$/HCl	67	16,5	10+10	4,5+4,5	4
III	$ZnCl_2$/HCl	82	8	8,5+8,5	8,5+8,5	8

EXPERIMENTAL METHOD

Synthesis of 1,7-C^{13}-Pimelic Acid. A solution of 58 g of pentamethylene bromide in 90 ml of absolute ether was added to 13.4 g of Mg in 300 ml of absolute ether. Toluene (100 ml) was added to the Grignard reagent oil, and the same amount of ether was removed from the mixture by distillation. Carbon dioxide obtained from $BaC^{13}O_3$ (50% enrichment) was passed through the resulting homogeneous solution at −15 to 20° for 1.5 h. The mixture was then decomposed with 10% H_2SO_4. The ether solution was treated with 10% NaOH to extract the pimelic acid. Cyclohexanone (2.8 g) was isolated from the residual ether solution. The alkaline solution was acidified with hydrochloric acid and evaporated to dryness, and 21.7 g of pimelic acid was extracted from the solid residue with ether.

Synthesis of 1-C^{13}-Cyclohexanone. A mixture of 21.7 g of pimelic acid and 0.93 g of $BaCO_3$ was heated at 340-360° for 6 h to give 9 g of 1-C^{13}-cyclohexanone.

Preparation of 1-C^{13}-Cyclohexanol (I). Reduction of 1-C^{13}-cyclohexanone with $LiAlH_4$ yielded 7.1 g of 1-C^{13}-cyclohexanol with bp 64-66° (15-16 mm) (bp 159° [4]).

Reaction of 1-C^{13}-Cyclohexanol with Hydrochloric Acid. A mixture of 1.4 g of 1-C^{13}-cyclohexanol (25% enrichment) in 6 ml of hydrochloric acid saturated with HCl was heated in an ampul at 100° for 15 h. The product isolated had bp 140-141° and was pure cyclohexyl chloride: the PMR spectrum did not contain proton signals from the methylene group of cyclopentylcarbinyl chloride (δ 3.44 ppm).

Reaction of 1-C^{13}-Cyclohexanol with the Lucas Reagent. A mixture of 1.5 ml of 1-C^{13}-cyclohexanol (25% enrichment) and 5.5 ml of a $ZnCl_2$/HCl solution (1 g of $ZnCl_2$ in 1 ml of solution) was heated at 50° for 6 h to give 0.97 g of cyclohexyl chloride with bp 140-141.5° (bp 141-142° [5]).

CONCLUSIONS

1. The intermediate cation formed in the reactions of 1-C^{13}-cyclohexanol with concentrated HCl and the Lucas reagent is isomerized due to hydride transfers.

2. The C^{13} distribution in the cyclohexyl chloride formed was established by means of the double NMR spectra.

LITERATURE CITED

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