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structural formulas of compounds I-VII

Figure 1: structural formulas of compounds I-VII

Abstract

Full Text

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ISOMERIZATION OF BICYCLIC HYDROCARBONS OF COMPOSITION C_9H_{16} IN THE PRESENCE OF $AlCl_3$

(Presented by Academician B. A. Kazanskii, January 16, 1965)

The isomeric transformations of alkanes and monocycloalkanes have been studied rather thoroughly, whereas there is very little information on the isomeric transformations of bicyclic hydrocarbons. At the same time, in recent years, owing to the use of new methods of analysis, detailed investigations of the individual hydrocarbon composition of ligroin and kerosene fractions of petroleum have shown that they contain appreciable amounts of condensed and bridged bicyclic hydrocarbons ([1–3]). The study of transformations of individual bicycloalkanes is of great importance for identifying the thermodynamically most stable compounds and for studying the reactivity of various spatial and structural isomers.

In the present communication we give the results of an investigation of the composition of equilibrium mixtures obtained in the isomerization of a number of bicycloalkanes of composition C_9H_{16} using $AlCl_3$ as catalyst.

We studied the transformations of the following bridged and condensed bicycloalkanes: 2-ethylbicyclo-(2,2,1)-heptane (I), 2-methylbicyclo-(3,2,1)-octane (II), 3-methylbicyclo-(3,2,1)-octane (III), 1-methylbicyclo-(3,2,1)-octane (IV), 2-methylbicyclo-(2,2,2)-octane (V), 1-methyl-cis-pentalane (1-methyl-cis-bicyclo-(3,3,0)-octane, VI), and hydrindane* (bicyclo-(4,3,0)-nonane, VII):

Transformations of hydrocarbons I-VI in the presence of $AlCl_3$ had not previously been studied; in the isomerization of hydrindane with $AlBr_3$, only the isomeric 1-, 2-, and 3-methyl-cis-bicyclo-(3,3,0)-octanes were found ([4]).

It turned out that at 50° in the presence of $AlCl_3$ one and the same equilibrium mixture of bicyclic hydrocarbons is formed, regardless of which compound (I-VII) is taken as the starting material. The chromatogram of such a mixture (obtained in the isomerization of V) is shown in Fig. 1, and as examples Table 1 gives the quantitative composition of several of the mixtures obtained. The equilibrium composition of the mixture was confirmed by us in a large number of experiments carried out with different contact times of the hydrocarbons with $AlCl_3$.

It is noteworthy that the resulting equilibrium mixture contains, in greatest amount, hydrocarbons with the bicyclo-(3,2,1)-

* The transformations of hydrindane were studied jointly with Prof. M. B. Turova-Pollak and I. E. Sosnina.

octane (57.8%), less with the structure of bicyclo-(3,3,0)-octane, still less cis- and trans-hydrindanes and methylbicyclo-(2,2,2)-octanes, and compounds with the strained structure of bicyclo-(2,2,1)-heptane are completely absent:

[[displayed chemical-structure scheme: five skeletal formulas in decreasing order, separated by ">"; labels include CH_3 on the first, second, and fourth structures and C_2H_5 on the fifth; percentages shown beneath the second through fifth structures: 21.2%, 12.4%, 6.8%, 0]]

In addition, it should be noted that one of the 16 identified compounds, namely 1-methylbicyclo-(3,2,1)-octane (IV), is present in the mixture in a considerably larger amount (43%) than the other hydrocarbons, which indicates its increased thermodynamic stability. Trans-hydrindane (VII) is present in the mixture obtained at 50° in an amount 1.5 times greater than the cis isomer, which is in good agreement with previously known data (5). Of the two possible isomers II, the endo isomer is considerably more stable than the exo isomer, and they are present in the mixture in a ratio of 8 : 1. Of the two 2-methyl-cis-bicyclo-(3,3,0)-octanes, the exo isomer is present in the mixture predominantly, whereas the content of endo- and exo-3-methyl-cis-bicy-

Fig. 1. Chromatogram of the mixture of hydrocarbons obtained by isomerization of 2-methylbicyclo-(2,2,2)-octane with $AlCl_3$ (50°). Capillary column, squalane, 70°, 1.5 atm He. Peaks 1 and 2 were recorded at sensitivity 1/10, and peaks 3—17 at sensitivity 1/3; consequently the area of peaks 3—17 is increased by a factor of 3.3 compared with the area of peaks 1 and 2.

Table 1

Composition of the mixture obtained in the isomerization of bicyclic hydrocarbons of composition C_9H_{16} in the presence of $AlCl_3$ (50°)

Peak no. in Fig. 1	Hydrocarbon	I	II + III	V
1	1-Methyl-cis-bicyclo-(3,3,0)-octane (VI)	6.9	7.0	6.7
5	Exo-2-methyl-cis-bicyclo-(3,3,0)-octane	7.0	7.4	7.0
9	Endo-2-methyl-cis-bicyclo-(3,3,0)-octane	1.0	1.1	1.1
6	Exo-3-methyl-cis-bicyclo-(3,3,0)-octane	3.1	3.2	3.3
4	Endo-3-methyl-cis-bicyclo-(3,3,0)-octane	2.7	2.8	3.0

Peak no. in Fig. 1	Hydrocarbon	I	II + III	V
2	1-Methylbicyclo-(3,2,1)-octane (IV)	42.3	43.0	43.0
15	Exo-2-methylbicyclo-(3,2,1)-octane (exo II)	0.8	0.6	0.8
11	Endo-2-methylbicyclo-(3,2,1)-octane (endo II)	6.2	6.7	6.3
7	3-Methylbicyclo-(3,2,1)-octane (III)	4.4	4.2	4.4
3	1-Methylbicyclo-(2,2,2)-octane (?)	6.1	5.8	5.7
12	2-Methylbicyclo-(2,2,2)-octane (V)	1.2	0.9	0.9
14	Trans-hydrindane (trans VII)	7.2	7.5	7.4
17	Cis-hydrindane (cis VII)	5.4	4.8	5.2
18	Bicyclo-(3,2,2)-nonane	0.2	0.3	0.3
8	Exo-6-methylbicyclo-(3,2,1)-octane (IX)	2.9	2.6	2.9
10	Not identified	1.7	1.5	1.5
13	Endo-6-methylbicyclo-(3,2,1)-octane (IX)	0.6	0.3	0.3
16	Not identified	0.2	0.1	0.1

clo-(3,3,0)-octanes is approximately the same. To some extent this may be compared with the relative stability of monocyclic hydrocarbons. It is known that in the case of 1,2-disubstituted cyclopentanes the trans isomer is considerably more stable, whereas in the case of 1,3-disubstituted cyclopentanes the stabilities of the cis and trans isomers are close (6, 7).

Thus, all the bicyclic hydrocarbons with five- and six-membered rings that we investigated, on interaction with $AlCl_3$ (50°), are converted into a mixture of hydrocarbons (in Fig. 1 and Table 1).

Experimental section

Gas-chromatographic analysis. Determination of the purity of the starting compounds and quantitative analysis of the hydrocarbon mixtures were carried out on a Hitachi KGL-2B chromatograph (capillary column, U—90/0.25, squalane) using an integrator from the firm "Pye."

Starting hydrocarbons. The synthesis of compounds II, III, and V will be published. The synthesis of hydrocarbon I has been described previously (8). Hydrindane (VII) was obtained by hydrogenation of indene and, after distillation, contained 99% cis and 1% trans isomer. 1-Methyl-cis-bicyclo-(3,3,0)-octane (VI) and 1-methylbicyclo-(3,2,1)-octane (IV) were isolated during the distillation of the catalyzates of 2-ethylbicyclo-(2,2,1)-heptane and hydrindane with $AlCl_3$ (see below).

Experimental procedure. The hydrocarbon (from 1 to 60 g in different experiments) and sublimed $AlCl_3$ (3:1 in moles) were kept in a thermostat at 50° for 8–55 h; then the principal amount of the catalyzate was decanted from $AlCl_3$, after which the latter was treated with n-pentane to extract the remaining amount of hydrocarbons. The catalyzate was washed with water and with a solution of soda, dried, and analyzed. The catalyzate (yield 90–95%) did not give a positive formalite reaction, i.e., it did not contain impurities of aromatic hydrocarbons.

Identification of exo- and endo-II, III, V, cis- and trans-VII, VI, bicyclo-(3,2,2)-nonane, IX, and endo- and exo-2-methyl-cis-bicyclo-(3,3,0)-octanes* was carried out by the GLC method by adding reference hydrocarbons to the mixture. The presence in the catalyzate of exo- and endo-3-methyl-cis-bicyclo-(3,3,0)-octanes was confirmed from their relative retention volumes (4). 1-Methylbicyclo-(3,2,1)-octane (IV) has not been described in the literature. Its structure was confirmed as follows. According to the NMR spectrum,** IV contains one methyl group ($\tau = 9.1$). The fact that this methyl group is not attached to a tertiary carbon atom but to a quaternary one is confirmed by the chemical behavior of hydrocarbon (IV does not isomerize with 99.6% H_2SO_4 even at 120°). Consequently, a hydrocarbon of composition C_9H_{16} containing one methyl group at a quaternary carbon atom could have the structure of 1-methylbicyclo-(3,3,0)-octane (VI), 1-methylbicyclo-(2,2,2)-octane (VIII), or 1-methylbicyclo-(3,2,1)-octane (IV). The structure of 1-methylbicyclo-(3,3,0)-octane (VI) is excluded for the hydrocarbon identified by us, since it was found in the catalyzate and

(structural formula of 1-methylbicyclo-(2,2,2)-octane, labeled (VIII), with CH_3 *substituent)*

has different physical properties. The choice between structures IV and VIII can be made unambiguously in favor of the first, if one takes into account the considerably greater thermodynamic stability of the bicyclo-(3,2,1)-octane system ([9]).

Isolation of 1-methylbicyclo-(3,2,1)-octane (IV). 133 g of catalyst obtained in various experiments were distilled on a 100-theoretical-plate column. In this way it was possible to isolate 1-methylbicyclo-(3,2,1)-octane with a purity of 96% (10 ml, b.p. 146.2°/720 mm; m.p. 3.2-3.7°, n_D^{20} 1.4622, d_4^{20} 0.8643). The forefractions from the distillation contained only 1-methyl-cis-bicyclo-(3,3,0)-octane (VI) and 1-methylbicyclo-(3,2,1)-octane (IV) in ratios from 1 : 1 to 1 : 20. These fractions were used to study the isomerization of IV and VI with $AlCl_3$.

A more detailed study of the transformations described in the present communication and the final establishment of the structure of 1-methylbicyclo-(3,2,1)-octane (IV) are continuing.

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* A sample of 1-methyl-cis-bicyclo-(3,3,0)-octane (VI) was kindly supplied to us by E. S. Balenkova, and 2-methyl-cis-bicyclo-(3,3,0)-octane by Al. A. Petrov and IX by E. M. Milvitskaya.

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