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Abstract

Full Text

CHEMISTRY

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TRANSFORMATIONS OF METHYLCYCLONONANE IN THE PRESENCE OF AN IRON-PLATINUM CATALYST

It was previously established by us that, in the catalytic transformations of cyclononane over platinized carbon at 300°, two main primary reactions occur: transannular dehydrocyclization of cyclononane to hydrindane and direct hydrogenolysis of the nine-membered ring with formation of *n*-nonane (1).

Using cyclopropane and cyclopentane hydrocarbons as examples, B. A. Kazanskii and co-workers established that the presence of substituents has a definite influence on the direction of the catalytic transformations of these hydrocarbons in the presence of platinum catalysts (2). It seemed of interest to us to study the behavior of methylcyclononane under conditions of dehydrogenation catalysis, in order to elucidate the influence of the substituent on the nature of the transformation of the nine-membered cyclane.

The methylcyclononane synthesized by us was passed over an iron-platinum catalyst at 310°, with a space velocity of 0.7 hr^{-1}; the degree of conversion of the hydrocarbon was 60%. By gas-liquid chromatography it was established that the products of the catalytic transformations of methylcyclononane are: cis-8-methylhydrindane (9%), hydrindane (3%), 1,1-dimethyl-2-ethylcyclohexane (or 1,2-dimethyl-1-ethylcyclohexane) (23%), indane (12%), 1- and 2-methylindanes (13%), 4-methylindane (15%), 5-methylindane (15%), 1,3-dimethyl-4-ethylbenzene (3%), 1,2-diethylbenzene (1%), and also 2-methylnonane (6%).

cis-8-Methylhydrindane could be formed by transannular dehydrocyclization of the initial methylcyclononane with participation of the hydrogen at the tertiary carbon atom bearing the methyl substituent. Cleavage of the methyl group in 8-methylhydrindane under catalysis leads to formation of hydrindane, and dehydrogenation of the six-membered ring in the latter—to indane. Hydrogenolysis of the five-membered cycle in 8-methylhydrindane leads to the formation of dimethylethylcyclohexanes. Thus, about 50% by weight of the catalyst consists of cis-8-methylhydrindane and secondary products of its transformations; hence it follows that methylcyclononane is characterized by such a type of transan-

Reaction scheme for the transformations of methylcyclononane in the presence of an iron–platinum catalyst, showing formation of methylhydrindanes, methylindanes, ethylmethylbenzenes, dimethyl- and ethyl-substituted cyclohexanes, and ring-opening products.

Figure 1: Reaction scheme for the transformations of methylcyclononane in the presence of an iron–platinum catalyst, showing formation of methylhydrindanes, methylindanes, ethylmethylbenzenes, dimethyl- and ethyl-substituted cyclohexanes, and ring-opening products.

nular dehydrocyclization in which preferential formation of methylhydrindane with an angular position of the methyl group occurs.

An X-ray structural study of the structure of the nine-membered ring carried out in 1960 ([3,4]) showed that substituted cyclononane exists in the form of two conformational isomers, the carbon skeletons of which are completely asymmetric and, although very close in the general arrangement of the carbon atoms, differ both in the valence angles C—C—C and in torsion angles. All 18 hydrogen atoms in completely asymmetric cyclononane are nonequivalent. However, for practical purposes, Dunitz and Prelog ([4]) propose to divide them into two groups: 6 intraannular hydrogen atoms, located inside the ring, and 12 extraannular hydrogen atoms. Substituents in cyclononane can probably occupy only extraannular positions. The distances between intraannular atoms

hydrogen atoms are 1.8–2.25 Å (Fig. 1). Formation of the C—C bond in transannular dehydrocyclization occurs precisely between those carbon atoms (1 and 5 or 3 and 8) that have closely situated intraannular hydrogen atoms. Apparently, dehydrocyclization proceeds with elimination of these closely situated hydrogen atoms.

The preferential formation of methylhydrindane with an angular position of the methyl group indicates that the transannular dehydrocyclization reaction occurs mainly with elimination of the intraannular hydrogen located at the carbon bearing the substituent. However, the presence in the catalyzate of 1-, 2-, 4-, and 5-methylindanes indicates the possibility that other intraannular hydrogen atoms also participate in this reaction.

It is unclear what determines the directed transannular dehydrocyclization—the presence of hydrogen at a tertiary carbon atom or the conformational features of methylcyclononane. As in the case of cyclononane, in the catalytic transformations of methylcyclononane hydrogenolysis of the nine-membered ring was observed, as indicated by the formation of 2-methylnonane.

The behavior of methylcyclononane in the presence of an iron–platinum catalyst may be expressed by the following scheme:

Scheme for synthesis of methylcyclononane from cyclononanone via reaction with methylmagnesium iodide, dehydration, and hydrogenation over Pt.

Figure 2: Scheme for synthesis of methylcyclononane from cyclononanone via reaction with methylmagnesium iodide, dehydration, and hydrogenation over Pt.

Fig. 1

Figure 3: Fig. 1

Experimental Part

A. Synthesis of hydrocarbons.

1. Methylcyclononane was obtained according to the scheme:

The cyclononanone required for the Grignard reaction was synthesized by the method of acyloin condensation (^{5}). The yield of methylcyclononane, calculated on the ketone, was 60%.

The hydrocarbon had: b.p. 192.5° (737 mm); n_D^{20} 1.4622; d_4^{20} 0.8413. Lit.: n_D^{20} 1.4600 (^{6}).

2. cis-8-Methylhydrindane. By the interaction of 1-formylcyclopentene with butadiene-1,3, cis-8-formyl-4,7,8,9-tetrahydrindane was obtained in quantitative yield; through the hydrazone it was converted into

cis-8-methyl-4,7,8,9-tetrahydrindane. Hydrogenation of the latter led to the formation of cis-8-methylhydrindane, b.p. 175° (740 mm); n_D^{20} 1.4700; d_4^{20} 0.8760. Lit. (^{7}): b.p. 176° (765 mm); n_D^{25} 1.4671; d_4^{25} 0.8756.

B. Catalytic transformations of methylcyclononane. In a quartz tube were placed 10.7 g (40 ml) of an iron-platinum catalyst (^{8}) containing 19.6% platinum, 2% iron, and 78.4%

Fig. 1. Conformation of the nine-membered ring

Fig. 2. Chromatogram of the paraffin–naphthene fraction of the catalyzate of methylcyclononane.
1 —2-methylnonane; 2 —1,1-dimethyl-2-ethylcyclohexane (or 1,2-dimethyl-1-ethylcyclohexane); 3 —hydrindane; 4 —cis-8-methylhydrindane; 5 —methylcyclononane

Fig. 3. Chromatogram of the aromatic fraction of the catalyzate of methylcyclononane.

Fig. 2

Figure 4: Fig. 2

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Fig. 3

Figure 5: Fig. 3

1 —1,2-diethylbenzene; 2 —1,3-dimethyl-4-ethylbenzene; 3 —indane; 4 —1- and 2-methylindane; 5 —5-methylindane; 6 —4-methylindane

activated carbon, and 27 g of methylcyclononane was passed over the catalyst at 310° with a space velocity of 0.7 hr^{-1}. The iron-platinum catalyst was chosen here by us because, under certain conditions, while actively effecting the dehydrogenation reaction of hexamethylene hydrocarbons, it carries out hydrogenolysis of the nine-membered ring only to a small extent, in contrast to platinized carbon, which in our case makes it possible to reduce the occurrence of secondary processes.

As a result of the catalysis of methylcyclononane, 24 g of liquid catalyzate with n_D^{20} 1.4986, d_4^{20} 0.9713, and 3.3 liters of gas were obtained; the gas consisted of 13% methane and 87% hydrogen. Chromatography of the catalyzate on silica gel afforded 14.6 g of a paraffin-naphthene fraction with n_D^{20} 1.4568; d_4^{20} 0.8294, and 8.4 g of an aromatic fraction with n_D^{20} 1.5272; d_4^{20} 0.9335.

Analysis of the fractions was carried out on a laboratory chromatograph with a katharometer as detector. The column length was 6 m, the internal diameter 4 mm; the stationary phase was polyethylene glycol adipate deposited on diatomaceous brick. The column temperature was 175°; the nitrogen flow rate at the outlet was 40 ml/min.

The chromatogram of the paraffin-naphthene fraction is shown in Fig. 2. The retention times of the transformation products contained in the fraction and of the corresponding individual hydrocarbons are given in Table 1.

The paraffin-naphthene part of the catalyzate could contain gem-substituted trialkylcyclohexanes formed through hydrogenolysis of the five-membered ring of cis-8-methylhydrindane (such hydrocarbons could be 1,1-dimethyl-2-ethylcyclohexane and 1,2-dimethyl-1-ethylcyclohexane). To confirm this supposition, the cis-8-methylhydrindane synthesized by us was subjected to catalysis under conditions analogous to those under which the catalysis of methylcyclononane was carried out. In the chromatogram of the naphthene part of the catalyzate of 8-methylhydrindane there was a peak completely corresponding in retention time to peak No. 2 of the chromatogram of the paraffin-naphthene part of the methylcyclononane catalyzate. Thus it was established that peak No. 2 in the chromatogram of the paraffin-naphthene fraction of the methylcyclononane catalyzate corresponds to the transformation product of 8-methyl-

Table 1

Peak No.	Retention time, min	Hydrocarbon	Amount of individual hydrocarbon in the fraction, % based on the transformed portion	Content of individual hydrocarbon in the catalyzate, %
Paraffin-naphthene fraction	**Paraffin-naphthene fraction**	**Paraffin-naphthene fraction**	**Paraffin-naphthene fraction**	**Paraffin-naphthene fraction**
1	5	2-Methylnonane	15	6
2	7	1,1-Dimethyl-2-ethylcyclohexane; 1,2-Dimethyl-1-ethylcyclohexane	56	23
3	10	Hydrindane	7	3
4	11	cis-8-Methylhydrindane	22	9
5	13	Methylcyclononane	–	–
Aromatic fraction	**Aromatic fraction**	**Aromatic fraction**	**Aromatic fraction**	**Aromatic fraction**
1	21	1,2-Diethylbenzene	2	1
2	29	1,3-Dimethyl-4-ethylbenzene	5	3
3	34	Indane	20	12
4	35	1- and 2-Methylindane	22	13
5	47	5-Methylindane	26	15
6	51	4-Methylindane	25	15

hydrindane, apparently one of the above-mentioned gem-trialkylcyclohexanes. The chromatogram of the aromatic fraction of the catalyzate is shown in Fig. 3;

the retention times corresponding to the transformation products of this fraction and the corresponding individual hydrocarbons are given in Table 1.

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