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Abstract

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Catalytic Transformations of Cyclododecane in the Presence of Platinized Carbon

In studying the catalytic transformations of eight- to ten-membered cyclanes, belonging to hydrocarbons with a medium ring size, in the presence of platinized carbon at 300°, it was established (1–3) that these hydrocarbons undergo transformations along two main pathways: 1) transannular dehydrocyclization with formation of bicyclic hydrocarbons and 2) direct hydrogenolysis of the ring with formation of normal paraffinic hydrocarbons.

It was of interest to determine whether the established regularity would be observed in the catalytic transformations of cyclododecane, the last representative of hydrocarbons with a medium ring size, which, in terms of its conformational features, lies at the boundary between medium and large cyclanes.

The cyclododecane synthesized by us was passed in a stream of hydrogen at 300° over 5% platinized carbon. The degree of conversion of cyclododecane was approximately 50%. Upon chromatography of the catalyzate on silica gel, paraffin-naphthene and aromatic fractions were isolated, which were then studied by gas-liquid chromatography. The paraffin-naphthene fraction consisted of unconverted cyclododecane and *n*-dodecane, which could have formed only through direct hydrogenolysis of the twelve-membered ring.

The chromatogram of the aromatic portion of the catalyzate (Fig. 1) indicated the presence of five hydrocarbons in it.

Peak 4, by retention time, corresponded to benzpentalane. The appearance of benzpentalane in the catalyzate can be explained as follows: as a result of catalytic dehydrocyclization, cyclododecane is converted into benzocyclooctane, and the latter then undergoes a C_5-dehydrocyclization reaction of the eight-membered ring with formation of benzpentalane.

The fact of formation of unsubstituted pentalane during catalytic dehydrocyclization of cyclooctane itself under analogous experimental conditions was established by us earlier (1).

[reaction scheme: cyclododecane → bicyclic intermediate → benzocyclooctane → benzpentalane]

Under the experimental conditions, benzpentalane can undergo hydrogenolysis of one of the five-membered rings with formation of substituted indane. Therefore it was likely to suppose that the catalyzate of cyclododecane contains products of further transformations of benzpentalane.

In order to confirm this supposition, benzpentalane specially synthesized by us was passed over platinized carbon under the same experimental conditions as cyclododecane. The chromatogram of the benzpentalane catalyzate (Fig. 2) consisted of three peaks, the last of which belonged to the starting hydrocarbon, while the other two, by retention time—

···corresponded completely to peaks 1 and 2 of the chromatogram of the aromatic fraction of the cyclododecane catalyzate (Fig. 1).

Thus it was established that peaks 1 and 2 in the chromatogram of the aromatic fraction of the cyclododecane catalyzate belong to products of benzenetralin transformations, apparently substituted indanes. Peak 3 of this chromatogram should probably be assigned to benzocyclooctane.

The retention time corresponding to peak 5 of the chromatogram of the aromatic fraction of the cyclododecane catalyzate was identical with that of individual 2,7-dimethylnaphthalene, the formation of which can be represented by the following scheme:

cyclododecane framework $\longrightarrow$ [fused bicyclic intermediate] $\longrightarrow$ [dimethyl-substituted decalin-type intermedi

Thus, the aromatic fraction, which constitutes 50% of the converted portion of the cyclododecane catalyzate, contains benzenetralin ($\sim$ 18%), products of its catalytic transformations—substituted indanes ($\sim$ 17%), dimethylnaphthalene ($\sim$ 6%) and, apparently, benzocyclooctane ($\sim$ 9%). The remaining 50% of the converted portion of the catalyzate is accounted for by *n*-dodecane—the product of direct hydrogenolysis of the twelve-membered ring.

Consequently, in the catalytic transformations of cyclododecane in the presence of a platinum catalyst, the same regularities are observed as for other medium rings: transannular dehydrocyclization and direct hydrogenolysis of the ring.

The catalytic transformations of cyclododecane over platinized carbon may be expressed by the following scheme:

$$\begin{tikzcd}
n\text{-C}_{12}\text{H}_{26} & \text{cyclododecane} \arrow[l] \arrow[d] \arrow[rr, shift left] & & \text{cyclododecane isomeric framework} \arrow[ll, shift left] \arrow[d] \\
& \text{[benzocyclooctane precursor]} \arrow[d] & & \text{[decalin-type precursor]} \arrow[d] \\
& \text{benzenecyclooctane-type intermediate} \arrow[d] & & \text{[dimethyl-decalin-type intermediate]} \arrow[d] \\
\text{propylindane} & \text{benzenetralin} \arrow[l] \arrow[r] & \text{ethylmethylindane} & \text{2,7-dimethylnaphth}
\end{tikzcd}$$

Experimental Part

Synthesis of cyclododecane.

By trimerization of divinyl by the method of Wilke (4) in the presence of a mixed catalyst consisting of titanium tetrachloride and triisobutylaluminum, cis-, trans-, trans-cyclododecatriene-1,5,9 was synthesized; hydrogenation of it over skeletal nickel in an autoclave at room temperature and a hydrogen pressure of 130 atm gave cyclododecane with m.p. 60°. Literature data: (5) m.p. 60—61°.

Synthesis of benzpentalane (6)

$$\text{benzene+cyclopentenecarboxylic acid chloride} \xrightarrow{\text{AlCl}_3} \text{benzpentalone} \xrightarrow[\text{HCl}]{\text{Zn/Hg}} \text{benzpentalane}$$

From cyclopentenecarboxylic acid chloride and benzene, in the presence of aluminum chloride, benzpentalone was synthesized in 55% yield. B.p. 147—149° (13 mm); n_D^{17} 1.5745.

Literature data: (6) b.p. 145° (12 mm); n_D^{17} 1.5740.

The ketone obtained was reduced with amalgamated zinc to benzpentalane. Yield 58%. B.p. 116—117° (19 mm); n_D^{20} 1.5501; d_4^{20} 1.0062.

Literature data: (6) b.p. 107—109° (12 mm); n_D^{17} 1.5511.

Fig. 1. Chromatogram of the aromatic fraction of the cyclododecane catalyzate

Catalytic conversions of cyclododecane.

Into a quartz tube was placed 60 cm^3 (14.7 g) of 5% platinized charcoal, over which, at 300° and a space velocity of 0.2 h^{-1}, in a stream of hydrogen, 35 g of cyclododecane dissolved in 14 g of n-hexane was passed. After

Fig. 1. Chromatogram of the aromatic fraction of the cyclododecane catalyzate

Figure 1: Fig. 1. Chromatogram of the aromatic fraction of the cyclododecane catalyzate

Fig. 2. Chromatogram of the benzpentalane catalyzate

Figure 2: Fig. 2. Chromatogram of the benzpentalane catalyzate

Fig. 2. Chromatogram of the benzpentalane catalyzate

distillation of the solvent, the catalyzate (32.3 g) was subjected to chromatography on silica gel. As a result, 24.1 g of a paraffin-naphthene fraction was isolated, from which the initial cyclododecane (15.8 g) was separated by freezing out. The residue (8.3 g), distilled in vacuo, had b.p. 114—116° (27 mm); n_D^{20} 1.4224; d_4^{20} 0.7495.

Literature data for *n*-dodecane: (7) b.p. 216° (760 mm); n_D^{20} 1.4216; n_D^{20} 0.74869.

The aromatic fraction obtained by chromatography (8.2 g) had b.p. 103—120° (9 mm); n_D^{20} 1.5223; d_4^{20} 0.9325.

Analysis of the fractions was carried out on a laboratory chromatograph with a katharometer as detector. The column length was 4 m, internal diameter

4 mm; stationary phase: polymethylphenylsiloxane oil (15 wt %), deposited on diatomaceous brick.

The column temperature in the analysis of the paraffin fraction was 176°; in the analysis of the aromatic fraction, 187°. The nitrogen flow rate was, respectively, 20 cm^3/min and 19 cm^3/min.

The chromatogram of the paraffin fraction consisted of a single peak, coinciding in retention time (12 min) with individual *n*-dodecane. The chromatogram of the aromatic fraction (Fig. 1) consisted of five peaks with the retention times given in Table 1.

Table 1

Peak No.	Retention time, min	Hydrocarbons of the aromatic part of the catalyzate
1	12	Substituted indanes
2	16	Substituted indanes
3	19	Benzcyclooctane (?)
4	22	Benzpentalan

Peak No.	Retention time, min	Hydrocarbons of the aromatic part of the catalyzate
5	33	2,7-Dimethylnaphthalene

The retention times corresponding to peaks 1 and 2 were identical with the retention times of the products of catalytic transformations of benzpentalan (see below); peak 4 corresponded to individual benzpentalan, peak 5 to 2,7-dimethylnaphthalene, and peak 3, apparently, should be assigned to benzcyclooctane.

Catalytic transformations of benzpentalan. Over 5% platinized carbon at 300° in a stream of hydrogen, 4 g of benzpentalan were passed. 2.8 g of catalyzate with n_D^{20} 1.5262 were obtained. The chromatogram of the catalyzate is presented in Fig. 2, where the retention times corresponding to the peaks of the chromatogram are also given.

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named after M. V. Lomonosov

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