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Abstract

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CONTACT TRANSFORMATIONS OF CYCLODECANE IN THE PRESENCE OF PLATINIZED CARBON

There are many data on the catalytic action of platinum on cyclanes with the number of carbon atoms in the ring from three to eight ([1,2]), but cyclodecane had not been studied in this respect, and comparison of it with other members of the series would be of undoubted interest. True, the contact transformations of cyclodecane were investigated by Prelog and Schenker ([3]), who showed as early as 1953 that at 340° in the presence of palladium on carbon this hydrocarbon gives up to 20% azulene and 4.5% naphthalene. However, their results cannot be compared with data obtained for other cyclanes on platinum, since the catalytic properties of these two metals sometimes differ considerably ([1]). Therefore, investigation of the behavior of cyclodecane on platinized carbon deserved attention; moreover, it was of interest from another point of view as well. Indeed, until now it had been considered that cyclodecane is converted directly into azulene.

However, in connection with the discovery of the C_5-dehydrocyclization reaction ([4]), the question arose whether the formation of azulene is only a secondary process, whereas initially decahydroazulene is formed (transannular C_5-dehydrocyclization), which is then dehydrogenated to azulene. Analogously, naphthalene could be obtained from decalin—a product of transannular C_5-dehydrocyclization. Unfortunately, the authors mentioned did not investigate the residue after separation of the aromatic hydrocarbons, and the question remained open.

In the present work an attempt was made to approach the clarification of the possibility of such a course of the reaction, first of all on platinized carbon (5 and 20% Pt), on which the investigations on C_5-dehydrocyclization had also been carried out. The experiments were performed at 300 and 310° without a carrier gas. Under the adopted conditions, most of the cyclodecane passed over the catalyst underwent transformation. To study the catalyzates, fractional rectification on efficient columns was used, as well as chromatography on silica gel for separating aromatic hydrocarbons from paraffinic and naphthenic ones, and examination of Raman spectra. Analysis of the spectra of the fractions, especially the naphthenic ones, was made difficult by the presence in many of them of components whose spectra are as yet unknown. In general, the catalyzate proved to be very complex: it contained paraffinic, mono- and bicyclic naphthenic, and aromatic hydrocarbons. Among the latter, naphthalene and *o*-diethylbenzene occupy the principal place. In small quantities there were also detected: α-methylindan, *n*-butylbenzene, indan, and *o*-methylethylbenzene. Of particular interest is the paraffin–naphthene portion, in which approximately equal amounts of *n*-decane, *cis*-decahydroazulene, and 1,2-diethylcyclohexane were found, a small quantity of *trans*-decalin, and some hydrocarbon whose spectrum is unknown. Evidently, the formation of decalin and naphthalene is the result of transannular C_6-dehydrocyclization, while decahydroazulene is obtained in the transannular C_5-dehydrocyclization of cyclodecane. Consequently, C_5- and C_6-dehydrocyclization can indeed take place not only through the closure of open chains, but also within a ring, with the formation of bicyclic systems.

Of special significance is the presence of *n*-decane in the catalyzate, since it could have formed only by rupture of the ten-membered ring. Since

Since until now hydrogenolysis had been known only for rings having no more than five carbon atoms in the ring, the observation made is of fundamental importance. The origin of *o*-diethylbenzene and 1,2-diethylcyclohexane, of which more than 30% in all is formed at 300°, remains unclear. It should be noted that none of the reactions known so far can serve to explain this fact.

The experimental material obtained makes it possible to conclude that, in the presence of platinized charcoal, cyclodecane reacts according to the following scheme:

$$\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}$$

$$\uparrow$$

[reaction scheme with decalin, naphthalene, open-chain decane, fused-ring intermediates, 1,2-diethylcyclohexane, and *o*-diethylbenzene]

All other hydrocarbons found in the catalyzate are probably products of subsequent transformations.

Experimental Part

Cyclodecane with b.p. 70.5° (11 mm); m.p. 11.0°; n_D^{20} 1.4715; d_4^{20} 0.8583; degree of purity (from the freezing curve) 99.5%. **Catalyst**—platinized charcoal prepared according to Zelinsky (5) (5% Pt in experiments at 300° and 20% Pt in experiments at 310°).

Contact transformations of cyclodecane at 310°. Over the catalyst in two successive experiments, 84.1 g of cyclodecane was passed at a space velocity of 0.2 h^{-1}, and 76.1 g of catalyzate and 25 l of hydrogen containing only 1.5% methane, i.e. another 2.6 g, were collected; the losses amounted to 6.5%. Properties of the catalyzates obtained: I n_D^{20} 1.5000, bromine number 2.45; and II n_D^{20} 1.4959, d_4^{20} 0.8799; the specific gravity of the first catalyzate was not determined, since it contained many crystals. Both catalyzates were cooled to 0°, and the crystals that separated were filtered off; from catalyzate I, 3.8 g of crystals was isolated; from catalyzate II, 2.9 g of crystals. The filtrates had n_D^{20} 1.4898 and 1.4883, respectively. The crystals obtained had the odor of naphthalene and, after recrystallization from alcohol, melted at 80.0–80.2°.

Table 1

Results of distillation of the paraffin-naphthene portion of the cyclodecane catalyzate (310°)

Fraction No.	Boiling range, °C/760 mm	Fraction weight, g	n_D^{20}	d_4^{20}
I	172.5–174.7	2.3	1.4182	0.7466
II	174.7–184.2	2.45	1.4318	0.7796
III	184.2–193.6	2.65	1.4681	0.8667
IV	193.6–195.2	2.8	1.4730	0.8779
V	195.2–198.5	2.7	1.4730	0.8740
VI	198.5–201.0	3.1	1.4720	0.8635
Residue	–	7.9	1.4717	0.8592

A mixed sample with known naphthalene melted at the same temperature. After chromatography on silica gel, the catalyzate freed from aromatics (25.0 g) was distilled on a column with an efficiency of 40 theoretical plates. The results of the distillation are given in Table 1. The aromatic portion was not investigated.

Contact transformations of cyclodecane at 300°. Over the catalyst, 190 g of cyclodecane was passed at a space velocity of 0.2 h^{-1}. By fractionating the catalyzate on a column with an efficiency of 80 theoretical plates, naphthalene and unreacted cyclodecane were separated. The latter was again subjected to catalysis. After three repetitions of such operations, 41.5 g of naphthalene, 128.1 g of liquid catalyzate, and 91.3 l of hydrogen containing only 1% methane, i.e. another 3.7 g, were obtained; the losses amounted—

were 6.0%. The fractions obtained in the above distillation that had n_D^{20} below 1.4820 were combined and chromatographed on silica gel to separate the paraffin-naphthenic hydrocarbons from the aromatic ones. Fractions from the same distillation with higher refractive indices were regarded as aromatic hydrocarbons, although, as was shown subsequently, they contained a certain amount of bicycloalkanes. To these fractions were also added the aromatic hydrocarbons isolated by chromatography. In this way, 69.1 g of aromatic and 49.1 g of paraffin-naphthenic hydrocarbons were obtained; these were separately subjected to distillation in vacuo on the same column. The results of the distillation of the paraffin-naphthenic portion are analogous to those given in Table 1; the results of the distillation of the aromatic portion are given in Table 2.

Table 2

Results of distillation of the aromatic portion of the catalyzate from experiments at 300°

Fraction No.	Boiling range, °C/17 mm	n_D^{20}	d_4^{20}	Weight of fraction, g
I	62.7–71.9	1.5052	0.9007	2.7
II	71.9–73.3	1.5100	0.9189	3.3
III	73.3–74.9	1.4960	0.8806	3.9
IV	74.9–76.1	1.5000	0.8772	6.1
V	76.1–76.5	1.5013	0.8772	7.7
VI	76.5–76.6	1.5020	0.8778	9.8
VII	76.6–76.8	1.5020	0.8784	8.5
VIII	76.8–78.4	1.5018	0.8800	7.1
IX	78.4–80.0	1.4890	0.8869	6.6
X	80.0–80.8	1.4755	0.8790	10.5
Residue	–	1.4880	0.8890	2.2
Losses	–	–	–	0.6

Fractions VII–X from the distillation of the paraffin-naphthenic portion were combined (17.5 g) and treated with a methanolic solution of urea. Decomposition of the isolated urea complex gave 8.3 g of *n*-decane with b.p. 172–173°/743 mm; n_D^{20} 1.4122; d_4^{20} 0.7302, which is very close to the literature data (^{6}).

Table 3

Results of spectral analysis of the paraffin-naphthenic fractions of cyclodecane catalyzate (310°)

	1	2	3	4	5	6
n-Decane	++	+	–	–	–	
2-Methylnonane	+	–	–	–	–	–
1,2-Diethylcyclohexane	+	++	+	?	–	–
trans-Decalin	+	++	++	+	–	–
Decahydroazulene	–	Traces	+	++	++	+
Unknown hydrocarbon	–	+	++	+++	++	+
Cyclodecane	–	–	Traces	+	++	+

Note. The number of crosses does not reflect the quantitative composition of the fractions, but is only a measure of the relative content of the given hydrocarbon in neighboring fractions.

Investigation of the composition of the fractions by means of combination-scattering spectra. The method used has already been described ([7,8]). Most of the spectra of individual hydrocarbons used for identification of the components of the fractions were taken from the cited monograph ([8]), and the refined spectrum of *o*-diethylbenzene from the catalog of the American Petroleum Institute ([9]). The spectra of cyclodecane, α-methylindane, and cis-decahydroazulene were obtained by us and will be published elsewhere. To interpret the spectra of the frac-

…could not be fully carried out because of the presence of lines whose assignment is unknown. In some cases it was possible to indicate a series of lines whose intensities from fraction to fraction first increase and then decrease. One set of such lines in the spectra of the paraffin–naphthenic fractions

$$393(3), 419(4), 448(4), 487(5), 528(5), 561(4), 580(5), 751(7), 780(5), 828(2), 847(6), 995(4), 1026(4), 1035(4), 1083$$

was assigned to 1,2-diethylcyclohexanes, which was confirmed by dehydrogenation of the combined fractions 3–5, leading to the appearance of intense lines of *o*-diethylbenzene. It is nevertheless not excluded that some of these lines belong to other hydrocarbons.

Another series of bright lines

$$421(3), 473(8), 906(7)$$

was found in the spectra of the paraffin–naphthenic fractions of the catalyzate obtained at 310°, and also in the aromatic fractions from experiments at 300°, which were not subjected to chromatography (see above). It is possible that these lines belong to the spectrum of trans-decahydroazulene or 8-methylhydrindane. The results of the analysis—quantitative or semiquantitative—are summarized in Tables 3 and 4; the composition of the paraffin-naphthenic part of the catalyzate obtained at 300° differs little from that given in Table 3 and is not presented separately.

Table 4

Results of spectral analysis of fractions of the aromatic part of the cyclodecane catalyzate (300°) (content is given in weight percent per fraction)

Hydrocarbon		2	3	4	5	6	7	8	9	10	11
n-Butylbenzene*	5-10	~5	25	20	20	15	10	5	—	—	—

Hydrocarbon		2	3	4	5	6	7	8	9	10	11
1-Methyl-2-ethylbenzene	55	10	–	–	–	–	–	–	–	–	–
1,2-Diethylbenzene	–	10	40	75	80	85	90	95	Present	–	–
Indane	35	50	15	–	–	–	–	–	–	–	–
α-Methylindane	–	–	–	–	–	–	–	–	+	++	+
Trans-decalin**	–	25	20	5	–	–	–	–	–	–	–
Decahydroazulene**	–	–	–	–	–	–	–	–	+	++	+
Unknown hydrocarbon**	–	–	–	–	–	–	–	–	+	++	+

* In the first fraction the presence of *n*-propylbenzene is possible.
** As noted above, the aromatic fractions were not chromatographed, and some of the bicyclanes entered them during fractionation.

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