CHEMISTRY

S. I. KHROMOV, E. S. BALENKOVA, O. E. LISHENOK

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

S. I. KHROMOV, E. S. BALENKOVA, O. E. LISHENOK
and Academician B. A. KAZANSKII

CATALYTIC TRANSFORMATIONS OF CYCLO ONANE IN THE PRESENCE OF PLATINIZED CHARCOAL

In studying the behavior of polymethylenes with an average ring size under conditions of catalytic dehydrogenation over platinized charcoal at 300–310°, we showed that over platinum these hydrocarbons undergo transformations different from those observed by Prelog and co-workers in the catalysis of these hydrocarbons in the presence of palladized charcoal at 400° (^1).

Over platinum, cyclooctane is converted mainly into cis-bicyclo-(0,3,3)-octane (^2). The behavior of cyclooctane in the presence of palladium was not studied by Prelog. Over platinized charcoal, cyclodecane undergoes direct hydrogenolysis, as a result of which *n*-decane is formed, C5-dehydrocyclization with the formation of perhydroazulene, and C6-dehydrocyclization, which leads to trans-decalin and naphthalene (^3). The fact of direct hydrogenolysis of a ten-membered ring attracted attention, since until now it had been known that direct ring opening in the presence of platinum occurs only with three-, four-, and five-membered polymethylenes.

It was of interest to determine what transformations cyclononane would undergo under analogous experimental conditions. The cyclononane synthesized for this purpose was passed over platinized charcoal at 300°. The liquid catalyzate was examined by careful fractionation on a highly efficient column, and its individual fractions were studied by spectroscopic methods and chemically.

The experimental data showed that the predominant amount of the cyclononane passed over the catalyst underwent transformation (~96%). In the reaction products were found ~68% indane, ~22% 1-methyl-2-ethylbenzene, ~2% *n*-propylbenzene, and ~7% *n*-nonane. The formation of indane, the main product of the catalytic transformations of cyclononane over platinized charcoal, can be explained by catalytic dehydrocyclization of cyclononane to hydrindane, which under the experimental conditions is then dehydrogenated to indane. The possibility of formation of a new bond within the nine-membered ring between the first and fifth carbon atoms is apparently associated with the spatial arrangement of the carbon atoms of the cyclononane molecule. The 1-methyl-2-ethylbenzene and *n*-propylbenzene detected in the catalyzate were obtained as a result of further transformations of indane. It is known (^4) that both indane and hydrindane, when passed over platinized charcoal at 330°, undergo hydrogenolysis of the five-membered ring and are converted into 1-methyl-2-ethylbenzene. The presence in the catalyzate of a certain amount of *n*-propylbenzene indicates that, during hydrogenolysis of the five-membered ring in indane, not only the carbon–carbon bond one carbon atom removed from the benzene ring is cleaved, but also the bond adjacent to the benzene ring, although to a lesser extent. The *n*-nonane found in the catalyzate testifies

···indicates that cyclononane, like cyclodecane, is capable of undergoing direct cleavage of a carbon–carbon bond in the presence of a platinum catalyst.

Thus, in the catalytic transformations of cyclononane over platinum, two main processes occur: first, dehydrocyclization of cyclononane to hydrindane, which under the experimental conditions is dehydrogenated to indane; second, direct hydrogenolysis of the nine-membered ring, as a result of which *n*-nonane is formed.

The catalytic transformations of cyclononane proceed according to the scheme:

$$\text{cyclononane} \xrightarrow[-H_2]{} \text{[bicyclic hydrocarbon]} \xrightarrow[-H_2]{} \text{hydrindane} \xrightarrow[-H_2]{} \left\{\begin{array}{l}\text{indane,}\\ \text{methylcyclohexane derivative}\end{array}\right. \qquad \text{and}$$

Experimental Part

1. Synthesis of cyclononane was carried out according to the scheme:

$$\text{dimethyl azelate} \xrightarrow[\text{Na}]{} \text{cyclononanolone-2} \xrightarrow[\text{Zn/HCl}]{} \text{cyclononanone} \xrightarrow[NH_2NH_2]{} \text{cyclononane}$$

Cyclononanolone-2. From azelaic acid and absolute methanol, dimethyl azelate was prepared in a yield of 78.8% of theory, with b.p. 149–150.5° (16 mm); d_4^{20}1.0079; n_D^{20}1.4370. Literature data (5): b.p. 142–150° (10 mm); n_D^{20}1.4350–1.4363.

The cyclization of dimethyl azelate was carried out in an atmosphere of dry nitrogen freed from traces of oxygen, with effective stirring by a mechanical stirrer (giving up to 7000 rpm). Into the reaction were taken 139 g (0.64 mole) of dimethyl azelate in 80 ml of dry xylene and 60 g of metallic sodium in 1400 ml of xylene. The reaction was continued at 130–135° for 10 hours.

41.6 g of cyclononanolone-2 was obtained, with b.p. 88–92° (6 mm); yield 41.6% of theory. On recrystallization from ligroin, pale-yellow crystals of the ketol alcohol were obtained, with m.p. 42°. Literature data (6): b.p. 110–124° (12 mm); m.p. 43°.

Cyclononanone. To 40 g (0.25 mole) of cyclononanolone-2 dissolved in 100 ml of CH_3COOH, with stirring, were added 100 g of zinc dust and 100 ml of chemically pure conc. HCl. The reaction mixture was heated to 100-105°, and to it 100 ml portions of HCl were added three times at half-hour intervals. After cooling, the mixture was strongly diluted with saturated NaCl solution and extracted with ether. The ether solution was washed and dried over magnesium sulfate. The ether was distilled off, and the reduction product was distilled in vacuo. 26 g of cyclononanone was obtained, with b.p. 77-78° (7 mm); m.p. 34.5-35.0°. Yield 74.3% of theory. Literature data (6): b.p. 92-95° (12 mm).

Cyclononane. From 140 g (1 mole) of cyclononanone and 166.9 g (3 moles) of 90% hydrazine hydrate in 280 ml of ethyl alcohol, 153.6 g of cyclononanone hydrazone was obtained. Yield 99.7% of theory. Decomposition of the hydrazone was carried out in diethylene glycol in the presence of KOH at 200-210°. The hydrocarbon was chromatographed on silica gel and distilled in vacuo on a column of 80 theoretical plates. 95.5 g of cyclononane was obtained. Yield,

75% of theory. Cyclononane had: b.p. 68.5° (20 mm); n_D^{20} 1.4665; d_4^{20} 0.8499. Crystallization temperature 10.1°. Degree of purity: 99.7 mol. %. Literature data (7): b.p. 178.44° (760 mm); n_D^{20} 1.46663; d_4^{20} 0.8502.

2. Catalytic transformations of cyclononane. 163.8 g of cyclononane were passed over 5% platinized charcoal (without a carrier gas), at a space velocity of 0.2. 150.6 g of liquid catalyzate with n_D^{20} 1.5150 and 96670 ml of gas were obtained. Gas analysis showed that it consisted only of hydrogen.

Investigation of the liquid catalyzate. The catalyzate was distilled on a column with an efficiency of 80 theoretical plates. The results of the distillation are presented in Table 1 and in Fig. 1.

Table 1

Fraction No.	Boiling limits at 752 mm	Fraction content, g	Fraction content, %	n_D^{20}	d_4^{20}
1	134.5—150.0	3.9	2.6	1.4250	0.7209
2	150.0—152.1	3.2	2.2	1.4270	0.7228
3	152.1—159.0	2.6	1.8	1.4460	0.7340
4	159.0—163.5	9.9	6.6	1.4910	0.8649
5	163.5—169.5	26.9	18.1	1.5020	0.8798
6	169.5—174.5	6.3	4.2	1.5030	0.8981
7	174.5—177.5	87.4	58.7	1.5386	0.9635
8	Residue	8.6	5.8	1.5395	0.9646

Fig. 1. Distillation curve of the cyclononane catalyzate

Figure 1: Fig. 1. Distillation curve of the cyclononane catalyzate

Fraction No.	Boiling limits at 752 mm	Fraction content, g	Fraction content, %	n_D^{20}	d_4^{20}
	Total . . .	148.8			

The 1st, 2nd, and 3rd fractions were combined and chromatographed on silica gel, as a result of which 8.1 g of dearomatized substance with n_D^{20} 1.4165 was obtained. On treating it with a methanolic solution of urea, a crystalline complex was obtained, which decomposes with distilled water. The hydrocarbon layer was separated, dried, and distilled. 5.2 g of hydrocarbon was obtained with b.p. 150–151° (757 mm); n_D^{20} 1.4058; d_4^{20} 0.7175. Comparison of the constants of this hydrocarbon with the literature data for *n*-nonane showed that the hydrocarbon was very pure *n*-nonane. Literature data for *n*-nonane (8): b.p. 150.798° (760 mm); n_D^{20} 1.40542; d_4^{20} 0.71763.

Fig. 1. Distillation curve of the cyclononane catalyzate

4th fraction (b.p. 159.0–163.5°). Upon oxidation of a small amount of this fraction with an aqueous solution of potassium permanganate (9), benzoic and *o*-phthalic acids were obtained. On the basis of the constants of the 4th fraction and the results of the analysis it may be concluded that it consists mainly of *n*-propylbenzene and 1-methyl-2-ethylbenzene.

5th fraction (b.p. 163.5–169.5°), upon oxidation, gave *o*-phthalic acid. Comparison of the oxidation results and the constants of this fraction shows that it is mainly 1-methyl-2-ethylbenzene.

6th fraction (b.p. 169.5-174.5°). As can be seen from the catalyst distillation curve (see Fig. 1), this fraction is intermediate and consists of a mixture of 1-methyl-2-ethylbenzene, contained in the 5th fraction, and indane, constituting the 7th fraction.

7th fraction (b.p. 174-177.5°) and the residue from fractionation, as indicated by the constants, represent fairly pure indane. Literature data for indane (10): b.p. 177.5-178.5°; n_D^{20} 1.5383; d_4^{20} 0.9639. Indane was identified in the form of 1,2,3-tribromoindane (11). On bromination of a small amount of the 7th fraction in boiling chloroform, a crystalline bromide was obtained which, after recrystallization from alcohol, melted at 134°. A mixed melting-point test with bromide from known pure indane gave no depression.

In addition, the composition of fractions 4-7 was established by studying their spectra of combinational light scattering*. The results of the spectral study are presented in Table 2.

Table 2

Hydrocarbons included in the fractions	Fraction No. 4, wt. %	Fraction No. 5, wt. %	Fraction No. 6, wt. %	Fraction No. 7, wt. %	Residue, wt. %
n-Propylbenzene	15	5	–	–	–
1-Methyl-2-ethylbenzene	75	75	50	+	–
Indane	3	15	30	95	100
Cyclononane	–	–	20	5	–
Paraffins, monocyclic naphthenes (?)	7	5	–	–	–

On the basis of the results of fractionation and of chemical and optical investigations of the fractions, the approximate composition of the transformed portion of the cyclononane catalyst was calculated.

Moscow State University
named after M. V. Lomonosov

Received
28 VII 1960

REFERENCES CITED

1. V. Prelog, V. Boarland, S. Polyak, *Helv. chim. Acta*, **38**, 434 (1955).
2. E. A. Shokova, S. I. Khromov, V. T. Aleksanyan, Kh. E. Sterin, B. A. Kazanskii, DAN, **133**, No. 5 (1960).
3. B. A. Kazanskii, S. I. Khromov, A. L. Liberman, E. S. Balenkova, T. V. Vasina, V. T. Aleksanyan, Kh. E. Sterin, DAN, **135**, No. 2, 76 (1960).
4. M. B. Turova-Polyak, ZhOKh, **6**, 947 (1936).

5. H. Brown, M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).
6. V. Prelog, L. Frenkiel, M. Kobelt, P. Borman, *Helv. chim. Acta*, **30**, 1822 (1947).
7. S. Kaarsemaker, J. Coops, *Rec. trav. chim.*, **71**, 261 (1952).
8. F. Rossini *et al.*, *Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Pittsburgh, 1953.
9. B. L. Moldavskii, G. D. Kamusher, M. V. Kobylskaya, ZhOKh, **7**, 167 (1937).
10. E. Evans, *J. Inst. Petrol.*, **24**, 537 (1938).
11. R. Meyer, W. Meyer, *Ber.*, **51**, 1581 (1918).

* The spectra were studied by Kh. E. Sterin and V. T. Aleksanyan in the laboratory of the Spectroscopy Commission of the Academy of Sciences of the USSR; we express our gratitude to them.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.