Academician B. A. KAZANSKII, E. A. LYUKOVA, S. I. KHROMOV,

V. T. ALEKSANYAN, and Kh. E. STERIN

1960

SovietRxiv

conformational formulas of cyclooctane labeled (I) and (II)

Figure 1: conformational formulas of cyclooctane labeled (I) and (II)

Abstract

Full Text

Academician B. A. KAZANSKII, E. A. LYUKOVA, S. I. KHROMOV,
V. T. ALEKSANYAN, and Kh. E. STERIN

CONTACT TRANSFORMATIONS OF CYCLOOCTANE IN THE PRESENCE OF PLATINIZED CARBON

In their studies on the manifestation of the transannular effect in polymethylenes with a medium ring size under conditions of catalytic dehydrogenation (5% Pd on carbon at 400°), Prelog and co-workers observed transformations of hydrocarbons of composition C_9—C_{18} (1). In this process, depending on the number of carbon atoms in the ring, various polycyclic—aromatic and pseudoaromatic—hydrocarbons are obtained with elimination of hydrogen (indene, azulene, naphthalene, fluorene, phenanthrene, etc., up to triphenylene).

Bearing in mind that platinum is a more active catalyst for dehydrocyclization than palladium (2), and that in a number of cases products of dehydrocyclization of nonaromatic character can also be obtained in the presence of platinum, we decided to see how polymethylenes with medium rings would behave in the presence of platinized carbon and at lower temperatures than those cited in Prelog' s works. It also seemed of interest to us to repeat, in essence, the unfinished work of N. D. Zelinskii and G. M. Freiman (3), in which they came to the conclusion that at 300° in the presence of platinized carbon, bicyclo-(0,3,3)-octane and methylcycloheptane are obtained from cyclooctane, although, however, they gave no experimental confirmation of such a course of the reaction. As noted above, in Prelog' s works cyclooctane does not figure as an object of investigation.

According to modern conformational concepts, cyclooctane can exist chiefly in two most stable forms: the "crown" (I) and the "boat" (II) (4):

The latter is apparently energetically much less favorable than the former, and therefore its relative content in cyclooctane must be very small. In the centrosymmetric form (I), four equatorial hydrogens are situated above the mean plane of the ring and four below it; they approach one another very closely, which is clearly seen on the Briegleb-Stuart model. Upon the elimination of any pair of them in the 1,5 position, a transannular C—C bond may arise with formation of cis-bicyclo-(0,3,3)-octane (cis-pentalane).

In the present work, transformations of cyclooctane on platinized carbon at 310° were investigated in the absence and in the presence of hydrogen. In both cases a quantitative transformation of cyclooctane was observed. In the absence of hydrogen the main reaction product was cis-bicyclo-(0,3,3)-octane (cis-pentalane), amounting to ~51% by weight of the catalyst. In appreciable

trans-1-Methyl-2-ethylcyclopentane (~23%) and *n*-propylcyclopentane (~20%) were also found in comparable amounts; 4-methylheptane was formed in a smaller amount (~6%); a very small amount of aromatic hydrocarbons was also detected in the catalyzate. These reaction products give grounds to suppose that it proceeds according to the following scheme:

$$\text{cyclooctane} \xrightarrow{-H_2} \text{cis-pentalane} \xrightarrow{+H_2} \begin{cases} \text{trans-1-methyl-2-ethylcyclopentane,} \\ n\text{-propylcyclopentane} \end{cases} \xrightarrow{+H_2} \text{4-methylheptane.}$$

Thus, the first stage is apparently the formation of cis-pentalane, which then undergoes hydrogenolysis at the expense of the hydrogen liberated during its formation, giving trans-1-methyl-2-ethylcyclopentane and *n*-propylcyclopentane; hydrogenolysis of the latter leads to 4-methylheptane.

In the presence of hydrogen the same substances were obtained, but in different ratios: only ~6% cis-pentalane, ~15% trans-1-methyl-2-ethylcyclopentane, ~37% cis-1-methyl-2-ethylcyclopentane, and only 2-3% *n*-propylcyclopentane. Such ratios are explained by the fact that, in the presence of hydrogen, hydrogenolysis of the five-membered ring naturally proceeds much more intensely, and pentalane and *n*-propylcyclopentane undergo hydrogenolysis more readily than 1-methyl-2-ethylcyclopentane. Confirmation of this is the presence in the catalyzate of a considerable amount of 4-methylheptane (~33%)—the product of hydrogenolysis of *n*-propylcyclopentane. Methylcyclopentane, to which N. D. Zelinsky and G. M. Freiman referred, was not found in the reaction products.

A small amount (~1-2%) of aromatic hydrocarbons (toluene, ethylbenzene, and *o*-xylene) was also formed.

All the hydrocarbons listed were identified mainly by studying the Raman spectra of the fractions obtained by distillation of the catalyzate on an efficient column. The aromatic hydrocarbons were isolated by chromatography on silica gel.

Experimental Part

The cyclooctane used in the present work was obtained according to the following scheme:

$$\text{cyclohexanone} \xrightarrow[(5)]{\mathrm{CH_2N_2}} \text{cycloheptanone} \xrightarrow[(5)]{\mathrm{CH_2N_2}} \text{cyclooctanone} \xrightarrow[(6)]{\mathrm{NH_2NH_2}} \text{cyclooctanone hydrazone} \xrightarrow[(7)]{\mathrm{KOH}} \text{cyclooct}$$

and had the following constants: b.p. 149.5°/745 mm; n_D^{20} 1.4592; d_4^{20} 0.8369. Literature data (8): b.p. 150.70°/760 mm; n_D^{20} 1.45851; d_4^{20} 0.8362.

Contact transformations of cyclooctane without carrier gas. A quartz tube was charged with 63 ml (16.6 g) of 5% platinized charcoal, prepared by the method of N. D. Zelinsky (2), which showed high activity in the dehydrogenation of cyclohexane. Over the catalyst, 44.5 g (0.4 mole) of cyclooctane was passed at 310° with a space velocity of 0.2. The results of the experiments are presented below:

Run	n_D^{20}	Amount of evolved gas, ml	Weight of catalyst, g
1	1.4435	5883	40.74
2	1.4435	850	38.18
Total	–	6733	38.18

The gaseous products were analyzed on a VTI apparatus. Results of the analysis: H_2 99.4%; $C_{nH_{2n+2}}$ 0.6%.

Study of the catalyzate. To separate the paraffin-naphthene hydrocarbons from the aromatic hydrocarbons (the presence of which was detected by means of the formalite reaction), the catalyzate was subjected to chromatography on silica gel, after which it was fractionated on a column of 60 theoretical plates. The results of the distillation are presented in Table 1.

Table 1

Fraction No.	Boiling limits at 745 mm	n_D^{20}	d_4^{20}	Amount, g
1	114–120	1.4173	0.7541	2.78
2	120–125.5	1.4216	0.7689	7.03
3	125.5–129.5	1.4260	0.7776	2.30
4	129.5–132	1.4334	0.7952	2.23
5	132–134.5	1.4431	0.8220	3.08
6	134.5–135.5	1.4538	0.8495	6.10
7	135.5–136	1.4595	0.8635	4.35
8	Residue	1.4603	0.8608	6.00
Total	–	–	–	33.87

The aromatic part of the catalyzate, which had n_D^{20} 1.4920, could not be studied because of its extremely small amount (less than 0.1 g). The composition of fractions 1–8 was established by studying their spectra of combinational light scattering. The results of the spectral study are presented in Table 2.

Table 2

Hydrocarbons constituting the fractions	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 6	Fraction 7	Fraction 8	Total in catalyzate, g	Total in catalyzate, wt.%
4-Methylheptane	20	20	5	–	–	–	–	–	2	6
n-Propylcyclopentane	–	10	40	65	50	30	10	–	7	20
Trans-1-methyl-2-ethylcyclopentane	70	60	40	10	–	–	–	–	8	23
Cis-bicyclo-(0,3,3)-octane	7	10	15	25	Main content of the fraction	Main content of the fraction	Main content of the fraction	Main content of the fraction	17	53

Contact transformations of cyclooctane in the presence of hydrogen. The experiments were carried out under conditions analogous to those described above. For catalysis, 20.7 g of cyclooctane was taken. The results of the experiments are given below.

Run	n_D^{20}	Amount of catalyzate, g
1	1.4260	14.80
2	1.4150	13.91

Study of the catalyzate. The catalyzate (13.9 g) was subjected to rectification on a column of 60 theoretical plates. The distillation results are presented in Table 3.

Table 3

Fraction no.	Boiling limits at 736 mm	n_D^{20}	d_4^{20}	Weight, g	Weight, %
1	98.5–113.9	1.4110	0.7336	1.10	7.9
2	114.0–118.5	1.4072	0.7227	3.32	23.8
3	118.5–121.5	1.4120	0.7435	5.37	38.6
4	121.5–126.5	1.4189	0.7602	2.20	15.8
5	Residue	1.4412	0.7995	1.92	13.8

The composition of all fractions was established by studying their combination-scattering spectra. The results of the spectral investigation are presented in Table 4.

Table 4

Hydrocarbons included in the fractions	Fraction no. 1+2, hydrocarbon content, wt.%	Fraction no. 3, hydrocarbon content, wt.%	Fraction no. 4, hydrocarbon content, wt.%	Fraction no. 5, hydrocarbon content, wt.%	Total in catalyzate, g	Total in catalyzate, wt.%
4-Methylheptane	70	30	–	–	4.5	33
n-Propylcyclopentane	–	–	–	20	0.4	3
trans-1-Methyl-2-ethylcyclopentane	10	70	40	–	5.1	37
cis-1-Methyl-2-ethylcyclopentane	–	+	50	50	2.1	15
cis-Bicyclo-(0,3,3)-octane	–	–	+	20	0.4	3
Toluene	2	–	–	–	0.08	0.6
Ethylbenzene	–	–	2	+	0.04	0.3

Hydrocarbons included in the fractions	Fraction no. 1+2, hydrocarbon content, wt.%	Fraction no. 3, hydrocarbon content, wt.%	Fraction no. 4, hydrocarbon content, wt.%	Fraction no. 5, hydrocarbon content, wt.%	Total in catalyzate, g	Total in catalyzate, wt.%
o-Xylene	–	–	+	10	0.19	1.4

The method of obtaining and measuring combination-scattering spectra used in the present work is described in detail in the monograph by G. S. Landsberg, B. A. Kazanskii, et al. (9). The intensities of the lines were estimated visually. Most of the spectra of individual hydrocarbons used in analyzing the composition of the fractions were taken from the same monograph. The spectra of the cis- and trans-isomers of 1-methyl-2-ethylcyclopentane were taken from the work of B. A. Kazanskii, A. L. Liberman, et al. (10), and the spectrum of cis-pentalane from the work of the same authors (11). The relative content of the components in each fraction was estimated by visual comparison of the intensities of the lines in its spectrum.

Moscow State University
named after M. V. Lomonosov

Commission on Spectroscopy
Academy of Sciences of the USSR

Received
11 V 1960

CITED LITERATURE

1. V. Prelog, V. Boarland, S. Polyak, Helv. chim. acta, **38**, 434 (1955).
2. N. D. Zelinskii, M. B. Turova-Polyak, Selected Works of Academician N. D. Zelinskii, 2, Publ. House of the Academy of Sciences of the USSR, 1941, p. 150.
3. N. D. Zelinskii, G. M. Freiman, Ber., **63**, 1487 (1903).
4. N. L. Allinger, J. Am. Chem. Soc., **81**, 5727 (1959).
5. E. Mosettig, A. Burger, J. Am. Chem. Soc., **52**, 3456 (1935).
6. M. B. Turova-Polyak, K. Yu. Novitskii, ZhOKh, **14**, 337 (1944).

7. Huang-Minlon, J. Am. Chem. Soc., **68**, 2487 (1946).

8. S. Kaarsemaker, J. Coops, Rec. trav. chim., **71**, 261 (1952).

9. G. S. Landsberg, B. A. Kazanskii, et al., *Determination of the Individual Composition of Straight-Run Gasolines*, Publ. House of the Academy of Sciences of the USSR, 1959.

10. B. A. Kazanskii, A. L. Liberman, et al., Izv. AN SSSR, OKhN, 1959, no. 6, 1071.

11. B. A. Kazanskii, A. L. Liberman, et al., DAN, **133**, no. 2 (1960).

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