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Abstract

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C_5-DEHYDROCYCLIZATION OF ALKYLCYCLOPENTANES INTO BICYCLIC HYDROCARBONS

Recently we published (¹) a detailed investigation of the C_5-dehydrocyclization of *n*-octane in the presence of platinized carbon. In that work it was shown that *n*-octane, on cyclization, gives the expected *n*-propyl- and 1-methyl-2-ethylcyclopentanes in approximately equal amounts, but with a small total yield (2.2–4.5%). In addition, it was noted that the catalyst contained some other cyclization product of saturated character. Indeed, in the combination-scattering spectrum of the residue obtained on distillation of the catalyst, after preliminary removal of a small admixture of unsaturated and aromatic compounds, an intense line at 762 cm^{-1}* was found; this line could not be assigned to any paraffinic or cyclopentane hydrocarbon with eight carbon atoms in the molecule. It was then suggested that this line belonged to pentalane, which could have been formed from *n*-propylcyclopentane or from 1-methyl-2-ethylcyclopentane as a result of secondary C_5-dehydrocyclization:

$$\begin{tikzcd}
& \mathrm{CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3} \arrow[dl] \arrow[dr] & \\
(n\text{-propylcyclopentane}) \arrow[dr] & & (\text{1-methyl-2-ethylcyclopentane}) \arrow[dl] \\
& \text{pentalane} &
\end{tikzcd}$$

This was also consistent with the fact that in the spectra of catalysts obtained by an analogous route from *n*-propylcyclopentane, the named line was likewise present. However, the spectra of cis- and trans-pentalanes were at that time unknown, and it was impossible to confirm the proposed assumption without synthesizing these hydrocarbons. Since the C_5-dehydrocyclization of paraffins or alkylcyclopentanes into bicyclic hydrocarbons had previously been observed by no one, we considered it expedient to carry out such a synthesis. This was of still greater interest because pentalane and methylpentalane had recently been found in petroleum (²), and therefore proof of the fundamental possibility of the reaction under consideration would make it possible to judge the possible routes of their formation in petroleum.

In the present work we confined ourselves to the synthesis and study of the combination-scattering spectrum of only one of the stereoisomeric pentalanes —its cis form. However, it turned out that precisely this was needed for our purposes—hydrocarbon, since not only the line at 764 cm^{-1}, but also some other previously unassigned lines in the spectrum of the above-mentioned catalyst fraction from *n*-octane belong to it. Thus, the question of the possibility of catalytic C_5-dehydrocyclization of paraffins and alkylcyclopentanes to pentalanes is undoubtedly answered in the affirmative.

The relatively large yield of pentalane from *n*-octane (0.25% of the catalyzate) is noteworthy, although it is a secondary product of the conversion of cyclopentanes, which themselves are obtained in low yield. Recalculated on the cyclopentanes formed, the yield of pentalane is $\sim$ 5%. This seems especially remarkable in comparison with the very low yield of pentalane from individual *n*-propylcyclopentane under comparable conditions: $\sim$ 1% at 310°; even at 320 and 330° only $\sim$ 1.5% pentalane is formed. This suggests that the main source of pentalane in the cyclization products of *n*-octane is 1-methyl-2-ethylcyclopentane, which may cyclize considerably faster than *n*-propylcyclopentane.

Experimental Part

cis-Pentalane was obtained according to a scheme similar to that developed by Fossen[3], and purified by distillation on a column with an efficiency of 100 theoretical plates. It had the following properties: b.p. 138.5°/760 mm; n_D^{20} 1.4625; d_4^{20} 0.8693. According to the literature data[4], the properties of cis-pentalane are as follows: b.p. 136°/755 mm; n_D^{18} 1.4629; d_4^{18} 0.8718.

The **spectrum of cis-pentalane** was obtained and measured by the procedure described earlier[5].

$\Delta\nu$ (cm^{-1}) : 194(6, sh), 288(2), 313(0), 334(1), 352(1), 388(9), 432(1), 470(1), 513(5), 532(8), 541(8), 585(12), 600(2), 617(2), 638(1), 727(2), 764(100), 815(1), 828(20), 856(3), 874(5, sh), 900(74), 912(15), 946(12), 1009(35), 1034(23), 1050(30), 1073(2), 1126(10), 1169(12), 1187(10), 1223(15), 1249(3, sh), 1275(6), 1294(10), 1310(18), 1335(5), 1447(76, sh), 1474(15), 2859(320), 2901(200, sh), 2922(100, ph), 2937(350, ph), 2954(450, ph).

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* In more precise measurements, 764 cm^{-1}.

Pentalane content in the *n*-octane catalyzate. The residue from the distillation of the catalyzate obtained earlier[1] was quantitatively analyzed from its combination-scattering spectrum[6]. Found: *n*-octane 30%, *n*-propylcyclopentane 55%, and cis-pentalane 15%. Thus, recalculated to the total catalyzate, the yield of pentalane from *n*-octane is 0.25%, since the residue amounted to 1.7% of the catalyzate.

Table 1

Results of experiments on C_5-dehydrocyclization of *n*-propylcyclopentane to pentalane

Experiment no.	Temp., °C	*n*-Propylcyclopentane passed, g	Catalyzate collected, g	n_D^{20} of catalyzate before chromatography	n_D^{20} of catalyzate after chromatography	Content of unsaturated compounds by bromine number, %	Aromatics content, %	Taken for distillation, g	Residue, g	n_D^{20} of residue	Pentalane yield, %
1	310	30.8	28.4	1.4261	1.4257	2.7	~ 0.2	18.0	2.15	1.4293	~ 1
2	320	39.3	33.4	1.4272	1.4263	Not determined	Not determined	29.7	3.2	1.4314	~ 1.5
3	330	38.7	37.4	1.4274	1.4262	6.9	~ 0.4	32.5	3.4	1.4303	~ 1.5

Cyclization of *n*-propylcyclopentane to pentalane. *n*-Propylcyclopentane, distilled on a column with an efficiency of 100 theoretical plates and having b.p. 130.9°/760 mm; n_D^{20} 1.4264 and d_4^{20} 0.7765, was passed over platinized carbon at a space velocity of 0.2 h^{-1} at temperatures of 310, 320, and 330°. Each experiment was carried out on a freshly prepared portion of catalyst. The content of unsaturated compounds was determined by

the bromine number, and the content of aromatics from the change in refractive index during chromatography on silica gel (taking into account the indeterminate components). The chromatographed catalyzate was then fractionated on columns with an efficiency of 50 theoretical plates to separate most of the unreacted *n*-propylcyclopentane and the products of its hydrogenolysis—paraffinic hydrocarbons; the cis-pentalane content in the residue was determined refractometrically. The presence in the spectra of such residues of the line characteristic of cis-pentalane at 762 cm^{-1} had been shown earlier[1]. The experimental results are summarized in Table 1.

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REFERENCES

1. B. A. Kazansky, A. L. Liberman et al., *Izv. AN SSSR, OKhN*, **1959**, 1071.
2. B. J. Mair, P. E. Eberly et al., *Anal. Chem.*, **30**, No. 3, 393 (1958).
3. G. Vossen, Inaugural-Dissertation, Bonn, 1910. See also G. Schroeter, *Ann.*, **426**, 1 (1922).
4. J. W. Barrett, R. P. Linstead, *J. Chem. Soc.*, **1935**, 436.
5. B. T. Aleksanyan, Kh. E. Sterin, *Optics and Spectroscopy*, **2**, 562 (1957).
6. G. S. Landsberg, B. A. Kazansky et al., *Determination of the Individual Hydrocarbon Composition of Straight-Run Gasolines by a Combined Method*, Publishing House of the Academy of Sciences of the USSR, 1959.

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