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1964

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Abstract

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MUTUAL TRANSFORMATIONS OF STEREOISOMERIC 1,3-DIMETHYLCYCLOPENTANES DURING ANALYTICAL DEHYDROGENATION

(Presented by Academician B. A. Kazanskii, June 9, 1964)

Dehydrogenation of hexamethylene hydrocarbons according to N. D. Zelinskii is widely used in the detailed analysis of hydrocarbons of gasoline fractions ($^{1-3}$).

The reliability of analytical data obtained by this method depends on the selectivity of the process and on the suppression or allowance for possible side reactions. The principal side reaction—hydrogenolysis of pentamethylene rings—is known to be suppressed by adding iron to platinized carbon (^{1}). Dehydrocyclization of paraffin hydrocarbons under the conditions recommended for analysis proceeds to a very slight extent. However, the mutual transformations of stereoisomeric cyclopentanes had not been taken into account, although as early as 1948 B. A. Kazanskii and co-workers (^{4}) pointed out their possibility. In a recent work by B. A. Kazanskii, A. L. Liberman, and co-workers (^{5}), it was proved that an isomerization reaction of cis- and trans-1,2-dimethylcyclopentanes takes place over a platinum catalyst. At the same time, the rate of mutual conversion of the cis and trans forms "considerably exceeds the rate of hydrogenolysis," and the resulting mixture is close in composition to the thermodynamically equilibrium mixture for the corresponding temperature.

We carried out a detailed study of the chemistry of transformations of bicyclic hydrocarbons under conditions of destructive hydrogenation, which required extensive use of analytical dehydrogenation. During dehydrogenation of fractions boiling within the range 88—92°, we also found mutual transformation of cis- and trans-1,3-dimethylcyclopentanes. These transformations are demonstrated qualitatively by comparing chromatograms of the fractions before and after dehydrogenation. Subsequent determination of the quantitative composition of the fractions and of their dehydrogenation products made it possible to estimate, with an accuracy of 3–5%, the extent of isomerization of cis- and trans-1,3-dimethylcyclopentanes.

Experimental Part

The fractions were obtained by sharp rectification of 15 liters of a dearomatized hydrogenate of bicyclic hydrocarbons on a column with an efficiency of 58 theoretical plates. Each fraction was collected within narrow limits. For detailed study, 5 such fractions were selected, each in an amount of 10-25 ml, in which either the cis or the trans isomer of 1,3-dimethylcyclopentane predominated (Table 1).

Table 1

Conditional designation of fractions	Boiling range, °C at 760 mm Hg	Specific gravity of fractions d_4^{20}	Refractive index n_D^{20} before dehydrogenation	Refractive index n_D^{20} after dehydrogenation
I	88.1	–	1.3978	1.3991
II	88.6—88.9	0.7104	1.3967	1.3975
III	89.3	–	1.3998	1.4006
IV	91.2—91.3	0.7282	1.4032	1.4058
V	91.2	0.7268	1.4035	1.4045

Fractions were dehydrogenated in a flow system over a catalyst containing 20% Pt and 2% Fe on carbon, at a temperature of 300°, in a weak stream of hydrogen with a space velocity of 0.8-0.9 h^{-1}.

Gas-liquid chromatography was carried out on a chromatographic apparatus consisting of a glass U-shaped column measuring 220 × 0.54 cm, a Scott micropulse hydrogen detector ([6]), and an EPP-09-2M electronic potentiometer with a 10 mV scale. Diisoamyl phthalate, deposited in an amount of 20% of the sorbent weight (diatomaceous brick), was used as the stationary liquid phase. Column temperatures were 60° and 70°; carrier-gas velocity (H_2) was 55 ml/min. The qualitative hydrocarbon composition was determined from physical constants and Raman spectra, and the quantitative composition mainly from the chromatograms. Figure 1 shows chromatograms of the fractions and their dehydrogenates.

In calculating the content of each component (Table 2), the normalization method ([7]) was used. Peak areas were measured with a planimeter. For incompletely separated peaks, the area was outlined by dropping a perpendicular from the point of inflection to the baseline. This procedure, of course, reduced the accuracy of the analysis; however, in study ([8]) it was shown that, with analogous processing of chromatograms, deviations were within 1-2% absolute from the true value. Since the content of cis-1,3-dimethylcyclopentane (see Table 2) varied within 7-33%, and that of the trans isomer within 7-37%, the relative error in most cases did not exceed 3-5%.

Table 2

Composition of the fractions (hydrocarbon content in wt. %)

No.	Hydrocarbons included in the fraction	I before dehydrogenation	I after dehydrogenation	II before dehydrogenation	II after dehydrogenation	III before dehydrogenation	III after dehydrogenation	IV before dehydrogenation	IV after dehydrogenation	V before dehydrogenation	V after dehydrogenation
1	2,3-Dimethylpentene	4.0	4.0	5.0	5.0	5.0	5.0	–	–	–	–
2	2-Methylhexane	32.0	32.0	35.2	34.9	21.5	21.2	10.0	9.8	1.5	1.4
3	3-Methylhexane	15.1	15.2	17.6	17.8	16.8	16.5	21.3	22.0	28.0	28.4
4	Cyclohexane	1.8	–	1.0	–	1.0	–	–	–	–	–
5	1,1-Dimethylcyclopentane	17.4	17.2	6.2	6.5	–	–	–	–	–	–
6	3-Ethylpentane	–	–	–	–	–	–	2.0	2.0	5.3	5.3
7	cis-1,3-Dimethylcyclopentane	21.4	13.3	25.7	15.2	33.0	19.9	24.0	23.3	6.8	9.6
8	trans-1,3-Dimethylcyclopentane	7.3	15.5	8.3	18.6	12.7	26.4	27.7	27.9	37.4	34.4
9	trans-1,2-Dimethylcyclopentane	1.0	0.8	1.0	0.8	10.0	7.9	12.0	9.5	20.0	15.4
11	cis-1,2-Dimethylcyclopentane	–	0.2	–	0.2	–	2.1	–	2.5	–	4.5
12	Methylcyclohexane	–	–	–	–	–	–	3.0	–	1.0	–
13	Benzene	–	1.8	–	1.0	–	1.0	–	–	–	–
14	Toluene	–	–	–	–	–	–	–	3.0	–	1.0

Because of the absence of samples of hydrocarbons whose presence was assumed in the fractions under study, the calibration method was not applied. But since it is known that, on nonselective stationary phases, hydrocarbons of one homologous series appear on the chromatogram according to their boiling points, and the spectral-analysis data made it possible to judge the hydrocarbons present in the fraction, interpretation of the chromatograms presented no particular difficulties.

Nevertheless, in order to verify the correctness of the adopted arrangement of the components on the chromatograms, fractions II and V were additionally

Fig. 1. Chromatograms of fractions before and after dehydrogenation

Figure 1: Fig. 1. Chromatograms of fractions before and after dehydrogenation

separated on a preparative gas-liquid chromatography column with the same stationary phase.

From fraction II there was isolated, as shown by the dotted line, the portion corresponding to peaks 1, 2; in its physical constants it corresponded to 85-90% 2-methylhexane (n_D^{20} 1.3861, d_4^{20} 0.6821)–this was confirmed by spectral analysis and the second component was shown to be 2,3-dimethylpentane. The sample corresponding to peak 3 (V) contained, as the main component (more than 93%), 3-methylhexane (n_D^{20} 1.3894; d_4^{20} 0.6890). Similarly, portions of the fractions corresponding to peaks 7 (fraction II) and 8, 9 (fraction V) were isolated and spectrally investigated; they proved to be, respectively,

Fig. 1. Chromatograms of fractions before and after dehydrogenation (with primes):
1 –2,3-dimethylpentane, **2** –2-methylhexane,
3 –3-methylhexane, **4** –cyclohexane, **5** –1,1-dimethylcyclopentane, **6** –3-ethylpentane, **7** –cis-1,3-dimethylcyclopentane,
8 –trans-1,3-dimethylcyclopentane, **9** –trans-1,2-dimethylcyclopentane, **11** –cis-1,2-dimethylcyclopentane

cis-1,3-dimethylcyclopentane (n_D^{20} 1.4097; d_4^{20} 0.7450) and a mixture of trans-1,2- and trans-1,3-dimethylcyclopentanes (n_D^{20} 1.4100; d_4^{20} 0.7478). Thus it was determined which hydrocarbons correspond to each peak. Among the 1,3-dimethylcyclopentanes the cis isomer appears first, since 1,3-dimethylcyclopentanes do not obey the Aue-Skita rule (9).

For an additional check on the correctness of determining the composition of the fractions from the chromatograms, the refractive indices and specific gravities of each fraction were calculated for the composition given in Table 2, assuming additivity of these quantities. The calculated refractive indices and specific gravities differed from the experimentally determined values (Table 1) by no more than 0.0004.

Comparing the chromatograms of the fractions and the chromatograms of the dehydrogenation products, it may be noted that the ratios between the magnitudes of peaks 1, 2 and 3 are preserved, i.e., the amounts of these components –paraffinic hydrocarbons–do not change. The amount of cyclohexane (Table 2, No. 4), which appears together with 3-methylhexane, is very small; therefore peak 3 (I′ and II′) decrea-

is unnoticeable. At the same time, in fractions I and II peak 7, corresponding to cis-1,3-dimethylcyclopentane, clearly decreases after dehydrogenation (see Fig. 1, I and I′, II and II′), whereas the indistinctly outlined inflection 8, 9 on the chromatograms of the dehydrogenates becomes a clear peak.

In these fractions trans-1,3-dimethylcyclopentane appears together with trans-1,2-dimethylcyclopentane (peaks 8, 9), but the content of the latter is small (1%), so that the change taking place applies only to trans-1,3-dimethylcyclopentane. An analogous redistribution of the amounts of the cis- and trans-1,3-dimethylcyclopentane isomers occurs in fraction III: before dehydrogenation the cis isomer appeared as a clear peak, while the mixture of the trans isomers of 1,2- and 1,3-dimethylpentanes appeared only as an inflection; after dehydrogenation (III′) they respectively give an inflection and a peak. In the next fraction (IV) the change is insignificant, i.e., the ratio of the isomers was practically preserved; while in fraction V, in which the trans isomer predominated, there is observed a certain decrease of its peak and a clearer manifestation of the inflection corresponding to the cis isomer, i.e., a reverse isomerization of the trans isomer into the cis isomer takes place.

It was of interest to determine whether the mutual transformations of cis- and trans-1,3-dimethylcyclopentanes reach equilibrium concentrations. The ratio of these concentrations (cis : trans) calculated from the data of (10) for the experimental temperature (300°) is 0.62. Table 3 gives the ratios of the isomer concentrations in the fractions studied.

Table 3

Fraction Nos.	cis : trans before dehydrogenation	cis : trans after dehydrogenation	Fraction Nos.	cis : trans before dehydrogenation	cis : trans after dehydrogenation
I	2.93	0.86	IV	0.87	0.84
II	3.10	0.82	V	0.19	0.28
III	2.60	0.75			

Thus, the conversion of cis-1,3-dimethylcyclopentane into the trans isomer proceeds up to concentrations close to equilibrium, while the reverse conversion occurs to a relatively small extent. However, the latter data may be underestimated because of mutual overlap of the peaks corresponding to cis- and trans-1,3-dimethylcyclopentanes, which makes an exact calculation difficult.

In Fig. 1 one can also trace the appearance of the peak of cis-1,2-dimethylcyclopentane in the fractions after dehydrogenation. Consequently, conversion into the cis form of trans-1,2-dimethylcyclopentane takes place; the content of the latter in fractions III, IV, and V is considerable.

Received
6 VI 1964

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