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Abstract

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SYNTHESIS OF 1,2-DIALKYLCYCLOPENTANES AND THEIR SEPARATION INTO CIS- AND TRANS-ISOMERS

(Presented by Academician B. A. Kazanskii, July 14, 1958)

A study of the chemical composition of gasolines has shown that most of them contain a significant amount of cyclopentane hydrocarbons. As for the ligroin-kerosene fractions, the nature of the hydrocarbons contained in them has been insufficiently studied, and the structure of the cyclopentane hydrocarbons has been almost entirely uninvestigated. In recent years, however, the question of studying the hydrocarbon composition of ligroins and kerosenes has become especially urgent in connection with the importance they have acquired as fuels for jet engines and Diesel engines. Such study is limited to a considerable extent by the lack of standard hydrocarbons, which are necessary, in particular, for the successful application of spectral methods of analysis.

We set ourselves the task of synthesizing 1,2-dialkylcyclopentanes of composition $C_{10}H_{20}$–$C_{13}H_{26}$ and separating them into cis- and trans-isomers.

In studying the individual composition of gasolines from a series of domestic petroleums, it was shown that they contain mono-, di-, and trisubstituted cyclopentane hydrocarbons ([1,2]). It was also shown that the 1,2-dimethylcyclopentane and 1-methyl-2-ethylcyclopentane contained in gasolines are mixtures of trans- and cis-isomers with a considerable predominance of the former (61.3–87.3% of the sum of both stereoisomers) ([1,3]). Up to the present time only a small number of 1,2-dialkylcyclopentanes have been obtained synthetically. The cis- and trans-isomers of 1,2-dimethylcyclopentane, 1-methyl-2-ethylcyclopentane ([4]), 1,2-diethylcyclopentane ([5]), 1-methyl-2-*n*-propylcyclopentane ([6]), and 1-methyl-2-*n*-butylcyclopentane ([7]) have been isolated in the individual state. In addition, there are reports in the literature on the preparation of 1,2-diheptylcyclopentane, 1,2-dioctylcyclopentane, 1-butyl-2-dodecylcyclopentane, 1-hexyl-2-decylcyclopentane, and 1-heptyl-2-nonylcyclopentane; however, in this work ([8]) there are no indications either of the spatial structure of these hydrocarbons or of the structure of the alkyl substituents.

In the present work we synthesized, according to the scheme given below, 1-ethyl-2-*n*-propyl-, 1-ethyl-2-*n*-butyl-, and 1,2-di-*n*-butylcyclopentanes:

$$\begin{array}{ccccccc} \begin{array}{c}\text{cyclopentanone derivative}\\ \text{R}\end{array} & \xrightarrow{\text{R}'\text{MgBr}} & \begin{array}{c}\text{R}\\ \text{R}'\\ \text{OH}\end{array} & \xrightarrow{-\text{H}_2\text{O}} & C_{nH_{2n-2}} & \underset{\text{Pt/C}}{\xrightarrow{+\text{H}_2}} & \begin{array}{c}\text{R}\\ \text{R}'\end{array} \\ \text{(I)} & & \text{(II)} & & \text{(III)} & & \text{(IV)} \end{array}$$

$$\text{(I)}^A \quad R = C_2H_5; \qquad \text{(II)}^A,\ \text{(IV)}^A \quad R' = n\text{-}C_3H_7; \qquad \text{(II)}^B,\ \text{(IV)}^B \quad R' = n\text{-}C_4H_9,$$
$$\text{(I)}^B \quad R = n\text{-}C_4H_9; \qquad \text{(II)}^B,\ \text{(IV)}^B \quad R' = n\text{-}C_4H_9.$$

From ketones (I), purified through their semicarbazones, and alkylmagnesium halides, the corresponding tertiary alcohols (II) were obtained in 50—

72% of theory; these alcohols were mixtures of cis- and trans-isomers and therefore distilled over a wide temperature range. By dehydration of the alcohols in the presence of iodine (1,2-di-*n*-butylcyclopentanol-1) or a saturated solution of oxalic acid (1-ethyl-2-*n*-propylcyclopentanol-2 and 1-ethyl-2-*n*-butylcyclopentanol-2), unsaturated hydrocarbons (III) were obtained in yields of 65-78% of theory. Their constants are given in Table 1.

Table 1

Constants of the obtained unsaturated hydrocarbons

No.	Hydrocarbon	B.p.	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.	Yield, % of theory
1	$C_{10}H_{18}$	60-60.5°/15 mm	1.4532	0.8157	45.82	45.71	65.3
2	$C_{11}H_{20}$	60-60.7°/5 mm	1.4545	0.8158	50.59	50.33	78.7
3	$C_{13}H_{24}$	70.5-71.0°/3 mm	1.4570	0.8244	59.57	59.57	77.7

Notes. I. All hydrocarbons crystallize on cooling. II. For No. 1. Found, %: C 86.32; 86.14; H 12.86; 12.97. $C_{10}H_{18}$. Calculated, %: C 86.88; H 13.12. For No. 2. Found, %: C 86.90; 87.06; H 13.07; 13.14. $C_{11}H_{20}$. Calculated, %: C 86.76; H 13.24. For No. 3. Found, %: C 86.07; 86.36; H 13.48; 13.50. $C_{13}H_{24}$. Calculated, %: C 86.58; H 13.42.

Since dehydration of the alcohols (II) can proceed in three directions, (III) may be a mixture of compounds of the following three types:

$$\underset{\text{(V)}}{\text{R}} \quad \text{and} \quad \underset{\text{(VII)}}{\text{R}}$$

[[unclear: structural formulas (V), (VI), and (VII) shown schematically on the page]]

The composition of these mixtures can be judged from Raman spectra. *In the case of the unsaturated hydrocarbons obtained from 1-ethyl-2-*n*-butylcyclopentanol-2 and 1,2-di-*n*-butylcyclopentanol-1, two lines were found in the region of the frequencies of the stretching vibrations of the double bond: 1652(5) and 1676(10) cm*$^{-1}$ *and, respectively, 1652(4) and 1673(8) cm*$^{-1}$. *This indicates that the unsaturated hydrocarbons studied are mixtures of isomers with different positions of the double bond. If these spectra are compared with the spectra of 1-alkylcyclopentenes-1 and 1,2-dialkylcyclopentenes (*[9]*), it may be assumed that the mixture obtained from 1-ethyl-2-*n*-butylcyclopentanol-2 consists of 70-85% 1-ethyl-2-*n*-butylcyclopentene-1 and 15-30% 1-ethyl-2-*n*-butylcyclopentene-2, possibly with an admixture of 1-ethyl-2-*n*-butylidenecyclopentane. The composition of the mixture obtained from 1,2-di-*n*-butylcyclopentanol-1: 60-80% 1,2-di-*n*-butylcyclopentene-1 and 20-40% 1,2-di-*n*-butylcyclopentene-2, possibly with an admixture of 1-*n*-butyl-2-*n*-butylidenecyclopentane. Thus, in both mixtures structures (V) predominate. The dehydration products of 1-ethyl-2-*n*-propylcyclopentanol-2 were not examined spectrally.

Owing to the closeness of the boiling points of the unsaturated hydrocarbons obtained by dehydration of the same alcohol, their separation was not carried out, and the mixtures were subjected to hydrogenation. From each such mixture, upon hydrogenation, one and the same saturated hydrocarbon should have been formed. Hydrogenation was carried out in alcoholic solution at room temperature in the presence of platinized charcoal (5% Pt), activated with palladium chloride ([10]). The resulting 1-ethyl-2-*n*-propylcyclopentane, 1-ethyl-2-*n*-butylcyclopentane and 1,2-di-*n*-butylcyclopentane,

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

preliminarily purified by chromatographic adsorption on silica gel, were separated into cis- and trans-isomers by distillation in vacuum on an 80 theoretical-plate column with metal packing. For the distillation curves and the change in constants by fractions, see Fig. 1. The constants of the hydrocarbons obtained are given in Table 2.

Fig. 1. Distillation curves of hydrocarbons and physical constants of fractions. 1

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—1-ethyl-2-*n*-propylcyclopentane, 2—1-ethyl-2-*n*-butylcyclopentane, 3—1,2-di-*n*-butylcyclopentane

Table 2

Constants of the cis- and trans-isomers of the hydrocarbons obtained

No.	Hydrocarbon	Conformation	B.p., °C at 30	B.p., °C converted to 760 mm*	n_D^{20}	n_D^{25}	d_4^{20}	d_4^{25}	MR_D^{20} found	MR_D^{20} calc.	Yield of isomer, % of the amount of hydrogenated hydrocarbon
1a	1-ethyl-2-*n*-propylcyclopentane	trans-	72.9	170.8	1.4337	1.4317	0.7898	0.7857	46.22	46.18	82.7
b	Same	cis-	77.4	176.4	1.4391	1.4371	0.8008	0.7965	46.08	46.18	12.3
2a	1-ethyl-2-*n*-butylcyclopentane	trans-	91.0	193.0	1.4376	1.4354	0.7950	0.7913	50.90	50.80	81.0
b	Same	cis-	95.3	198.1	1.4426	1.4404	0.8054	0.8017	50.75	50.80	13.8

No.	Hydrocarbon	Configuration	B.p., °C at 30 mm	B.p., °C converted to 760 mm*	n_D^{20}	n_D^{25}	d_4^{20}	d_4^{25}	MR_D^{20} found	MR_D^{20} calc.	Yield of isomer, % of the amount of hydrogenated hydrocarbon
3a	1,2-di-*n*-butylcyclopentane	trans-	122.6	231.1	1.4427	1.4409	0.8028	0.7993	60.18	60.08	80.9
b	Same	cis-	125.4	234.5	1.4467	1.4449	0.8111	0.8077	60.03	60.08	15.6

Note. I. trans-1,2-di-*n*-butylcyclopentane (No. 3a) has m.p. −62.7°; the melting point recalculated to zero impurity is 62.55°; degree of purity 99.75%. All the remaining hydrocarbons, as well as cis-1,2-di-*n*-butylcyclopentane, vitrify.

II. For No. 1. Found, %: (No. 1a) C 85.53; 85.53; H 14.20; 14.18; (No. 1b) C 85.52; 85.56; H 14.23; 14.14. $C_{10}H_{20}$. Calculated, %: C 85.63; H 14.37. For No. 2. Found, %: (No. 2a) C 85.58; 85.54; H 14.30; 14.30; (No. 2b) C 85.91; 85.86; H 14.31; 14.40. $C_{11}H_{22}$. Calculated, %: C 85.63; H 14.37. For No. 3. Found, %: (No. 3a) C 85.81; 85.73; H 14.16; 14.18; (No. 3b) C 85.54; 85.61; H 14.28; 14.36. $C_{13}H_{26}$. Calculated, %: C 85.63; H 14.37.

* The recalculation was made according to tables (11).

Stereoisomers with relatively higher boiling point, refractive index, and density and lower molecular refraction were assigned, according to the Auwers-Skita rule, the cis configuration. In the present work the cis and trans isomers were obtained in ratios from 1 : 5.2 to 1 : 6.7. For trans-1,2-di-*n*-butylcyclopentane, the crystallization temperature and the degree of purity were determined; the latter was found to be 99.75% (12). For cis-1,2-di-*n*-butylcyclopentane, the cis and trans isomers of 1-ethyl-2-*n*-butylcyclopentane, and 1-ethyl-2-*n*-propylcyclopentane, the crystallization temperatures could not be determined, because these hydrocarbons vitrify on cooling.

Fig. 2. Change in Δt for 1,2-dialkylcyclopentanes as a function of the number

Fig. 2. Change in Δt for 1,2-dialkylcyclopentanes as a function of the number of carbon atoms in the molecule. a —hydrocarbons obtained in the present work

Figure 2: Fig. 2. Change in Δt for 1,2-dialkylcyclopentanes as a function of the number of carbon atoms in the molecule. a —hydrocarbons obtained in the present work

of carbon atoms in the molecule. *a* —hydrocarbons obtained in the present work

The data obtained by us, as is evident from Fig. 2, confirm and supplement the results of B. A. Kazanskii and A. L. Liberman et al. (13), who showed that the differences in boiling temperatures of stereoisomeric dialkylcycloalkanes known up to the present time are in a linear dependence on the number of carbon atoms in the molecule. The differences in boiling temperatures of the stereoisomers synthesized by us fit this dependence well; it follows from this that 1,2-dialkylcyclopentanes of composition $C_{10}H_{20}$—$C_{13}H_{26}$ must obey the Auwers-Skita rule. Thus, the configurations that we assigned to the stereoisomeric hydrocarbons obtained in the present work may be considered correct.

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