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Abstract

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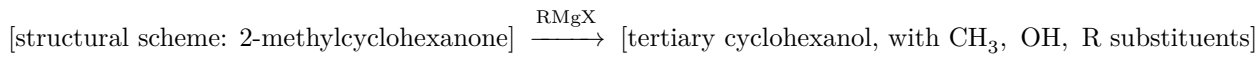
Stereoisomeric 1-Methyl-2-alkylcyclohexanes

There is still very little information in the literature on stereoisomeric dialkylcyclohexanes. Even in the comparatively better-studied series of cis- and trans-1,4-derivatives, reliable data on physical properties are at present available for only five pairs of stereoisomers ([1–5]): 1,4-dimethyl-, 1-methyl-4-ethyl-, 1-methyl-4-isopropyl-, 1-methyl-4-tert.-butyl-, and 1,4-diisopropylcyclohexanes. In the series of 1,2- and 1,3-derivatives, only 1,2- and 1,3-dimethylcyclohexanes ([1]), 1-methyl-2-ethylcyclohexanes ([6]), and 1-methyl-3-tert.-butylcyclohexanes ([4]) have so far been separated with complete reliability. Therefore, the study of this class of compounds is extremely interesting, although it also presents considerable experimental difficulties.

Considering the relatively small amount of data belonging here, we encounter certain unexpected features. Thus, it turns out that the cis form of 1,4-diisopropylcyclohexane boils lower than the trans isomer ([5]), although according to the Auwers–Skita rule it should have boiled higher. The reason for this peculiar inversion of boiling points remains unclear and deserves further study. In particular, it was of interest to determine whether similar exceptions occur in other series of dialkylcyclane hydrocarbons, for example in the series of 1,2-dialkylcyclohexanes. To this end we decided to synthesize and separate into stereoisomers several 1-methyl-2-*n*-alkylcyclohexanes. The syntheses were carried out according to a general scheme:



where R = *n*-propyl, *n*-hexane, and *n*-heptyl. The stereoisomers were separated in vacuo on rectification columns with an efficiency of 100 theoretical plates, the distillation being carried out continuously over several days. Judging from the results of fractionation, all stereoisomers were obtained in a very pure state. It proved that the constants of all hydrocarbons obtained in the present work were in agreement with the Auwers–Skita rule. The search for exceptions to this rule is continuing.

1-Methyl-2-*n*-hexyl- and 1-methyl-2-*n*-heptylcyclohexanes had not been mentioned in the literature, while 1-methyl-2-*n*-propylcyclohexane had previously

Fig. 1. Freezing curve of methylcyclohexanone-1

Figure 1: Fig. 1. Freezing curve of methylcyclohexanone-1

been obtained only as a mixture of stereoisomers ([7]), which was not separated further by the authors of the cited work.

Experimental Part

Fractionations of the starting, intermediate, and final products were carried out on two columns (Nos. 1 and 2) with efficiencies, respectively, of 20

and 60 theoretical plates with a glass packing, and three columns with an efficiency of 100 theoretical plates with a copper packing; these latter columns are completely equivalent, and all will be referred to as column No. 3.

2-Methylcyclohexanone-1 of various origins was carefully purified by distillation in vacuum on column No. 3, fractions of 15–20 ml being collected. For each of them the freezing curve was determined, and for further work only fractions with a freezing point not lower than -13.2° were taken. Fractions unsatisfactory in purity were subjected to repeated distillation. In this way 911 g of ketone were obtained, having the following constants: freezing point -13.2°, n_D^{20} 1.4488; d_4^{20} 0.9251. The purest fraction of ketone obtained by us had the constants: b.p. $70.5^\circ/31.5$ mm, freezing point -12.7° (see Fig. 1); the other constants did not differ from those given above. Judging from the freezing curve and from the cryoscopic constant found by us (0.0165 mole fraction/degree), the purity of the main portion of ketone was 99.2%, and that of the purest fraction not less than 99.9%. The most reliable literature data ([8]) apparently correspond to a less pure preparation: b.p. $165.08^\circ/760$ mm, freezing point -14°, d_D^{20} 0.9250.

Fig. 1. Freezing curve of methylcyclohexanone-1

***n*-Propyl chloride** (commercial) was distilled on column No. 2. The collected fraction (440 g) had the following properties: b.p. $46.6^\circ/760$ mm, n_D^{20} 1.3882, d_4^{20} 0.8920. According to the literature data ([8]): b.p. $46.6^\circ/760$ mm, n_D^{20} 1.3888, d_4^{20} 0.8924.

***n*-Hexyl bromide** was obtained from commercial *n*-hexyl alcohol, previously distilled on column No. 1 and having the constants: b.p. $157.4^\circ/760$ mm, n_D^{20} 1.4780, d_4^{20} 0.8188. According to the literature data ([9]): b.p. $157.4^\circ/760$ mm, n_D^{20} 1.4779, d_4^{20} 0.8189. *n*-Hexyl bromide (394 g), obtained by the action on the alcohol of a mixture of hydrobromic and sulfuric acids ([10]), after distillation in vacuum had the following constants: b.p. $55.5^\circ/25$ mm, n_D^{20} 1.4476, d_4^{20} 1.1705.

According to the literature data ([9]): b.p. $156.0^\circ/760$ mm, n_D^{20} 1.4478, d_4^{20} 1.1705.

***n*-Heptyl bromide** was obtained from commercial *n*-heptyl alcohol, distilled in vacuum on column No. 1 and having the following constants: b.p. $82.4^\circ/16.5$ mm, d_D^{20} 1.4242, d_4^{20} 0.8219. According to the literature data ([11]): b.p.

176.8°/760 mm, n_D^{20} 1.4242, d_4^{20} 0.8219. *n*-Heptyl bromide was obtained in the same way as *n*-hexyl bromide. After distillation in vacuum, 495 g of *n*-hexyl bromide were obtained with the following constants: b.p. 76.0°/23 mm, n_D^{20} 1.4499, d_4^{20} 1.1336. According to the literature data ([11]): b.p. 180°/760 mm, d_4^{20} 1.1335.

2-Methyl-1-*n*-alkylcyclohexanols-1 were obtained by the Grignard reaction. In all cases a large excess of Grignard reagent was used in order to ensure more complete utilization of the ketone, which, because of the considerable difficulty of obtaining it in very pure form, was of relatively greater value than the alkyl halides. All data on the yields and constants of the carbinols obtained, which are apparently mixtures of the cis and trans forms, are summarized in Table 1.

1-Methyl-2-*n*-alkylcyclohexenes were obtained by dehydration of the corresponding carbinols in the presence of aqueous oxalic acid (methylethylcyclohexene) or 2–3 drops of concentrated sulfuric acid and were mixtures of isomers with different positions of the double bond.

···bond. Data on the yields and constants are given in Table 2.

1-Methyl-2-*n*-alkylcyclohexanes were obtained in 88.9–96.5% yields by hydrogenating the corresponding cycloalkenes over platinized carbon (20% Pt) in a catalytic furnace at 150°, and were chromatographed on silica gel to remove residues of unsaturated compounds. For separation into stereoisomers, 169.8 g of 1-methyl-2-*n*-propylcyclohexane, 81.4 g of 1-methyl-2-*n*-hexylcyclohexane, and 100.7 g of 1-methyl-2-*n*-heptylcyclohexane were taken. The separation was carried out under vacuum on columns No. 3. In the temperature-rise regions, collection was performed at a reflux ratio of 200–220; during the period of constant temperature the reflux ratio was reduced to 120–150. During the distillation, the distillate was collected in small fractions by volume (from 2 to 15 ml and only in rare cases smaller or larger than this value); for each of these the refractive index and specific gravity were determined. If the distillate in several consecutive fractions had exactly identical constants, it was regarded as an individual stereoisomer. Figure 2 shows the course of the constants of the fractions obtained during the distillation. The properties of the isolated stereoisomers are summarized in Table 3.

Fig. 2. Refractive indices and specific gravities of the fractions of 1-methyl-2-*n*-propylcyclohexane (**A**), 1-methyl-2-*n*-hexylcyclohexane (**B**), and 1-methyl-2-*n*-heptylcyclohexane (**C**).

Table 1

Yields and properties of 2-methyl-1-alkylcyclohexanols-1

R	Ketone, taken in one synthesis, mol	Alkyl halide, taken in one synthesis, mol	Yield, % of theory, calculated on ketone	Obtained in all syntheses, g	b.p., °C/mm Hg	n_D^{20}	d_4^{20}
n-Propyl *	2.27	2.70	84.1	294.4	87-88/13	1.4651	0.9120
n-Hexyl **	1.34	1.79	77.0	256.2	102.0/2.8	1.4655	0.8902
n-Heptyl **	1.20	1.40	69.2	250.9	106.0/2.2	1.4660	0.8916

* According to Signaigo and Cramer (7), b.p. 65-67°/2 mm, n_D^{20} 1.4653, d_{20}^{20} 0.913.
** Not described in the literature.

Table 2

Yields and properties of 1-methyl-2-*n*-alkylcyclohexenes

R	Yield of cyclene, % of theory	Cyclene obtained, g	b.p., °C/mm Hg	n_D^{20}	d_4^{20}
n-Propyl *	82.7	193.6	169.0-172.0/745	1.4612	0.8273
n-Hexyl **	88.3	200.5	78-80/2.5	1.4640	0.8312
n-Heptyl **	94.7	130.0	78-80/1.8	1.4655	0.8326

* Signaigo and Cramer (7) give the following constants for 1-methyl-2-*n*-propylcyclohexene-1: b.p. 177.3-177.5°/760 mm, n_D^{20} 1.4627, d_{20}^{20} 0.832.
** Not described in the literature.

Table 3

Properties of stereoisomeric 1-methyl-2-*n*-alkylcyclohexanes

Hydrocarbon	Isomer	b.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D, calc.	MR_D, found
1-methyl-2-*n*-propylcyclohexane	trans	66.8/20.5	1.4408	0.7997	46.18	46.30
1-methyl-2-*n*-propylcyclohexane	cis	69.9/20.5	1.4460	0.8127	46.18	46.02
1-methyl-2-*n*-hexylcyclohexane	trans	111.2/13.8	1.4490	0.8116	60.26	60.26
1-methyl-2-*n*-hexylcyclohexane	cis	114.0/14.0	1.4527	0.8208	60.26	60.06
1-methyl-2-*n*-heptylcyclohexane	trans	126.1/13.8	1.4503	0.8143	64.65	64.83
1-methyl-2-*n*-heptylcyclohexane	cis	127.9/13.8	1.4540	0.8229	64.65	64.61

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