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Abstract

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STEREOISOMERIC 1,4-DI-*n*-PROPYL- AND 1-METHYL-4^2-METHO-4-BUTYLCYCLOHEXANES

Earlier we showed (1,2,3) that the physical properties of certain 1,4-dialkylcyclohexanes differ from those usually observed in this series. Thus, in 1,4-diisopropyl- and 1,4-di-*tert*-butylcyclohexanes the lower-boiling isomer has the cis configuration, whereas in all other known cases trans-1,4-dialkylcyclohexanes boil lower. On comparing these facts with the reliable experimental data available in the literature, the idea was advanced that the differences in the boiling temperatures of stereoisomers ($\Delta t = t_{\text{cis}} - t_{\text{trans}}$) are in a linear relationship to molecular weight. The intersection of such straight lines with the abscissa axis could explain the inversion of the boiling temperatures of stereoisomers at a definite molecular weight (4). This relationship is well maintained in the series of 1,2-dialkylcyclopentanes, as has recently been confirmed (5) by new examples. In the series of 1,2-dialkylcyclohexanes, only the first member of the series departed from the linear relationship, which may be connected with the more complex geometry of the cyclohexane ring as compared with the cyclopentane ring and with the stronger interaction, resulting from this, of the 1,2-e,a-groups. The data for 1,4-dialkylcyclohexanes also seemed to confirm the presence of a linear relationship. However, in contrast to the cases considered above, here, because of the paucity of the available experimental material, not only hydrocarbons with primary alkyls in the side chains were included in the consideration, but also representatives with secondary radicals: methylisopropyl- and diisopropylcyclohexanes. In other words, in this case the possible influence of the structure of the side chain was not taken into account. The present investigation was undertaken in order to resolve precisely this question of influence.

For this purpose, 1,4-di-*n*-propyl- and 1-methyl-4^2-metho-4-butylcyclohexanes, which are structural isomers of 1,4-diisopropylcyclohexane, for which an inversion of the boiling temperatures of the stereoisomers was observed, were synthesized and separated into cis and trans isomers. The hydrocarbons were chosen so that in one case the side chains were identical, and in the other—different. This was to show to what extent asymmetry of the radicals can affect the magnitude of Δt. It turned out that for the stereoisomers obtained in the present work the trans form boils lower than the cis form, i.e., Δt in both cases has a positive value, whereas for 1,4-diisopropylcyclohexanes it was negative ([1],[4]). Thus, the primary, secondary, or tertiary character of the side chain substantially affects the ratio of the boiling temperatures of stereoisomeric dialkylcyclohexanes. The question of the existence of a linear relationship in the series of 1,4-dialkylcyclohexanes with primary radicals remains open until additional experimental data appear.

As in our previous works, the synthesis of the hydrocarbons was carried out by methods making it possible to obtain the purest reaction products, even at the expense of yield. Thus, 1,4-di-*n*-propylcyclohexanes were obtained from *p*-dibromobenzene and allyl chloride by the Grignard reaction, followed by hydrogenation of *p*-diallylbenzene.

Since *p*-dibromobenzene under ordinary conditions reacts with only one atom of magnesium ([6]), replacement of the bromine atoms by allyl radicals had to be carried out in two stages. 1-Methyl-4^2-methoxy-4-butylcyclohexanes were obtained from α-chloro-*p*-xylene according to the usual Grignard synthesis scheme.

The addition of hydrogen to the double bond of the intermediate butenyltoluene in the presence of platinum at room temperature was accompanied by partial hydrogenation of the benzene ring. However, the previously undescribed 4^2-methoxy-4-butyltoluene was nevertheless isolated in individual form by column fractionation. Also obtained for the first time was 4^2-hydroxy-4^2-methoxy-4-butyltoluene.

To ensure a high degree of purity of the final products, the starting substances were purified very thoroughly. Final separation of the stereoisomers was carried out by distillation on columns of 100 theoretical plates under vacuum, with very high reflux ratios. Fractionation was performed continuously over many days. The distillate was collected in small fractions (3-5 ml each), and the constants were determined for each of them. If the distillate had completely identical constants in several successive fractions, it was regarded as an individual substance. The configurations of all four stereoisomers, not previously described in the literature, were determined with the aid of their combination-scattering spectra* on the basis of the fact that in the spectra of the cis isomers of this series there is always present ([7]) a bright line at $\sim 630\ \mathrm{cm}^{-1}$. The physical constants of the stereoisomers and the lines characterizing their configuration are given in Table 1. For comparison, the previously published ([1]) properties of stereoisomeric 1,4-diisopropylcyclohexanes are also given there.

Table 1

Physical constants of synthesized stereoisomeric 1,4-dialkylcyclohexanes of composition $C_{12}H_{24}$

Hydrocarbon	Configuration	b.p., °C/mm	b.p., °C/760 mm*	Δt/760 mm	n_D^{20}	d_4^{20}	MR_D**	Characteristic spectral lines of the cis form
1,4-Di-*n*-propylcyclohexane	cis	96.9/14.0	221.0		1.4480	0.8138	55.28	634(13)
1,4-Di-*n*-propylcyclohexane	trans	96.1/14.0	220.0	+1.0	1.4440	0.8030	55.59	–
1-Methyl-4^2-methoxy-4-butylcyclohexane	cis	97.5/20.0	211.5		1.4469	0.8121	55.36	636(14)
1-Methyl-4^2-methoxy-4-butylcyclohexane	trans	90.5/16.0	209.0	+2.5	1.4418	0.7997	55.66	–
1,4-Diisopropylcyclohexane	cis	78.9/7.5	215.1		1.4524	0.8236	55.17	629(46)
1,4-Diisopropylcyclohexane	trans	80.4/7.5	217.1	−2.0	1.4485	0.8143	55.38	–

* Found by recalculation according to the tables of Dreisbach (^{8}).

** Calculated for $C_{12}H_{24}$, $MR_D = 55.42$.

As is evident from the data in Table 1, the refractive indices and specific gravities are higher for the cis forms in all cases, in accordance with the known Auwers-Skita rule, whereas the boiling points of the cis forms are sometimes higher and sometimes lower, depending on the structure of the side chains.

Experimental Part

p-Dibromobenzene, obtained by bromination of benzene with bromine in the presence of $AlBr_3$ and recrystallized three times from ether, melted at 87.5°.

p-Bromoallylbenzene was obtained by the Grignard method from *p*-dibromobenzene and

Figure 1. Refractive indices and specific gravities of fractions of the hydrocarbons studied. A—1,4-di-*n*-propylcyclohexanes. B—1-methyl-4^2-methoxy-4-butylcyclohexanes

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allyl chloride in 6 syntheses with a yield of 30–51%. After fivefold distillation from a Favorskii flask, *n*-bromoallylbenzene (550.2 g) had the constants: b.p. 73.0—74.0°/4.5 mm; n_D^{20} 1.5560; d_4^{20} 1.3220.

***n*-Diallylbenzene.** From 508.6 g of freshly distilled *n*-bromoallylbenzene and 248.6 g of allyl chloride, 143.6 g of *n*-diallylbenzene was obtained by the Grignard reaction (yield 35.2% of theory, calculated on the bromide), which after fourfold distillation from a Favorskii flask had the following constants: b.p. 68.0°/3.5 mm; n_D^{20} 1.5420; d_4^{20} 0.9131.

Fig. 1. Refractive indices and specific gravities of fractions of the hydrocarbons studied.
A—1,4-di-*n*-propylcyclohexanes.
B—1-methyl-4^2-methoxy-4-butylcyclohexanes.

***n*-Di-*n*-propylcyclohexanes.** *n*-Diallylbenzene was hydrogenated in a duck-shaped vessel in the presence of platinized charcoal activated by addition of H_2PtCl_6 (^{9}); then, for complete hydrogenation of the ring, the catalyst was passed over platinized charcoal at 150° in a stream of H_2 and chromatographed on silica gel to remove traces of aromatics.

Separation of stereoisomeric 1,4-di-*n*-propylcyclohexanes. 89.9 g of the chromatographed mixture of stereoisomers (n_D^{20} 1.4442; d_4^{20} 0.8070) was fractionated on a column at 9–10 mm with a dephlegmator

with a reflux ratio of 200–220. Twenty-six fractions were collected (Fig. 1A); losses did not exceed 1.8%. The properties of the isolated stereoisomers are summarized in Table 1.

***α*-Chloro-*p*-xylene** was obtained from *p*-xylene of a purity of ~99.9% (from the freezing curve) by chlorination in the vapor phase under illumination with a 500-watt lamp. The yield in different experiments was 30–50%, calculated on *p*-xylene. After fivefold distillation of the combined reaction product from a Favorskii flask, 334.2 g of *α*-chloro-*p*-xylene was obtained: b.p. 92.0–92.5°/20

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* All spectroscopic studies were carried out by staff members of the Commission on Spectroscopy of the Department of Physical and Mathematical Sciences of the Academy of Sciences of the USSR, V. T. Aleksanyan and Kh. E. Sterin, to whom we express our gratitude for the assistance rendered.

mm; n_D^{20} 1.5340; d_4^{20} 1.0510.

4^2-Oxy-4^2-methoxy-4-butyltoluene was prepared under the usual conditions of Grignard synthesis (in a nitrogen atmosphere) from 61.4 g of magnesium (2.53 g-atoms), 332.0 g of α-chloro-*p*-xylene (2.38 moles) in 700 ml of abs. ether, and 200.0 g of freshly distilled methyl ethyl ketone (2.77 moles) in 450 ml of ether. The 4^2-oxy-4^2-methoxy-4-butyltoluene obtained after the usual isolation and fourfold distillation from a Favorskii flask (220.2 g, yield 52.1% of theory, calculated on the chloride) had the following properties: b.p. 112.8-113.5°/6.5 mm; n_D^{20} 1.5120; d_4^{20} 0.9562. According to analysis, the substance corresponds to the composition $C_{12}H_{18}O$.

Found, %: C 80.63; 80.62; H 10.15; 10.13
$C_{12}H_{18}O$. Calculated, %: C 80.83; H 10.18

4^2-Methoxy-4-butenyltoluenes. A mixture of 200.0 g of 4^2-oxy-4^2-methoxy-4-butyltoluene (1.12 moles) and 69.2 g of boric acid (1.12 moles) was heated in a flask with a reflux condenser for 3 h. (^{10}), and then decanted. After drying over calcium chloride and distillation from a Favorskii flask, 145.7 g of a mixture of *p*-methobutenyltoluenes was obtained (yield 81.0%) with the following constants: b.p. 102.0-104.0°/13 mm; n_D^{20} 1.5160; d_4^{20} 0.8836. There are no data in the literature for these hydrocarbons.

4^2-Methoxy-4-butyltoluene. A portion of methobutenyltoluene (50.5 g) was hydrogenated in an autoclave as described above. Then 49.3 g of catalyst was removed on a column at 12.5 mm with a reflux ratio of 180-200, and 25.7 g of 4^2-methoxy-4-butyltoluene was obtained in the form of 12 fractions not differing in constants: b.p. 92.5°/12.5 mm; n_D^{20} 1.4899; d_4^{20} 0.8497.

1-Methyl-4^2-methoxy-4-butylcyclohexanes. 110.5 g of 4^2-methoxy-4-butyltoluene was hydrogenated by passing over platinized charcoal in a stream of H_2 at 150°, and then chromatographed on silica gel to remove traces of aromatic compounds.

Separation of stereoisomeric 1-methyl-4^2-methoxy-4-butylcyclohexanes. 105.1 g of the chromatographed mixture of stereoisomers (b.p. 81.5-82.5°/11 mm; n_D^{20} 1.4450; d_4^{20} 0.8159) was fractionated on a column at 10-12 mm with a reflux ratio of 200-220 (during the collection of fractions with constant refractive indices and specific gravities, the reflux ratio was reduced to 150-180). Twenty-eight fractions were collected (Fig. 1B); losses did not exceed 2.8%. The properties of the isolated stereoisomers are summarized in Table 1.

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