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Academician B. A. KAZANSKII, A. L. LIBERMAN, and N. I. TYUN' KINA

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Abstract

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DEVIATION OF STEREOISOMERIC 1,4-DI-tert-BUTYLCYCLOHEXANES FROM THE AUWERS-SKITA RULE

In 1956 we showed that 1,4-diisopropylcyclohexanes do not obey the Auwers-Skita rule; namely, in this case the lower-boiling isomer has the cis configuration ([1]). Later this was confirmed by stereospecific synthesis ([2]). In the course of the latter it became clear that the dimethyl esters of stereoisomeric cyclohexane-1,4-dicarboxylic acids likewise deviate from the Auwers-Skita rule in an entirely analogous way. Recently, Eliel and Haber ([3]) found that the boiling points of all six stereoisomeric methylcyclohexanols contradict the so-called conformational rule—the modern and more exact expression of the Auwers-Skita rule. Thus, in the case of 2- and 4-methylcyclohexanols the cis isomer boiled lower, whereas in the case of 3-methylcyclohexanols the lower-boiling form proved to be the trans form. These deviations were attributed by the American authors to the influence of hydrogen bonds. Such an explanation would be unacceptable for the complex esters that we studied, especially for hydrocarbons; however, it is not excluded that in compounds of different classes the causes of the phenomenon under discussion may be different. It was therefore of interest to try to find new examples of such deviations among hydrocarbons, where there can be no complicating influence of hydrogen bonds, polar atoms or groups, etc.

It seemed to us that 1,4-di-tert-butylcyclohexane might serve as such an example. Indeed, Mekhtiev and co-workers ([4]), having synthesized this hydrocarbon, found in attempting to separate it into stereoisomers that the lower-boiling isomer was a liquid, whereas the distillation residue solidified in the distillation flask and had m.p. 57°. Although these authors, on the basis of the Auwers-Skita rule, assigned the trans configuration to the lower-boiling isomer, the correctness of this assignment may be doubted, since in the series of 1,4-disubstituted cyclohexanes the trans forms are characterized by a higher melting point, which in the present case belonged to the higher-boiling isomer. We therefore decided to repeat the synthesis of the stereoisomeric 1,4-di-tert-butylcyclohexanes and to determine their relation to the Auwers-Skita rule. They were obtained by alkylation of benzene with isobutyl alcohol, with formation of *p*-di-tert-butylbenzene, and hydrogenation of the latter with Raney nickel. Then the lower-boiling isomer was distilled off on a column of 100 theoretical plates efficiency, and the residue was recrystallized repeatedly from alcohol until the melting point no longer changed in successive crystallizations. The properties of the stereoisomers obtained are given in Table 1. The constants of the lower-boiling form are close to those reported by Mekhtiev and co-workers (^{4}), although our preparation is evidently appreciably purer. However, the higher-boiling substance described by these authors, as is apparent from our results, was not an individual compound but a mixture of both forms containing considerable amounts of the lower-boiling isomer.

In a recently published work (^{5}) it was shown that all the stereoisomeric 1,4-dialkylcyclohexanes considered by its authors are characte- are characterized by the presence in the combination-scattering spectrum of the cis-isomers of a bright line at 630 cm^{-1}, absent from the spectra of the trans-isomers. A spectroscopic investigation of 1,4-di-tert.-butylcyclohexanes* based on this observation confirmed our assumption concerning the configuration of the stereoisomers obtained. Indeed, in the spectrum of the low-boiling

Table 1

Physical properties of stereoisomeric 1,4-di-tert.-butylcyclohexanes

Preparation	Isomer	B.p., °C/mm	B.p., °C/760 mm	M.p., °C	n_D^{20}	n_D^{90}	d_4^{20}	d_4^{90}	Cryoscopic constant of benzene, °C/mol	Degree of purity, %
This work	Cis-	120.0/20	234.9**	20.8	1.4580	1.4300	–	0.7852	0.0181	99.9
Mekhtiev et al. (4)	Low-boiling	96/10	239 – 240	18.5	1.4568	–	0.8309	–	–	96***
This work	Trans-	121.7 – 122*, 2/20	236.9** – 237.5	88.5	–	1.4290	–	0.7844	[0.0165	99.9
Mekhtiev et al. (4)	High-boiling	–	242 – 243	57	–	–	–	–	–	–

* In view of the high melting point of the substance, it was not possible to determine the boiling point accurately. The value given was obtained by distillation from a Claisen flask.
** Calculated from the tables of Dreisbach (5).
*** Calculated by us on the basis of the given cryoscopic constant and m.p. 18.5°.

isomer a line 629(26) was found, and, consequently, it must be assigned the cis-configuration. Thus, here we do indeed have a new case of violation of the Auwers—Skita rule.

Until very recently it was noted in the literature that deviations from this rule are observed only for entire series of compounds of the same type of structure (1,3-dialkylcyclopentanes and 1,3-dialkylcyclohexanes). At present, data are accumulating which indicate that even within a single series the Auwers—Skita rule may either be obeyed or violated. In this case either only the boiling points may undergo inversion (1,4-diisopropylcyclohexanes, methylcyclohexanols), or several constants at once. To the latter type of violation belong, as was shown quite recently (7), 1-phenyl-2-cyclopropyl- and 1,2-diphenylcyclopropanes. In these hydrocarbons the cis-forms not only boil lower, but also have a lower refractive index and specific gravity.

As is seen from Table 1, stereoisomeric 1,4-di-tert.-butylcyclohexanes deviate from the Auwers—Skita rule analogously to 1,4-diisopropylcyclohexanes.

Experimental Part

1,4-Di-tert.-butylbenzene. Benzene was alkylated with isobutyl alcohol in the presence of conc. H_2SO_4 (8). The starting alcohol had the following properties: b.p. 107.0–107.2°/739 mm; n_D^{20} 1.3960; d_4^{20} 0.8012. According to reliable literature data (9), b.p. 107.98°/760 mm; n_D^{20} 1.3959; d_4^{20} 0.80196. In several syntheses 400 g of 1,4-di-tert.-butylbenzene was obtained, which, after two recrystallizations from ether, had a freezing point of +76.2° (according to literature data (10), m.p. +77.7°). The freezing curve of the hydrocarbon is given in Fig. 1 **B**.

* The spectroscopic investigations were carried out by the scientific associates of the Commission on Spectroscopy of the Academy of Sciences of the USSR, V. T. Aleksanyan and Kh. E. Sterin, to whom we express our gratitude for their comradely assistance.

Stereoisomeric 1,4-di-tert-butylcyclohexanes. A solution of 150 g of 1,4-di-tert-butylbenzene in 250 g of *n*-heptane was hydrogenated in an autoclave at an initial hydrogen pressure of 140 atm and a temperature of 190–200°. Raney nickel, prepared as described earlier [1], served as the catalyst. After completion of the hydrogenation, the solution filtered from the catalyst was chromatographed twice on silica gel (174–180 g) to remove unreacted aromatic material; the heptane was then distilled off, and the residue (108.8 g), consisting of crystals and liquid, was filtered on a glass filter. The crystalline portion (70.0 g) was distilled on a column of 100 theoretical plates efficiency. The distillation was carried out continuously for several days with a high reflux ratio of 150-200. To avoid crystallization of the distilled substances on the cold parts of the apparatus, warm water was supplied to the column condenser, and all external parts of the receiver and column were wrapped with thin foil through which an electric current was passed. During the distillation, 14 small fractions of 1.5–5

Fig. 1. Freezing curves of the hydrocarbons studied. A —
trans-1,4-di-tert-butylcyclohexane. —1,4-di-tert-butylbenzene, —
cis-1,4-di-tert-butylcyclohexane

Figure 1: Fig. 1. Freezing curves of the hydrocarbons studied. A — trans-1,4-di-tert-butylcyclohexane. —1,4-di-tert-butylbenzene, —cis-1,4-di-tert-butylcyclohexane

ml were collected, for each of which freezing curves were made. Judging from them, the purest low-boiling substance was represented by four such fractions having identical constants, given in Table 1 as the properties of the cis isomer; the freezing curve is given in Fig. 1B. In all, 23.3 g* (33.3%) of the low-boiling isomer was collected, and 6.8 g (9.7%) of transition fractions with melting points gradually increasing from 23.4 to 40°. The residue, m.p. 58–68°, amounted to 39.2 g (56.0%). It was subjected to repeated recrystallization. Separation of the isomers proceeded with difficulty, and only after the eighth recrystallization was the pure high-melting isomer obtained (9.0 g), whose freezing curve is shown in Fig. 1A, while the constants are given in Table 1 as the properties of the cis isomer.

Fig. 1. Freezing curves of the hydrocarbons studied.
A —trans-1,4-di-tert-butylcyclohexane.
—1,4-di-tert-butylbenzene,
—cis-1,4-di-tert-butylcyclohexane.

The cryoscopic constants of both isomers given in Table 1 were determined by adding to each of them an impurity of the other isomer.

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* An additional 5.7 g of this isomer was isolated from the filtrate mentioned above.

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

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