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A. L. Liberman, B. M. Lerman, G. N. Zhizhin,

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Abstract

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A. L. Liberman, B. M. Lerman, G. N. Zhizhin,
Kh. E. Sterin

On the Sequence of Boiling Temperatures of Stereoisomeric 1-Methyl- and 1-Ethyl-4-tert.-butylcyclohexanes

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Considerable research over the last 40 years, beginning with the work of Auwers and Skita, has been devoted to the search for a dependence between the physical properties and the configuration of disubstituted cyclanes; they formulated their results in the form of the well-known rule. Subsequently, this rule was discussed several times and reformulated anew by other investigators in order to eliminate the contradictions into which it came with new facts. In connection with such discussion, our attention was drawn to data on the properties of stereoisomeric 1-methyl-4-tert.-butylcyclohexanes (1). The authors of the cited work did not assign definite configurations to the stereoisomers they had isolated. Meanwhile, the constants of the substances under discussion seemed unusual to us. On the one hand, according to the Auwers-Skita rule, one might think that the higher-boiling isomer, having higher n_D^{20} and d_4^{20}, is the cis form. On these grounds it is precisely in this way that it is regarded by Van Bekkum, Verkade, and coauthors (2). On the other hand, the higher-boiling isomer has a higher melting point, and there is a belief that in the series of 1,4-disubstituted cyclohexanes trans forms should melt higher than cis forms. In the literature one can find many cases in which configurations were assigned to stereoisomers solely on the basis of this criterion. Thus, if one proceeds from it, the cis configuration should be assigned to the lower-boiling stereoisomer of 1-methyl-4-tert.-butylcyclohexanes.

In recent years it has become clear that the sequences of boiling temperatures of stereoisomeric dialkylcyclohexanes obey certain specific regularities that go beyond both the Auwers-Skita rule and its subsequent variants (3-5). So far it has been possible to establish that the differences in boiling temperatures (Δt) of each pair of stereoisomers* are regularly related to the position, length, and structure of the side chains (5,6). True, the regularities found have been tested, with one exception, only on dialkylcyclohexanes that do not contain tertiary alkyls. The large conformational volume of the latter, however, does not permit the regularities found to be extended without preliminary experiments to dialkylcyclohexanes with tertiary alkyls, since the influence of steric effects on boiling temperatures is unclear. Therefore, exact knowledge of the configurations of the stereoisomeric 1-methyl-4-tert.-butylcyclohexanes—the simplest dialkylcyclohexanes with one tert.-alkyl group—seemed to us sufficiently important.

All these considerations prompted us to repeat the synthesis of stereoisomeric 1-methyl-4-tert.-butylcyclohexanes in order to resolve the question of their configuration with the aid of spectroscopic methods developed by us (^{7},8). In addition, for a more complete picture, we made an attempt to obtain the stereoisomers of the next homologue—1-ethyl-4-tert.-butylcyclohexane.

* The difference is expressed as $\Delta t = t_{ea} - t_{ee}$, where t_{ea} and t_{ee} are the boiling temperatures of the equatorial-axial (ea) and diequatorial (ee) forms, respectively. With this expression, Δt for stereoisomers obeying the Auwers–Skita rule in the modernized formulation of Pitzer (⁀9) will have a positive value; deviation from this rule corresponds to a negative value of Δt.

The syntheses were carried out according to the scheme:

$$\text{alkylbenzene with substituent } R \xrightarrow{(CH_3)_2C{=}CH_2} \text{dialkylbenzene with } C(CH_3)_3 \xrightarrow{+3H_2} \text{cyclohexane deriva}$$

The starting monoalkylbenzenes and the intermediate dialkylbenzenes were carefully purified by distillation on a highly efficient column. The separation of the stereoisomers was carried out on the same column. The constants of the synthesized preparations are summarized in Table 1.

Table 1

Physical properties of the hydrocarbons obtained

Hydrocarbon	Configuration	Boiling temperature, °C/mm Hg	Boiling temperature, °C/760 mm Hg	Freezing temperature, °C	n_D^{20}	d_4^{20}	Cryoscopic constant, mol. fraction/°C	Degree of purity, %
1-Methyl-4-tert.-butylcyclohexanes	trans	–	186.5*	−50.5	1.4418	0.8016	0.0322	99.7

Hydrocarbon	Configuration	Boiling temperature, °C/mm Hg	Boiling temperature, °C/760 mm Hg	Freezing temperature, °C	n_D^{20}	d_4^{20}	Cryoscopic constant, mol. fraction/°C	Degree of purity, %
1-Methyl-4-tert.-butylcyclohexanes	cis	–	188.8*	−34.0**	1.4488	0.8173	0.0328	99.0
Fractions of 1-ethyl-4-tert.-butylcyclohexane, most enriched in the corresponding stereoisomer	trans	~122/58	–	–	1.4482	0.8142	–	80–85

Hydrocarbon	Configuration	Boiling temperature, °C/mm Hg	Boiling temperature, °C/760 mm Hg	Freezing temperature, °C	n_D^{20}	d_4^{20}	Cryoscopic constant, mol. fraction/°C	Degree of purity, %
Fractions of 1-ethyl-4-tert.-butylcyclohexane, most enriched in the corresponding stereoisomer	cis	~122/58	–	–	1.4510	0.8203	–	80–85
p-tert.-Butyltoluene	–	104.0/48	193.4***	−52.4	1.4919	0.8610	0.0183[9]	99.9
p-tert.-Butylethylbenzene	–	127.0*/61	204.2***	−54.9	1.4933	0.8632	0.0159	99.3

* Determined in a special experiment.
** The melting temperature was determined, since for this substance equilibrium between the solid and liquid phases is established very slowly.
*** Recalculated according to Dreisbach’ s tables.

The purity of our *p*-tert.-butyltoluene (99.9%) was commensurate with the purity of the preparation described earlier[9]; the constants of both samples do not differ within the limits of measurement error. However, in the case of *p*-tert.-butylethylbenzene the situation was different. This hydrocarbon was described by Schletter and Clark[10], and, judging from the article, their preparation should have been regarded as fairly pure. The degree of purity of our preparation, determined from freezing curves, was 99.3%. Nevertheless, the freezing temperature found by us (−54.9°) is almost 17° lower than the value reported by Schletter and Clark (−38.35°). In this connection, the structure of our preparation was confirmed by spectroscopic and chemical methods. The *p*-tert.-butylbenzoic acid obtained from it by oxidation melted without depression in a mixed sample with an authentic preparation. The Raman spectrum of our preparation of *p*-tert.-butylethylbenzene contains the lines 648(4), 781(10), 1195(5), 1206(5), 1616(10)*, i.e., it possesses all the features characteristic of the spectra of *p*-dialkylbenzenes[11]; moreover, it lacks the lines characteristic of mono-, 1,2-, and 1,3-dialkylbenzenes[11,12]. All this confirms the 1,4-arrangement of the side chains in the substance obtained. Thus, the structure of the preparation synthesized by us is beyond doubt, and the freezing temperature reported in the work of Schletter and Clark must be regarded as erroneous.

The stereoisomeric 1-methyl-4-tert.-butylcyclohexanes were obtained in a substantially purer form than the preparations described earlier[1]. Study of the spectra of these preparations made it possible to establish their configurations. In the Raman spectrum of the higher-boiling isomer a rather intense line at 626 cm^{-1} is observed, and in the infrared spectrum—a band at 623 cm^{-1}. In the spectra of the lower-boiling isomer there is no such frequency. Consequently, according to ([7,8]), the lower-boiling isomer is the trans form, and the higher-boiling one is the cis form, which agrees with the Auwers–Skita rule and with the considerations cited in the literature ([2]). Thus, it turns out that here the cis form melts higher than its trans stereoisomer, contrary to the widespread opinion concerning the order of the melting temperatures of stereoisomers. However, after reviewing the data available in the literature over the last 20 years on the values of this constant for 1,4-disubstituted cyclohexanes, we became convinced that, although in most cases the trans forms do indeed melt higher, there is a fairly large number of exceptions. Usually these exceptions occur when one of the substituents is a tert-alkyl or another group with a large conformational volume. 1-Methyl-4-tert-butylcyclohexane also belongs precisely to this type of substance.

Whereas for 1-methyl-4-tert-butylcyclohexanes Δt proved to be equal to 2.3° and they were readily separated upon distillation, it proved impossible to isolate the individual stereoisomers of 1-ethyl-4-tert-butylcyclohexane by rectification on a column of 100 theoretical plates. Apparently, here Δt amounts to only fractions of a degree. Therefore, despite the great care taken in the distillation, the stereoisomers, as spectroscopic investigation showed, were obtained contaminated with one another (up to 15–20% impurity). Fractions enriched in the lower-boiling isomer had higher values of n_D^{20} and d_4^{20} than the higher-boiling fractions. An analogous course of the constants occurred for 1,4-diisopropylcyclohexanes, in which the lower-boiling isomer had the cis configuration ([13]). Despite the incomplete separation, from the frequency 622 cm^{-1} it could be stated with confidence that the cis form predominates in the lower-boiling fractions of 1-ethyl-4-tert-butylcyclohexane. Consequently, in this hydrocarbon the cis configuration must be assigned to the lower-boiling stereoisomer, in contrast to what was observed for 1-methyl-4-tert-butylcyclohexanes.

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* The numbers in parentheses denote visual intensities.

This result is highly significant. Such a small change in the side chain as replacement of methyl by an ethyl group changed, in the case under consideration, the sequence of boiling temperatures to the reverse one. Up to now, inversion of the boiling temperatures of stereoisomers had been observed only upon replacement of two primary radicals by two secondary or two tertiary ones, which allowed some investigators to regard such inversion as an exceptional phenomenon. Thus, in the work cited above (^{2}) the opinion was expressed that the inversion of boiling temperatures in 1,4-diisopropylcyclohexanes (^{13}) and in 1,4-di-tert-butylcyclohexanes (^{14}) is associated with the special compactness of the corresponding side chains, and not with the manifestation of some fundamental property. However, the argument concerning the compactness of radicals is not confirmed by experiment, since inversion of boiling temperatures is observed in 1,4-dialkylcyclohexanes with such noncompact radicals as 1-ethylpropyl and 1-propylbutyl (^{5}). The results of the present work, showing that inversion can be caused even by replacement of methyl by ethyl, make it possible finally to discard the supposition of some decisive role of the compactness of side chains in the sequence of boiling temperatures of stereoisomers.

Experimental Part

Distillations. For the distillations two full-condensation rectification columns were used: column No. 1, with an efficiency of 25 theoretical plates and a glass packing, and column No. 2, with an efficiency of 100 theoretical plates and a metal packing. Distillations on column No. 2 were carried out in vacuo around the clock with a reflux ratio of 170–200. The distillate was collected in small fractions (3.5–7 ml each), and only those containing not less than 99.0% of the principal substance were taken for further work. Some differences

were obtained only during fractionation of a mixture of stereoisomeric 1-ethyl-4-tert-butylcyclohexanes.

Toluene was purified by converting it into *p*-toluenesulfonic acid, followed by reverse hydrolysis of the latter, and then by distillation on column No. 1. The starting ethylbenzene, obtained by alkylation of benzene with ethylene, was distilled on column No. 1.

n-tert-Butyltoluene and n-tert-butylethylbenzene were synthesized by alkylation of toluene and ethylbenzene with isobutylene at 0° in the presence of 93% sulfuric acid (15) and were distilled on column No. 2. In all, 146.5 g of n-tert-butyltoluene was obtained (67.8%, based on toluene) and 148.0 g of n-tert-butylethylbenzene (58.0%, based on ethylbenzene). Analysis of n-tert-butylethylbenzene:

Found, %:	C 88.75; 88.88;	H 11.05; 11.04
$C_{12}H_{18}$. Calculated, %:	C 88.89;	H 11.11

Oxidation of n-tert-butylethylbenzene was carried out with a chromic mixture. n-tert-Butylbenzoic acid was obtained, which melted at 164–166°; a mixed sample with an authentic specimen (m.p. 163.5–165.5°) melted at 164.5–166°.

Stereoisomeric 1-methyl-4-tert-butylcyclohexanes. Into a rotating autoclave were placed 133.1 g of n-tert-butyltoluene, and hydrogenation was carried out at 150° and an initial hydrogen pressure of 150 atm in the presence of platinized charcoal activated with chloroplatinic acid (16). To remove traces of aromatic hydrocarbons, the catalyst was chromatographed on silica gel. Fractionation of 127.1 g of the substance obtained on column No. 2 gave 34.9 g of trans- and 48.2 g of cis-1-methyl-4-tert-butylcyclohexanes (the remainder consisted of intermediate fractions).

Stereoisomeric 1-ethyl-4-tert-butylcyclohexanes. Hydrogenation of n-tert-butylethylbenzene (129.4 g) was carried out in the same way as in the preceding case. Fractionation of the hydrogenation product (116.9 g) was carried out on column No. 2 with a reflux ratio of 200 throughout the entire distillation. The boiling temperature from the beginning to the end of the distillation remained unchanged within the limits of measurement accuracy (~122°/58 mm). The distillate was collected in small portions; in all, 23 such portions were collected. Their n_D^{20} and d_4^{20} remained approximately constant only for the first three portions, then gradually decreased up to the end of the distillation. For spectroscopic investigation, the portions with the most different constants were taken, i.e., III and a mixture of XXII with XXIII (Table 1). It turned out that the 622 cm^{-1} line in III is much more intense than in XXII–XXIII. A series of lines that are intense in III also appears in XXII–XXIII, and vice versa.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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