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Abstract

Full Text

Chemistry

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On the Synthesis of Cyclopentyl- and Cyclohexyl-Substituted Mesitylenes

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As has been shown in a number of works on the synthesis of alkylcycloalkylbenzenes, the introduction of cyclopentyl and cyclohexyl groups into the aromatic ring through the reaction of cyclopentene and cyclohexene with aromatic hydrocarbons in the presence of anhydrous aluminum chloride proceeds in many cases smoothly and in good yield (1).

However, in the case of some alkylbenzenes aluminum chloride causes isomerization of the starting aromatic hydrocarbon.

As a result of the alkylation of mesitylene with cyclopentene, we obtained the trimethylcyclopentylbenzene described by us earlier (b.p. 100°/2 mm, $n_D^{20}1.5330$, $d_4^{20}0.9424$, solidifying to a glass at −45° (2)). This hydrocarbon was later obtained by the same method by Kanyan et al.; for it the authors give b.p. 138-139°/15 mm, $d_4^{20}0.943$ and $n_D^{20}1.5212$ (3).

A comparatively simple and quite reliable method for establishing the positions of substituents in monocyclic aromatic hydrocarbons with alkyl and cycloalkyl substituents is the method of spectral analysis using absorption spectra in the near ultraviolet region (4-6). In this connection, the better-studied methylated benzenes can serve as comparison hydrocarbons.

Fig. 1. Absorption spectra. *I* –durol (4), *II* –cyclopentylpseudocumene (5), *III* –cyclohexylpseudocumene (5), *IV* –cyclopentylmesitylene, *V* –cyclohexylmesitylene.

The absorption spectrum in the near ultraviolet region of the synthesized trimethylcyclopentylbenzene is shown in Fig. 1, *II**. From the similarity of

Fig. 2. Absorption spectra. I –isodurol (7), II –pentamethylbenzene (7)

Figure 2: Fig. 2. Absorption spectra. I –isodurol (7), II –pentamethylbenzene (7)

this spectrum to the spectrum of durol (Fig. 1, *I*) and its sharp difference from the spectrum from isodurol (Fig. 2, *I*) it may be concluded that, in this trimethylcyclopentylbenzene, the substituents are in positions 1, 2, 4, 5. Hence it follows that, in the interaction of cyclopentene with mesitylene in the presence of aluminum chloride, mesitylene is isomerized to 1,2,4-trimethylbenzene, and the cyclopentyl radical enters position 5. The trimethyldicyclopentylbenzene formed in the same synthesis was a viscous liquid with b.p. 159–160°/3 mm, n_D^{20}1.5540, and solidified at −10° to a glass.

The absorption spectrum of this hydrocarbon is shown in Fig. 3, *II*. As was to be expected, this spectrum has a noticeable resemblance to the spectrum of pentamethylbenzene (Fig. 2, *II*)*. Not being able to determine precisely the mutual arrangement of the substituents in the molecule of the aromatic hydrocarbon–trimethyldicyclopentylbenzene–we nevertheless consider the structure 1,2,4-trimethyl-3,5-dicyclopentylbenzene to be very probable for it.

Fig. 2. Absorption spectra. *I* –isodurol (7), *II* –pentamethylbenzene (7)

Expecting to obtain cyclopentylmesitylene without isomerization of the starting product, we carried out the alkylation of mesitylene with cyclopentene in the presence of concentrated sulfuric acid.

The starting mesitylene had b.p. 163.5°/740 mm, n_D^{20}1.4993, and d_4^{20}0.8651, which corresponds to the literature data for mesitylene (8). The alkylation of mesitylene was carried out with cyclopentene under cooling in the presence of concentrated sulfuric acid.

From the reaction products a substance was isolated with b.p. 100.5–101.5°/3 mm and 266–267°/755 mm, n_D^{20}1.5343, d_4^{20}0.9441, and m.p. −8.7°, with the formula (analysis) $C_{14}H_{20}$. In its properties the hydrocarbon obtained differs from the trimethylcyclopentylbenzene of the durol type of structure described above.

The absorption spectrum in the near ultraviolet region of this hydrocarbon (Fig. 1, *IV*) also differs sharply from the absorption spectrum of the previously

* The absorption spectra of all hydrocarbons described in the present work were studied with a "Uviflex" photoelectric spectrophotometer with quartz optics and with a specially introduced thermostatting chamber for cuvettes, analogous in principle of operation to the Beckman and SF-4 spectrophotometers. The hydrocarbons were examined at a temperature of 20° as equimolar solutions (0.00250 and 0.00350 g-mol/l) in spectrally pure isooctane–2,2,4-trimethylpentane).

obtained trimethylcyclopentylbenzene (Fig. 1, *II*) and has a great similarity to the spectrum of isodurol (Fig. 2, *I*).

Hence it follows that, upon condensation of mesitylene with cyclopentene in the presence of concentrated sulfuric acid, isomerization does not occur, and the synthesized hydrocarbon is cyclopentylmesitylene (1,3,5-trimethyl-4-cyclopentylbenzene).

The residue boiling above 270° upon distillation over metallic sodium boiled within the range 155–160° at 3 mm. On standing, this product crystallized. After several recrystallizations from ethyl alcohol, a white crystalline substance with m.p. 63.7° was obtained. This solid hydrocarbon must have the structure of dicyclopentylmesitylene, or 1,3,5-trimethyl-2,4-dicyclopentylbenzene.

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* The different character of the substituting groups in trimethyldicyclopentylbenzene and in pentamethylbenzene, and their investigation on spectral instruments with different resolving power, affected the intensities of the maxima in the absorption spectra of these compounds.

The absorption spectrum in the near ultraviolet region of this hydrocarbon is shown in Fig. 3, *IV*. In appearance, position, and intensity this spectrum differs little from the absorption spectrum of 1,2,4-trimethyl-3,5-dicyclopentylbenzene (Fig. 3, *II*).

To obtain cyclohexylmesitylene, the alkylation reaction of mesitylene with cyclohexene was carried out in the presence of anhydrous aluminum chloride. The reaction was conducted with ice cooling.

The hydrocarbon isolated from the products of this reaction had b.p. 119—120°/2 mm, n_D^{20}1.5309, d_4^{20}0.9384, and freezing point $-19°$ in glass. The hydrocarbon previously obtained in an analogous way by Bodroux had b.p. 283—284°, n_D^{20}1.535, and d_4^{20}0.946 (^{9}), which is close to our data.

From the higher products of the reaction we carried out, a crystalline substance was isolated with m.p. 148°, not previously described in the literature, corresponding in its composition to the formula $C_{21}H_{32}$ (analysis).

The considerable similarity of the absorption spectrum in the near ultraviolet region of the liquid hydrocarbon (Fig. 1, *III*) to the spectrum of durol (Fig. 1, *I*) indicates that the interaction of cyclohexene with mesitylene in the presence of anhydrous aluminum chloride, even under cooling, proceeds with isomerization of mesitylene, quite analogously to the same reaction with cyclopentene.

The hydrocarbon synthesized is 1,2,4-trimethyl-5-cyclohexylbenzene.

In connection with the structure established for the liquid hydrocarbon, for the solid hydrocarbon (m.p. 148°) the most probable structure is 1,2,4-trimethyl-3,5-dicyclohexylbenzene. The absorption spectrum of this hydrocarbon is shown in Fig. 3, *I*.

Fig. 3

Figure 3: Fig. 3

Fig. 3. Absorption spectra. *I* —dicyclohexylpseudocumene (5), *II* —dicyclopentylpseudocumene, *III* —dicyclohexylmesitylene, *IV* —dicyclopentylmesitylene

In order to obtain non-isomerized reaction products, the condensation of cyclohexene with mesitylene was carried out in the presence of concentrated sulfuric acid at molar ratios mesitylene : cyclohexene : sulfuric acid = 2 : 1 : 2, with ice cooling.

From the reaction products a substance was isolated with b.p. 107—108°/2 mm, n_D^{20}1.5320, d_4^{20}0.9402, and freezing point 13.2° (in crystals). Its composition corresponded to the formula $C_{15}H_{22}$ (analysis).

In its properties the indicated hydrocarbon differs from the previously described cyclohexylpseudocumene.

The absorption spectrum of this compound (Fig. 1, *V*) has a great similarity to the spectrum of cyclopentylmesitylene (Fig. 1, *IV*). For the latter compound, an isodurol type of structure was established above; whence it follows that the structure of the synthesized hydrocarbon corresponds to 1,3,5-trimethyl-2-cyclohexylbenzene.

Thus, in the condensation of mesitylene with cyclohexene in the presence of concentrated sulfuric acid, isomerization does not occur, which is analogous to the same reaction with cyclopentene.

From the high-boiling fraction of the products of the described reaction was iso-

fraction with b.p. ~180-185°/3 mm, which distilled as a thick mass and crystallized on standing, was separated by distillation over metallic sodium. After several recrystallizations from alcohol, a substance crystallizing in the form of small needles with m.p. 127.8° was isolated. For it the composition $C_{21}H_{32}$ was found (analysis).

This solid hydrocarbon must have the structure of dicyclohexylmesitylene or 1,3,5-trimethyl-2,4-dicyclohexylbenzene.

The absorption spectrum of this hydrocarbon is shown in Fig. 3, *III*. The melting points of cyclopentylmesitylene, dicyclopentylmesitylene, cyclohexylmesitylene, and dicyclohexylmesitylene were determined by the thermographic method by N. I. Lyashkevich, to whom we express our gratitude.

A. P. Bogomolova took part in the work.

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