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Abstract

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INVESTIGATION OF ISOMERIC OCTALINS

Octalins have attracted the attention of many investigators. Hückel, in his well-known works on the stereochemistry of bicyclic compounds, obtained and studied all the isomeric octalins. Turova-Polyak described the irreversible catalysis of trans-Δ-2,3-octalin over palladized asbestos (^{1}), and Linstead and co-workers investigated the disproportionation of the same hydrocarbon and of Δ-9,10-octalin in the presence of platinum and palladium catalysts (^{2}). The interaction of octalins with various oxidizing agents has been described repeatedly. Thus, ozonization of Δ-9,10-octalin under certain conditions leads to cyclodecanedione-1,6 ($^{3-5}$)—the starting product for the synthesis of the simplest azulene. Reduction of cyclodecanedione gave cyclodecanediol-1,6 (^{5}). This same diol was synthesized via octalin oxide, obtained by oxidation of Δ-9,10-octalin with hydrogen peroxide in formic acid (^{6}). Earlier, octalin oxide had been obtained by oxidation of the same hydrocarbon with benzoyl peroxide (^{3,7}). Octalins have been used in alkylation reactions (^{8}), acylation (^{9}), hydroformylation (^{10}), and others.

A large place in work on octalins is occupied by methods for their preparation and identification. In many cases synthesis gives mixtures of isomers that differ little from one another in properties. The difficulties in separating such mixtures have not always been overcome, as is evidenced by discrepancies in the properties of the same octalins described by different authors. As yet, there is no general method for the analysis of octalins. For the identification of octalins, nitrosochlorination and oxidation have until recently been used chiefly. The nitrosochloride of Δ-9,10-octalin (9-chloro-10-nitrosodecalin) consists of blue crystals with m.p. 91°; it can be obtained in good yield, and it is easily separated by dissolution in acetone from the white nitrosochlorides of cis-Δ-2,3- and Δ-1,9-octalins that are formed simultaneously in small amounts. These products melt with decomposition: the first at 186°, and the second, depending on the rate of heating, at about 121–135 or 142–143°.

Often, for the identification of octalins, their oxidation to the corresponding carboxylic acids is used, followed by determination of the melting points of the acids. To study the structure of cis-Δ-1,2- and Δ-1,9-octalins, oxidative hydrolysis of complexes of these hydrocarbons with osmium tetroxide was employed, leading to the formation of crystalline decalin-diols (^{11,12}). To determine the position of the double bond in Δ-9,10-octalin, this hydrocarbon was oxidized to octalin oxide, and the oxide was hydrated to the corresponding glycol, which was then dehydrated with formation of hexalin (7).

Spectral methods have been used comparatively little for the study of octalins. Cope recorded the infrared spectra of cis- and trans-Δ-1,2-octalins, as well as of Δ-1,9- and Δ-9,10-octalins (12). Sakuiro Kimura studied the spectra of cis-Δ-2,3-octalin in the ultraviolet region (13), and Kohlrausch—the combination-scattering spectra of trans-Δ-2,3-octalin (14). Hückel and Fech-

Tih identified Δ-1,9- and Δ-9,10-octalins in their mixture by means of the ultraviolet spectra of their iodine complexes (15).

In the present work, the Raman spectra of cis-Δ-2,3-octalin, Δ-9,10-octalin, and mixtures of Δ-1,9- and Δ-9,10-octalins were studied.

Experimental Part

The starting material for obtaining the octalins was cis-cis-decalol-2, m.p. 103°, isolated from a mixture of isomers by filtration and recrystallized from ligroin. Cis-Δ-2,3-octalin was prepared by dehydration of this decalol, while Δ-9,10-octalin was obtained as a result of the isomerization occurring during dehydration. The formation of Δ-9,10-octalin upon dehydration of a mixture of decalols in the presence of zinc chloride was shown by Hückel (3). Linstead obtained this hydrocarbon by dehydration of trans-decalol-2 in the presence of a mixture of orthophosphoric acid and phosphorus anhydride (16). At the same time it was shown that trans-Δ-2,3-octalin is readily isomerized with formation of Δ-9,10-octalin.

To obtain Δ-9,10-octalin, we gradually heated a mixture of 200 g of cis-cis-decalol-2 and 70 g of orthophosphoric acid, with mechanical stirring, to 200°, with continuous distillation of the reaction products. A total of 106 g (61%) of hydrocarbons was obtained; to remove unreacted decalol, these were boiled for 2 h over sodium. The isolated product was distilled over sodium and had: b.p. 188–189° (767 mm), d_4^{20} 0.9076, n_D^{20} 1.4940, and molecular weight 134. By the action of isoamyl nitrite and hydrochloric acid at −10°, 2.3 g (31%) of nitrosochlorides was obtained from 5.5 ml of substance. From these, with the aid of acetone, 0.1 g of white crystals with m.p. 125–127° and 2 g of blue crystals with m.p. 90° were isolated. The data obtained indicate that, under the experimental conditions, the Δ-2,3-octalin formed is partially converted into Δ-9,10- and Δ-1,9-octalins.

Pure Δ-9,10-octalin was isolated from the resulting mixture of octalin isomers through the nitrosochlorides. From the blue crystals accumulated in a series of experiments and recrystallized from acetone, 18 ml of octalin was obtained by decomposition according to Hückel (3). The purified product distilled over sodium at 193.5–195° (758 mm). It had: d_4^{20} 0.9170, n_D^{20} 1.4992, and an aniline point (1 : 1) below −30°. Preliminary determinations showed that the solubility of the blue nitrosochlorides is 1 part in 10 parts of acetone, and that of the white ones is correspondingly 1 part in 1000 parts of acetone. Consequently, the content of its isomers in the Δ-9,10-octalin does not exceed 1–2%.

To obtain cis-Δ-2,3-octalin, we first studied the dehydration of decalol in the presence of the cation-exchange resin KU-2 (hydrogen form). It is known that, in a number of cases, reactions of organic compounds over KU-2 proceed selectively, without formation of by-products.

The dehydration experiments were carried out by heating decalol with 20–30% KU-2 at temperatures of 140–170° for 2–3 h. The maximum yield of octalin in these experiments (55% of theory) was obtained by 3-hour heating of decalol with 30% KU-2 at 165–170°. The octalin, freed from decalol, boiled over sodium at 191.5–194° (766 mm) and had n_D^{20} 1.4975. From 5.5 ml of octalin, 1 g (14%) of nitrosochlorides was obtained, from which, with the aid of acetone, 0.8 g of blue crystals with m.p. 91° and 0.2 g of white crystals with m.p. 124–125° were isolated. Consequently, during dehydration of cis-cis-decalol-2 in the presence of KU-2, partial isomerization of the cis-Δ-2,3-octalin formed into Δ-1,9- and Δ-9,10-octalins occurs, and this method is unsuitable for obtaining pure cis-Δ-2,3-octalin intended for recording spectra. Subsequently we turned to the known method of dehydrating decalol in the presence of 200% freshly fused potassium bisulfate. The mixture was rapidly heated with mechanical stirring to 190–195°, with continuous distillation of the reaction products. After dehydration and remo-

of decalone, octalin was obtained (77.5% of theory), which distilled at 190–192° (770 mm). It had: d_4^{20} 0.9152, n_D^{20} 1.4967, an aniline point (1:1) equal to −3°. From 5.5 ml of the product, 0.4 g of slightly bluish nitrosochlorides was obtained. After washing them with acetone, white crystals with m.p. 176° were obtained. It was not possible to isolate blue nitrosochlorides from the acetone solution because of their insignificant content. On oxidation of a sample of octalin with an alkaline solution of potassium permanganate, a crystalline product with m.p. 159° was obtained, which corresponds to the m.p. of cis-cyclohexanediacetic acid-1,2. It may be considered that the cis-Δ-2,3-octalin prepared contains only traces of Δ-9,10-octalin.

We obtained Raman spectra of Δ-9,10-octalin, cis-Δ-2,3-octalin, prepared by the method described, and also of mixtures of Δ-1,9- and Δ-9,10-octalins obtained by dehydration of cis-cis-decalol-2 in the presence of orthophosphoric acid.

For obtaining and processing the spectrograms, standard methodology and apparatus were used: an ISP-51 spectrograph with a 270-mm camera, a vessel for recording spectra of 8 ml volume, and an IZA-2 comparator. All photographs were taken with strictly identical exposure and under one and the same lamp-burning regime.

Table 1

Frequencies of Raman lines of octalins (in cm^{-1})

Δ-9,10-octalin	cis-Δ-2,3-octalin	Δ-1,9- and Δ-9,10-octalins	Δ-9,10-octalin	cis-Δ-2,3-octalin	Δ-1,9- and Δ-9,10-octalins
316 (1)	316 (1)	318 (1)	1043	1046	1045
sh360	sh355	sh357	(1)1078	(5)1072 (6)	(3)1079 (4)
(0)418	(0)376	(0)375	(7)1098	f1109 (3)	f1107 (3)
(8)456	(6)382	(1)385	(4)1132 (3)	f1130 (3)	f1128 (1)
(1)509	(6)420 (2)	(1)418	f1182	f1158 (3)	f1180 (5)
(2)542	df475	(6)473	(8)1261	f1177 (4)	f1220
(2)620	(2)497	(1)498	(1)1270	f1200	(2)1243 (3)
(0)675	(2)538	(1)511	(7)1356	(0)1221	f1266 (5)
(8)808	(0)573	(1)540	(2)1375	(3)1240 (5)	f1332 (2)
(3)830	(3)648	(1)579	(3)1434	f1254 (5)	f1345 (3)
(4)884	(1)664	(1)599	(10)1449	f1266 (5)	f1357
(7)895	(4)694	(2)676	(6)1464	f1288	(2)1378
(4)988 (6)	(3)728	(5)728	(6)1684	(2)1332 (4)	(1)1438
	(6)774	(3)748	(10)2838286029322941	f1372 (1)	(10)1451
	(5)834	(4)772		f1442 (10)	(8)1656
	(0)846	(1)809		sh1652	(1)1672
	(3)872	(0)833		(8)1686	(2)1686
	(2)881	(0)859		(2)2838ff29383022	(7)28352858289829383022
	(2)896	(3)886			
	(3)935	(4)896			
	(0)966	(2)933			
	(4)986 (3)	(0)965			
		(0)988			
		(3)1014 (1)			

Table 1 gives the frequencies of the Raman lines; in parentheses are the visually estimated intensities on a 10-point scale. The line intensities in the spectrum of each compound were estimated relative to the line at 1684 cm^{-1} in the spectrum of Δ-9,10-octalin, whose intensity was taken as 10 units. The intensity of lines located in the region of the stretching-vibration frequencies of the C—H bond was not estimated.

It is evident from the table that in the spectrum of Δ-9,10-octalin, in the frequency region of the stretching vibrations of the C=C bond, there is one intense line at about 1684 cm^{-1}; in the spectrum of cis-Δ-2,3-octalin there is an intense line with a frequency of 1652 (8) cm^{-1} and a less intense line with a frequency of 1685(2) cm^{-1}. In the mixture of Δ-9,10- and Δ-1,9-octalins three lines are observed, with frequencies 1656(1), 1672(2), and 1686 (7) cm^{-1}.

Taking into account the sensitivity of the method of combination light scattering, as well as the fact that the Δ-9,10-octalin obtained by us could not contain more than 1-2% of other isomers, it may be considered with great confidence that impurity lines are absent from the spectrum of Δ-9,10-octalin. This is also confirmed by the comparatively small number of lines in the spectrum of this compound.

In the spectrum of cis-Δ-2,3-octalin, frequencies of Δ-9,10-octalin may be present, since, during the isolation of nitroso chlorides from cis-Δ-2,3-octalin, traces of the nitroso chlorides of Δ-9,10-octalin were obtained. In the spectrum of the mixture, the lines of all three isomers appear.

Taking all that has been said into consideration, the frequencies of the stretching vibrations of the C=C bond obtained for the compounds studied may be assigned in the following way.

The frequency of the stretching vibration of the C=C bond equal to 1684 cm^{-1} pertains to Δ-9,10-octalin, the frequency 1672 cm^{-1} to Δ-1,9-octalin, and the frequency 1652 cm^{-1} to cis-Δ-2,3-octalin.

On the basis of the obtained frequencies of the vibrations of the C=C bond of the octalins studied, it may be considered that the 9,10 bond is stronger than the 1,9 bond, and the 1,9 bond is stronger than the 2,3 bond.

This conclusion is in agreement with the phenomenon observed by us of the isomerization of cis-Δ-2,3-octalin into Δ-1,9- and Δ-9,10-octalins. Cases of reverse isomerization are unknown.

In the spectrum of Δ-9,10-octalin there is an intense line at about 675 cm^{-1}, absent from the spectrum of cis-Δ-2,3-octalin. In the mixture the intensity of this line is considerably reduced. Evidently this line is characteristic of Δ-9,10-octalin. The lines 418 and 830 cm^{-1} also stand out by their intensity in the spectrum of Δ-9,10-octalin.

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