[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Dehydration of *cis*- and *trans*-2-Phenylcyclohexanols

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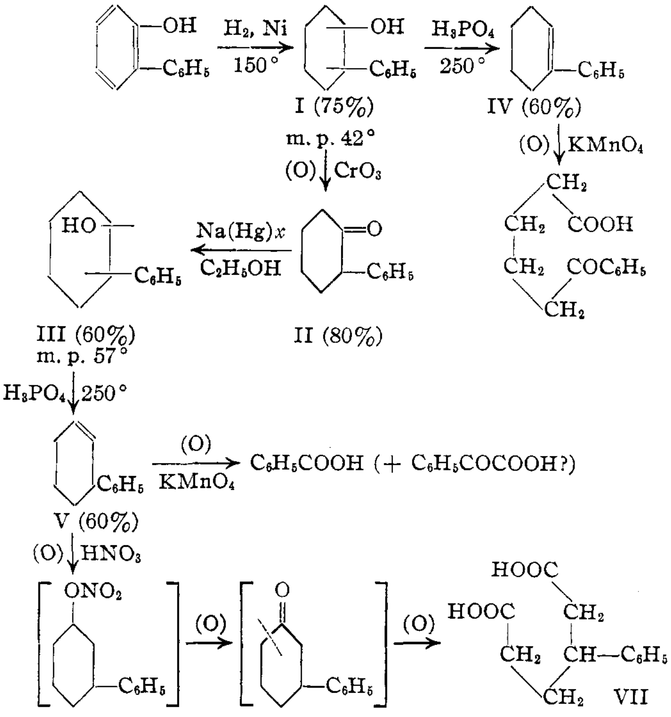
An investigation of the dehydration of *cis*- and *trans*-2-phenylcyclohexanols has been undertaken in order to obtain further evidence concerning the *trans*-elimination of water in such reactions. Vavon and Barbier[1] have observed that *cis*-2-alkylcyclohexanols are more easily dehydrated thermally or chemically than their *trans*-isomers, indicating that hydroxyl and hydrogen are more readily removed as water when they are in the *trans*-positions. They did not, however, determine the nature of the olefin formed in each case; it was with this purpose in view that the dehydration of the 2-phenylcyclohexanols has been investigated.

Only one of these two alcohols previously has beeen characterized and identified. From the catalytic reduction of *o*-phenylphenol with a nickel catalyst at temperatures above 200°, von Braun, Gruber and Kirschbaum[2] obtained a mixture of phenylcyclohexanol, cyclohexylcyclohexanol, cyclohexylbenzene and bicyclohexyl. The two alcohols were separated by oxidation to the ketones and subsequent reduction by sodium and alcohol; the 2-phenylcyclohexanol melted at 54–55°. Bedos[3] treated cyclohexene oxide with phenylmagnesium bromide and obtained a poor yield of a liquid which he suggested was a stereoisomer of the alcohol above, although it gave the same phenylurethan and phthalate. Cook, Lawrence and Hewitt,[4] however, pointed out that Bedos' alcohol may be contaminated by products of ring contraction. Using phenyllithium they obtained excellent yields of the alcohol, melting at 56–57° and identical with that reported by von Braun, Gruber and Kirschbaum.[2]

By the hydrogenation of *o*-phenylphenol with Raney nickel catalyst at 150° we have obtained an excellent yield of 2-phenylcyclohexanol melting at 41–42°. Since the compound crystallized only on standing for several days, the "viscous liquid" described by Ranedo and Leon[5] from a similar hydrogenation using platinum black in the cold may have been a slightly less pure sample of this isomer. The fact that this low-melting isomer has the *cis*-configuration is indicated by its method of preparation.[6]

Oxidation of the new low-melting *cis*-2-phenylcyclohexanol (I) with chromic acid yielded 2-phenylcyclohexanone (II) which was reduced to the high-melting isomer (III) by sodium amalgam and ethanol.



Dehydration of these two phenylcyclohexanols with phosphoric acid or anhydride gave chiefly 1-phenylcyclohexene (IV) from the *cis*-isomer (I) and 3-phenylcyclohexene (V) from the *trans* (III), another example of the well-known fact

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[1] Vavon and Barbier (*Bull. soc. chim.*, [4] **49**, 567 (1931)) and Hückel and Neunhoeffer (*Ann.*, **477**, 135 (1930)) found that *cis*-2-cyclohexylcyclohexanol was dehydrated readily to Δ^1-cyclohexylcyclohexene while the *trans*-isomer was dehydrated with difficulty to give this same olefin contaminated by a small amount of an isomer which they suggested was Δ^1-hexahydrobenzylcyclopentene. A similar study with *trans*-2-methylcyclohexanol[8] gave no evidence for such a ring contraction, but the formation of both Δ^1- and Δ^2-methylcyclohexenes was demonstrated.

[2] Von Braun, Gruber and Kirschbaum, *Ber.*, **55**, 3668 (1922).

[3] Bedos, *Compt. rend.*, **177**, 111 (1923); *Bull soc. chim.*, **39**, 292 (1926).

[4] Cook, Lawrence and Hewitt, *J. Chem. Soc.*, 71 (1936).

[5] Ranedo and Leon, *Añales soc. espan. fis. quim.*, **22**, 222 (1924).

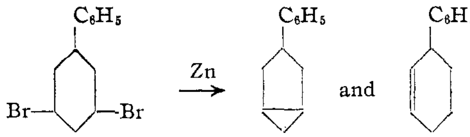
[6] See, *e. g.*, Vavon, *Bull. soc. chim.*, **41**, 1401 (1925); Bourguel, *Compt. rend.*, **180**, 1753 (1925); **187**, 383 (1928); Aronstein and Holleman, *Ber.*, **22**, 1181 (1899); Ott, *ibid.*, **61**, 2124 (1928).

that elimination to form a multiple link takes place most readily when the elements lost are *trans* to each other.[7]

In each case a small amount of the isomeric cycloölefin was obtained (Table I). In the second case (III) this could not have been due to isomerization after dehydration since the olefin (V) was unaffected when refluxed with phosphoric acid. The formation of a mixture must therefore be due either to the fact that some of the alcohol was isomerized before dehydration occurred or else *cis*- and *trans*-elimination must be competitive reactions; the first possibility seems the more likely.

The results differ somewhat from those with *trans*-2-methylcyclohexanol,[8] which gave nearly equivalent amounts of the two possible isomeric olefins. The *cis*-isomer of this compound has not yet been studied.

Of the two olefins above only 1-phenylcyclohexene (IV) has been reported previously in the literature.[9] Uspenski,[10] however, found that the treatment of 3,5-dibromo-1-phenylcyclohexane (VIII) with zinc yielded an olefin as well as the expected bicyclo compound. This olefin is identical in physical properties with the 3-phenylcyclohexene (V) above and is also similar in that no satisfactory products were obtained by permanganate oxidation (Uspenski obtained benzoic acid; we obtained benzoic, and possibly benzoylformic, acids).



VIII V

Oxidation of 3-phenylcyclohexene with dilute nitric acid gave a good yield of β-phenyladipic acid (VII). The formation of this acid was rather surprising; evidently the nitric acid attacks the double bond first by addition as indicated above.

Experimental

***cis*-2-Phenylcyclohexanol** (I).—*o*-Phenylphenol[11] was treated with hydrogen and Adams platinum catalyst in alcohol at 3–4 atmospheres at temperatures up to 70° but no hydrogen was absorbed.[5] When 680 g. of *o*-phenylphenol in 400 cc. of alcohol was treated with hydrogen at 135 atmospheres and 140–150° in the presence of Raney nickel until the theoretical amount of hydrogen had been absorbed, the product washed with 5% sodium hydroxide and distilled, 480 g. (75%) of *cis*-2-phenylcyclohexanol was obtained as a colorless, viscous oil, crystallizing after standing several days, b. p. 140–141° (16 mm.), m. p. 41–42°.[12]

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.14. Found: C, 81.44; H, 9.42.

Acidification of the alkaline extract above yielded 40 g. of starting material.

The **phenylurethan** was recrystallized readily from petroleum ether, m. p. 127.5–128°.

Anal. Calcd. for $C_{19}H_{21}O_2N$: N, 4.75. Found: N, 4.77.

Mixed with the phenylurethan from the *trans*-isomer (m. p. 136–137°) the melting point was 110–125°.

2-Phenylcyclohexanone (**II**).—The oxidation of the *cis*-cyclohexanol (I) was carried out by a modification of the method used by Cook, Lawrence and Hewitt.[4] To a solution of 31 g. of I in 50 cc. of glacial acetic acid, 14 g. of chromic oxide in 50 cc. of 80% acetic acid was added dropwise with vigorous stirring so that the temperature did not rise above 50°. After standing at room temperature for twenty-four hours, the mixture was poured into 250 cc. of water and extracted with one 200-cc. and two 100-cc. portions of benzene. The combined extracts were washed with sodium bicarbonate and with water, dried and distilled. The yield of 2-phenylcyclohexanone (II) was 25 g. (80%); b. p. 155–160° (16 mm.); m. p. 52.5–54.5°. The pure ketone melts at 63°[2,13]; the product reported by Cook, Lawrence and Hewitt[4] melted at 50–53°. The low-melting products are undoubtedly contaminated by a small amount of the unoxidized alcohol. The **semicarbazone** melted at 189–190°.[2,13]

***trans*-2-Phenylcyclohexanol** (**III**).—The ketone (II, 25 g.) was reduced by shaking with 433 g. of sodium amalgam (10 g. of sodium) in 175 cc. of alcohol for several hours. The mixture was partially evaporated, diluted with water and extracted with ether. The ether was washed, dried and distilled, yield, 15 g. (60%) of III, b. p. 152–155° (16 mm.), m. p. 52–54°. Recrystallized from petroleum ether, it melted at 56–57°.[2,4]

The **phenylurethan** had a melting point of 136–137°, in agreement with reports by other investigators.[2,3,4]

Dehydration.—Dehydration of the two alcohols was accomplished by refluxing with an equal weight of sirupy phosphoric acid for four hours. Ether and water were added and the ether washed, dried and distilled under diminished pressure. The composition of the fractions boiling from 115–130° (16 mm.) was determined by refractive index. These results are summarized in Table I. The physical constants of the purest samples of the two olefins are recorded in Table II.

One dehydration using phosphoric anhydride gave results very similar to those with phosphoric acid. The

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[7] Michael, *Ber.*, **34**, 4225 (1901); Pfeiffer, *Z. physik. Chem.*, **48**, 40 (1904); Chavanne, *Bull. soc. chim. Belg.*, **26**, 287 (1912); **28**, 234, 240 (1914); Van der Walle, *ibid.*, **27**, 209 (1913); **28**, 369 (1914).

[8] Price, THIS JOURNAL, **61**, 1847 (1939).

[9] Sabatier and Mailhe, *Compt. rend.*, **138**, 1323 (1904).

[10] Uspenski, *J. Russ. Phys.-Chem. Soc.*, **51**, 245 (1920).

[11] Dow Chemical Company, Midland, Michigan.

[12] All melting points are corrected.

[13] Le Brazidec, *Compt. rend.*, **159**, 774 (1914).

TABLE I

DEHYDRATION OF *cis*- AND *trans*-2-PHENYLCYCLOHEXANOLS

	% Yield from					
	cis-Isomer			*trans*-Isomer		
Product	Expt. 1	2	3[a]	4	5	6
1-Phenylcyclohexene (IV)	61.8	56	62	17.5	10	15.9
3-Phenylcyclohexene (V)	16.8	14.9	8.9	58.5	61	68.2

[a] Phosphoric anhydride.

TABLE II

PHYSICAL CONSTANTS OF 1- AND 3-PHENYLCYCLOHEXENES

	B. p. °C.	B. p. Mm.	n^{20}_D	d^{20}_4	M^{20}_D (calcd. 51.36)
1-Phenyl- (IV)	126-128	16	1.5670	0.9939	51.95
1-Phenyl-[9]	128	16	1.569 (14°)	.9939	
3-Phenyl-[a]	115-117	16	1.5530	.9800	51.62
3(?)-Phenyl-[10]	101	9.5	1.5528	.9801	51.60

[a] *Anal.* Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.81; H, 9.32.

dehydration mixture was heated so that the product would distil at 16 mm. This crude olefin was washed, dried and redistilled as above.

3-Phenylcyclohexene (V, 1 g., n^{20}_D 1.5528) and 1 g. of phosphoric acid were refluxed for four hours and 75% of the hydrocarbon was recovered unchanged (n^{20}_D 1.5529), indicating that the dehydration conditions are not sufficient to cause isomerization of the double bond, in spite of the fact that in this case the isomer should be more stable due to conjugation. This conjugation, incidentally, leads to a slight exaltation in the molecular refraction for the 1-phenylcyclohexene (Table II).

Oxidation of 1-Phenylcyclohexene (IV).—Five grams of (IV) and 10 g. of potassium permanganate were stirred for twenty-four hours, initially at 0° but gradually warming to room temperature. Filtration and acidification gave an acid which was recrystallized from water as plates, 2 g., m. p. 75–76°. This corresponds to δ-benzoylvaleric acid (VI), the expected product. Its semicarbazone melted at 183–185°.[4,14]

Oxidation of 3-Phenylcyclohexene (V).—This hydrocarbon (4.75 g.) was refluxed with 100 cc. of 5% nitric acid for six days with the addition of a total of 7 cc. of concentrated nitric acid at intervals. On cooling, 3 g. of solid acid was obtained. Recrystallization from water gave β-phenyladipic acid (VII), m. p. 147–148°.[15] The permanganate (20.7 g.) oxidation of this olefin (4.5 g.) was not very satisfactory. Only benzoic acid precipitated on acidifying the filtrate. Semicarbazide gave a semicarbazone melting at 178–180° (the mixture with the semicarbazone of benzoylvaleric acid melted below 110°), which was hydrolyzed to an acid melting at 64–65° (benzoylformic acid is reported as melting at 66°).[16]

Summary

cis-2-Phenylcyclohexanol has been prepared in 75% yield by hydrogenation of *o*-phenylphenol.

Oxidation of this alcohol with chromic acid is an easy and economical method for the preparation of 2-phenylcyclohexanone.

cis-2-Phenylcyclohexanol and the *trans*-isomer yield chiefly 1- and 3-phenylcyclohexene, respectively, on dehydration, products corresponding to the *trans*-elimination of the elements of water in each case.

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[14] Von Auwers and Treppmann, *Ber.*, **48**, 1217 (1915), report a melting point of 77–78° for the acid and 187° for the semicarbazone.

[15] Case, THIS JOURNAL, **55**, 2927 (1933), reported α-phenyladipic acid, m. p. 132–133°. Manske, *ibid.*, **53**, 1104 (1931), gives the melting point of β-phenyladipic acid as 146°. We found the neutral equivalent to be 109 (calcd.: 111).

[16] Claisen, *Ber.*, **10**, 431 (1877); Bougault, *Ann. chim.* [9], **5**, 341 (1916), reported the melting point of the semicarbazone as 200°, dec.