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THE ISOMERS OF 4-PHENYL- AND 4-CYCLOHEXYL-CYCLOHEXANOL

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The preparation and determination of configuration of the geometric isomers has been carried out only for a few simple 4-substituted alkyl cyclohexanols (1, 2, 3, 4). All of these are liquids. The similarity of the physical properties of the liquid isomers makes it difficult to ascertain the purity of a given preparation or to estimate the composition of mixtures of isomers. Since a pure liquid compound can be obtained with certainty only by regeneration from solid derivatives, unstable forms which might be present are lost. The present study was undertaken with the aim of preparing solid cyclohexanols which could be studied singly or in mixtures, before and after regeneration from derivatives.

The starting materials for this investigation, 4-phenyl- and 4-cyclohexylcyclohexanone, were obtained by oxidation of crude cyclohexanol mixtures and purified by regeneration from their oximes.

A mixture of 4-cyclohexylcyclohexanols is the main product when *p*-hydroxydiphenyl is hydrogenated at 210° (200 atm.) over Raney nickel catalyst. If the reduction is carried out at 140–170° in the presence of a small amount of the sodium salt of *p*-hydroxydiphenyl, the formation of the 4-phenylcyclohexanols is favored (5, 6).

Reduction of 4-phenylcyclohexanone with sodium and alcohol yields a nearly pure alcohol (I) melting at 117.2–118.5° which is identical with the substance isolated in this laboratory some time ago (5) and with the product of Musser and Adkins (7). The hitherto unknown isomer (II), m.p. 76–77°, is formed in good yield by the hydrogenation of this ketone with Raney nickel catalyst at room temperature under a slight pressure of hydrogen. The hydrogenation of this ketone with platinum catalyst in acetic acid solution is particularly unsatisfactory because of side reactions which affect the benzene ring and the hydroxyl group.

The product obtained by reducing 4-cyclohexylcyclohexanone with sodium and alcohol melts at 103–104° (III). It is identical with the "*cis*"-alcohol of Schrauth and Görig (10) and others (11) and with the cyclohexylcyclohexanol of Musser and Adkins (7, 5). The isomeric cyclohexanol (IV) cannot be separated directly from the mixture which results when the ketone is reduced with Raney nickel or platinum catalyst at room temperature. It is obtained by fractional crystallization of the dinitrobenzoates and hydrolysis of the pure ester, and melts at 92–93°. The compound described in the literature melting at 83–84° (10, 11) must be regarded as a mixture of isomers.

Since an absolute method for determining configuration is not available for 4-alkyl- and 4-aryl-cyclohexanols, the structures of the isomers in this series are assigned on the basis of methods of formation, physical properties, reaction rates, and isomerization studies.

The phenylcyclohexanol (I), m.p. 118–118.5° (after purification) is assigned the *trans*-configuration because of its method of formation (8) and because it is obtained from the *cis*-isomer (II), m.p. 76–77° by inversion with sodium at 200° (9). The *trans*-alcohol (I) shows a larger molecular weight in ethylene bromide than the isomer (II) (Fig. 4) which is in agreement with the generalization established by Hückel (17). The concentration dependency, on the other hand, appears to be reversed, since the molecular weight of the *cis*-alcohol (II) increases more rapidly with concentration than that of the alcohol (I). Abnormalities in the concentration dependency of the molecular weights of other cyclohexanols have been observed by Hückel and have been ascribed to the solvent (18). The small solubilities of the compounds unfortunately prevented the determination of the molecular weights in other solvents.

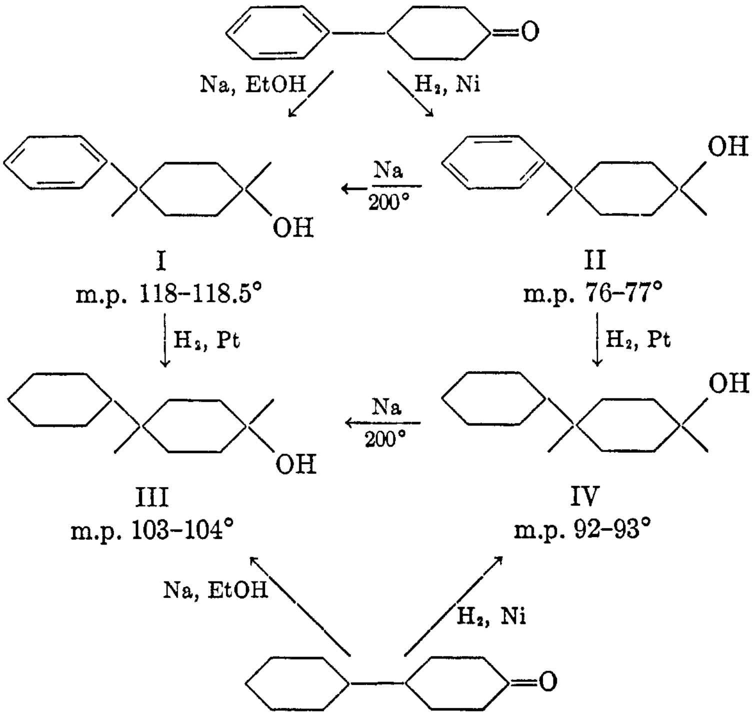

Fig. 1

The *trans*-configuration of the 4-cyclohexylcyclohexanol (III), m.p. 103–104°, is based upon its preparation from 4-cyclohexylcyclohexanone by reduction with sodium and alcohol (8). It is formed in good yield also from the *cis*-isomer (IV), m.p. 92–93°, by inversion with sodium (9) and its 3,5-dinitrobenzoate is saponified more easily than that of the *cis*-alcohol (IV) (12). The configuration of the *cis*-alcohol (IV) follows from its formation by catalytic hydrogenation of the corresponding ketone with platinum in acetic acid solution. The cryoscopic behavior of the 4-cyclohexylcyclohexanols parallels that of the 4-phenylcyclohexanols.

The pure phenylcyclohexanols have been converted to the corresponding cyclohexylcyclohexanols by hydrogenation with Adams' catalyst in acetic acid solution. The relationship of the compounds is given in Figure 1. The *cis*-alcohol (II) is hydrogenated nearly twice as fast as the isomer (I) (Fig. 2), the reaction continues after the aromatic ring is saturated, and the hydroxyl group is eliminated quantitatively to give dicyclohexyl. The rate of hydrogenolysis is greater for the *cis*-alcohol (IV) than for the *trans*-isomer (III) (Fig. 3). A similar relationship has been observed by Chiurdoglu in the hydrogenolysis of the 1,2-dialkylcyclopentanols (13) and the 1,2- 1,3- and 1,4-dialkylcyclohexanols (14). The alcohol with *cis*-configuration of hydroxyl and the second alkyl group is reduced more rapidly than its isomer.

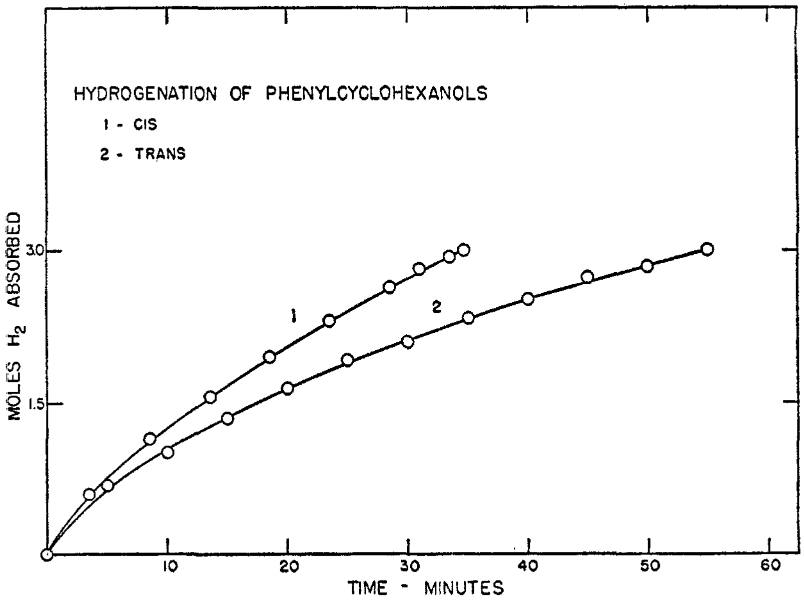

FIG. 2

The cyclohexanol mixtures which are obtained from the reduction of 4-phenyl- and 4-cyclohexyl-cyclohexanone have been found to correspond to mixtures of pure *cis*- and *trans*-isomers by comparison with the melting point-composition diagrams. It is particularly interesting to note that mixtures resulting from the reduction of the ketones with Raney nickel at room temperature correspond to eutectic points in the melting point diagrams.

Chromatographic adsorption on alumina has been found useful for the purification of both pairs of isomers although a complete separation by this method has succeeded only with the phenylcyclohexanols. The *trans*-alcohol in each case is more strongly adsorbed than the *cis*-isomer. This relationship appears to apply to 4-substituted cyclohexanols generally (15, 16) and is suggested as a method to determine configuration.

EXPERIMENTAL

All temperatures uncorrected.

Analyses by the students in my course in organic quantitative semimicro analysis.

Hydrogenation of p-hydroxydiphenyl. *p*-Hydroxydiphenyl (100 g.) was dissolved in a solution of sodium methoxide containing 0.06 g. of sodium in 100 cc. of absolute methanol. Raney nickel (6 g.) was added to the resulting solution and the mixture was immediately hydrogenated under an initial pressure of 2700 lbs. The temperature was raised rapidly to 140° and maintained until the absorption of hydrogen ceased or else it was raised to 170° and the reaction stopped at this point.

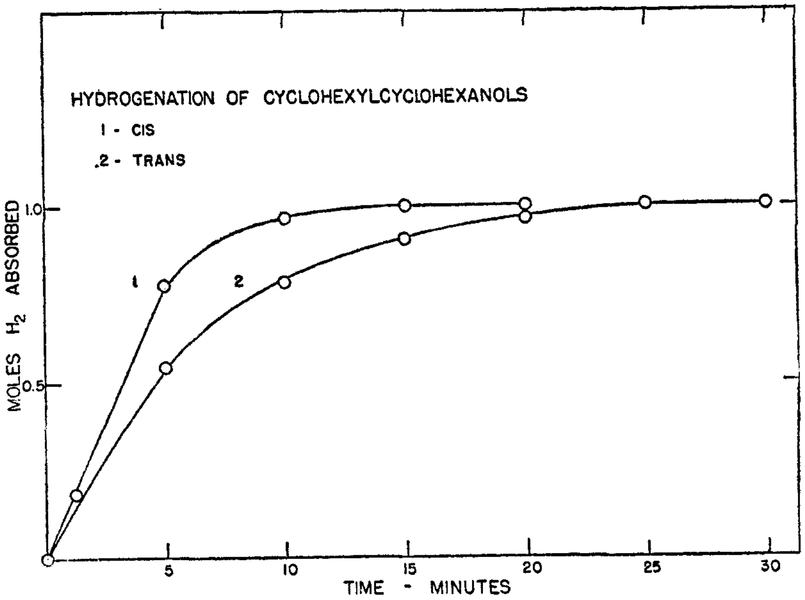

FIG. 3

The methanol solution was filtered from the catalyst and distilled to remove the solvent. The remaining glassy material was dissolved in benzene and was extracted with 5% aqueous potassium hydroxide solution to remove phenolic material. The benzene solution was washed with water, dried by removing the benzene-water azeotrope, and distilled. The residual oil (98 g.) consisted of a mixture of 4-phenyl- and 4-cyclohexyl-cyclohexanols. It was used directly for the preparation of 4-phenylcyclohexanone.

The alkali-soluble portion upon acidification gave nearly pure (approximately 95%) *p*-cyclohexylphenol melting at 127–129°. Crystallization from benzene raised the melting point to 129–130°; mixed melting point with authentic material 129–130°.

For the preparation of the cyclohexylcyclohexanols, the hydrogenation of *p*-hydroxydiphenyl (100 g.) was carried out by shaking the solution in 100 cc. of methanol with 12 g. of Raney nickel at 210° under a starting pressure of 3000 lbs. until the absorption of hydrogen ceased.

4-Phenylcyclohexanone. Concentrated sulfuric acid (66 g.) was added to 200 cc. of water contained in a 2-liter three-necked flask equipped with a thermometer and efficient stirrer.

The mixture was cooled to 20°. The crude mixture of 4-phenyl- and 4-cyclohexyl-cyclohexanols (182 g.) was added to this solution with stirring. To the resultant suspension was added 150 cc. of glacial acetic acid with stirring and the mixture was packed in ice. The addition of the oxidizing solution was started immediately, dropwise, with stirring at such a rate that the temperature did not rise.

The oxidizing solution consisted of 66 g. of concentrated sulfuric acid, 100 g. of sodium dichromate, and 200 cc. of water, and was cooled to 20° before the addition.

After completed addition, another 50-cc. portion of acetic acid was added, the ice-bath was removed, and the reaction mixture was immersed in a cold water-bath. The temperature of the mixture was raised to 60° during 2.5 hours, then it was allowed to stand overnight. The mixture was extracted with ether and the extract washed with water, 10% aqueous sodium hydroxide solution, and again with water. The ether layer was stirred vigorously with 1500 cc. of saturated aqueous sodium bisulfite solution for two hours. The addition compound was washed twice with 95% ethyl alcohol and twice with ether and air dried. The dry powder was stirred with 1000 cc. of cold 10% aqueous sodium hydroxide solution. The oily ketone was extracted with benzene. The extracts were washed with water, filtered, and distilled from a water-bath. The residual ketone (162 g.) was crystallized from petroleum ether (28–38°). The yield of 4-phenylcyclohexanone was 73 g., m.p. 77–78°.

4-Phenylcyclohexanone oxime. A mixture of 10 g. of ketone, 30 cc. of methanol, 10 g. of hydroxylamine hydrochloride in 15 cc. of water, and 10 g. of sodium acetate in 15 cc. of water gave 10.5 g. of dry oxime which melted at 110–111° after crystallization from ligroin (60–100°). Repeated crystallizations from the same solvent gave the constant melting point 112–113°.

Anal. Calc'd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40; M.W., 189.

Found: C, 75.99, 76.07; H, 8.10, 7.95; N, 7.40, 7.38, 7.34; M.W., 185 (Rast).

The oxime (5 g.) was hydrolyzed by heating with 100 cc. of 10% aqueous sulfuric acid. The ketone was isolated by steam distillation. After crystallization from ligroin (60–70°) the product showed the melting point 78–79° and the freezing point 77.7° (from the cooling curve).

Reconversion of this ketone to the oxime gave an excellent yield of a product melting at 112–113°.

The semicarbazone of the pure ketone (0.5 g.) prepared with 10 cc. of methanol, 0.7 g. of semicarbazide hydrochloride in 1.5 cc. of water, and 1.0 g. of sodium acetate in 1.5 cc. of water melted at 211–212° (dec.). Crystallization from methanol raised the melting point to 211.5–212.5° (dec.). The melting point of v.Braun and Weissbach (229° dec.) (19) was obtained for this material by using the Dennis bar method.

trans-4-Phenylcyclohexanol (I). Pure 4-phenylcyclohexanone (20 g.) was reduced with sodium (20 g.) and 200 cc. of absolute ethyl alcohol. The mixture was refluxed and, while still warm, was decomposed with 800 cc. of water. The product was taken up in benzene, washed with water, and distilled. The solid residue (20 g.) on crystallization from ligroin (60–70°) gave 13.0 g. of the alcohol melting at 116–117.5°. Another crystallization from ligroin (85–100°) raised the melting point to 117.2–118.5° (yield 12.2 g.). The mixed melting point of this material with the 4-phenylcyclohexanol (m.p. 116–117°) previously described (5) was 116–117.5°.

Phenylurethan. The phenylurethan prepared from 2.2 g. of the above alcohol by refluxing with 1.8 cc. of phenylisocyanate in 50 cc. of ligroin (85–100°), melted at 138–139.5°, yield 3.0 g. Several crystallizations from the same solvent gave the constant melting point 140–140.5°.

Anal. Calc'd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.16; N, 4.74; M.W. 295.3.

Found: C, 77.28, 77.33; H, 7.32, 7.27; N, 4.62; M.W. 275 (Rast).

The purified phenylurethan (3.93 g.) was ammonolyzed with 50 cc. of concentrated ammonia by heating under pressure at 160° for one hour. The reaction mixture was worked up as described previously (4). The product (2.41 g.), m.p. 109–112°, contained unchanged urethan which could not be separated by crystallization. Adsorption of the mixture on alumina (General Chemical Co., ignited powder, reagent) from ligroin (85–100°) solution and elution with the same solvent yielded 0.65 g. of pure phenylurethan, m.p. 140–140.5°. Subsequent elution with benzene gave 1.0 g. of pure *trans*-4-phenylcyclohexanol melting at 118–118.5° (from ligroin, 60–70°). Its mixture with the starting material melted at 117.2–118.5°.

Benzoate. Benzoylation of the *trans*-alcohol with benzoyl chloride in pyridine in the cold gave a benzoate melting at 104.5–105.5° (from ligroin, 60–70°).

Anal. Calc'd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19.
Found: C, 81.01, 81.23; H, 7.41, 7.64.

p-Toluenesulfonate. The *p*-toluenesulfonate, prepared in the usual way, was stable toward boiling methanol. It melted at 98.2–98.7° after several crystallizations from methanol. Hydrolysis of the *p*-toluenesulfonate gave only the olefin.

Anal. Calc'd for $C_{19}H_{22}O_3S$: C, 69.07; H, 6.71.
Found: C, 69.13; H. 6.71.

cis-4-Phenylcyclohexanol (II). 4-Phenylcyclohexanone (1.74 g., 0.01 mole) dissolved in 30 cc. of methanol was hydrogenated with 3 g. of Raney nickel under a pressure of 30 mm. of hydrogen. The absorption of hydrogen stopped when the theoretical amount was taken up. The mixture was filtered and the filtrate freed from solvent. The residue (1.61 g.) solidified on cooling and melted at 59–61°. Crystallization or adsorption on alumina from ligroin (85–100°) solution gave small amounts of the *trans*-alcohol melting at 117.5–118.2° but failed to separate the bulk of the material. A complete separation was effected by adsorbing the mixture (1.3 g.) on alumina from ligroin (30–60) solution. Elution with the same solvent yielded 0.50 g. of *cis*-isomer melting at 76–77°. The mixed melting point of this substance with the ketone (m.p. 77–78°) was 49–56° and the mixed melting point with the *trans*-alcohol (m.p. 118–118.5°) was 62–92°.

Anal. Calc'd for $C_{12}H_{16}O$: C, 81.78; H, 9.15.
Found: C, 81.77, 81.69, 81.81; H, 9.07, 9.01, 9.07.

Further elution of the column with benzene gave 0.16 g. of crystalline material melting at 62–66° which was a mixture of the isomers. The subsequent methanol eluate contained 0.13 g. of the *trans*-isomer melting at 118–118.5° which did not depress the melting point of an authentic specimen.

Phenylurethan. The crystalline phenylurethan of the *cis*-alcohol (II) melted at 140.5–141°. The mixture with the isomeric urethan (m.p. 140–140.5°) melted at 115–124°.

Anal. Calc'd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.16; N, 4.74; M.W., 295.3.
Found: C, 77.36; H, 7.34; N, 4.61, 4.78; M.W. 296 (Rast).

The alcohol (II) was recovered unchanged after standing for ten days at room temperature with 3,5-dinitrobenzoyl chloride in pyridine.

Inversion of cis-4-phenylcyclohexanol (II). The pure *cis*-alcohol (II) (0.5 g.) was heated with sodium at 200° for 3 hours as described previously (4). The reaction product (0.42 g.) after crystallization from ligroin (60–70°) melted at 105.5–116°, yield 0.30 g. Its mixture with the pure *trans*-isomer melted at 114–118°.

4-Cyclohexylcyclohexanone. The crude mixture of 4-cyclohexylcyclohexanol isomers (182 g.) (either from the hydrogenation of 4-hydroxydiphenyl or the Eastman technical grade) when oxidized with chromic acid as described for 4-phenylcyclohexanone yielded 160 g. of crude ketone. Without further purification this material, dissolved in 300 cc. of methanol, was converted to the oxime by treating with a solution of 120 g. of hydroxylamine hydrochloride in 180 cc. of water and a solution of 120 g. of sodium acetate in 180 cc. of water. The mixture was heated and the oxime was isolated in the usual way. The crude oxime melting at 72–89° weighed 179.6 g. Digestion with petroleum ether (28–38°) and crystallization from the same solvent gave 102.7 g. of pure oxime melting at 100–101°. Repeated crystallization gave the constant melting point 101–102°.

Anal. Calc'd for $C_{12}H_{21}NO$: C, 73.78; H, 10.84; N, 7.16; M.W., 195.
Found: C, 73.79, 73.62; H, 10.85, 10.97; N, 6.99, 7.20; M.W., 198 (Rast).

Hydrolysis of the oxime (102.7 g., m.p. 100–101°) with a solution of 100 cc. of concentrated sulfuric acid in 900 cc. of water at 90° for 1.5 hour gave 81.6 g. of ketone boiling at 70–72° (0.1 mm.). This material had the freezing point 29.2° (from the cooling curve). Reconversion to the oxime gave 95.4% of pure material melting at 101–102°.

The capillary melting point of the semicarbazone was 205–206° (dec.) (Schrauth and Görig give 204–205°) (10), whereas the Dennis bar method gave a value of 210°; v. Braun reports 216° (20).

trans-4-Cyclohexylcyclohexanol (III). Reduction of the pure ketone (20 g.) with sodium (20 g.) in 200 cc. of absolute alcohol gave 17.2 g. of crystalline alcohol which melted at 103–104° after several crystallizations from 60–70° ligroin.

Phenylurethan. The phenylurethan prepared from this alcohol melted at 156–156.8° (from methanol) and is undoubtedly identical with the substance described by v. Braun *et al.* (20).

Anal. Calc'd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03.
Found: C, 75.85, 75.80; H, 9.14, 9.09.

3,5-Dinitrobenzoate. Esterification of the alcohol (III) (0.54 g.) with 3,5-dinitrobenzoyl chloride (0.69 g.) in 8 cc. of pyridine at room temperature yielded 0.95 g. of ester melting at 138–139° after standing for four days. One crystallization from 85–100° ligroin raised the melting point to 149.5–150° which was unchanged by further crystallization.

Anal. Calc'd for $C_{19}H_{24}N_2O_6$: C, 60.63; H, 6.42.
Found: C, 60.75; H, 6.35.

Hydrolysis of the pure dinitrobenzoate (0.41 g.) with a solution of 0.4 g. of sodium hydroxide in 40 cc. of methanol and 40 cc. of water gave 0.10 g. of solid, m.p. 102–103.5°, which after one crystallization from 85–100° ligroin melted at 103.5–104°.

cis-4-Cyclohexylcyclohexanol (IV). 4-Cyclohexylcyclohexanone (5.39 g.) dissolved in 30 cc. of methanol was reduced with 3 g. of Raney nickel at 28° under a pressure of 30 mm. of hydrogen. The reduction stopped after absorbing 1 mole of hydrogen. The product melted at 80.5–81.5°, yield 5.10 g. Repeated fractional crystallizations and adsorption of this material or the substance obtained by reducing the ketone with platinum in acetic acid gave some *trans*-alcohol, m.p. 100–102°, and a mixture of isomers which melted at 83–87° and could not be further separated by crystallization or adsorption. It is presumably this material which Schrauth and Görig described as their "*trans*"-isomer (10). The fractions melting at 83–87° (3.7 g.) were esterified with 3,5-dinitrobenzoyl chloride in 50 cc. of pyridine at room temperature. The 3,5-dinitrobenzoates were obtained in 92% yield after three days, m.p. 128–147°. The dinitrobenzoates of other fractions were also prepared and all of them were fractionally crystallized. The highest melting fractions were combined and further crystallized until a homogeneous product was obtained which melted at 161–162° and depressed the melting point of the isomeric benzoate.

Anal. Calc'd for $C_{19}H_{24}N_2O_6$: C, 60.63; H, 6.42.
Found: C, 60.36; H, 6.15.

Hydrolysis of the dinitrobenzoate took place only very slowly with the dilute alkaline solution used for the isomeric benzoate. The pure *cis*-alcohol was obtained by hydrolysis of the dinitrobenzoate (4.88 g.) with 8.0 g. of potassium hydroxide in a solution of 40 cc. of water and 80 cc. of methanol. The product melting at 92–93° weighed 2.36 g. Its melting point was unchanged by crystallization from 28–38° petroleum ether. The mixture with the *trans*-isomer, m.p. 103–104° melted at 81.5–93.5°.

Anal. Calc'd for $C_{12}H_{16}O$: C, 81.78; H, 9.15.
Found: C, 81.73; H, 9.21.

Phenylurethan. The phenylurethan of the alcohol (IV) was crystallized from 60–70° ligroin. It showed two melting points, at 107–108° and 111–112°. The lower-melting form was converted to the higher-melting form by slow heating above its melting point. The reported phenylurethan melting at 103° (20) was probably impure.

Anal. Calc'd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03.
Found: C, 75.93; H, 9.16.

Rearrangement of cis-4-cyclohexylcyclohexanol. Heating of the pure *cis*-alcohol (IV)

(0.3 g.) with 0.039 g. of sodium at 200–210° brought about the expected inversion to the *trans*-isomer. The crude product (0.17 g.) after crystallization from 60–70° ligroin melted at 102.5–104° and did not depress the melting point of an authentic sample.

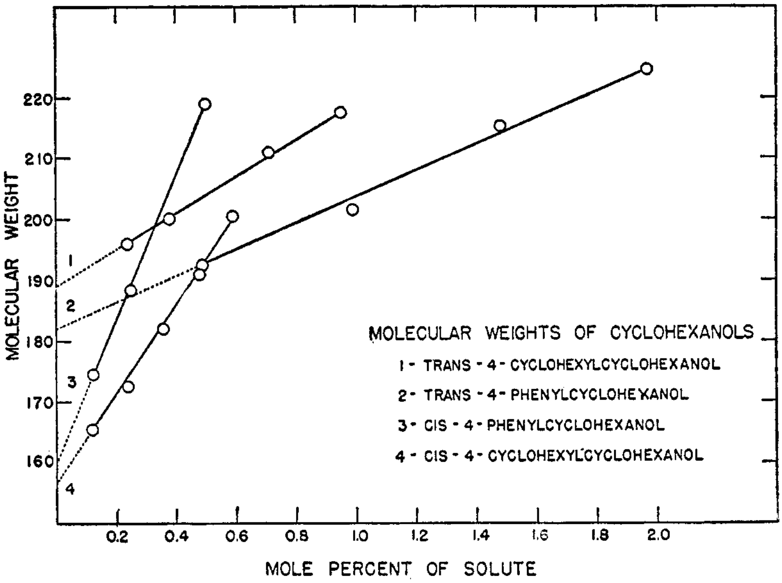

Fig. 4

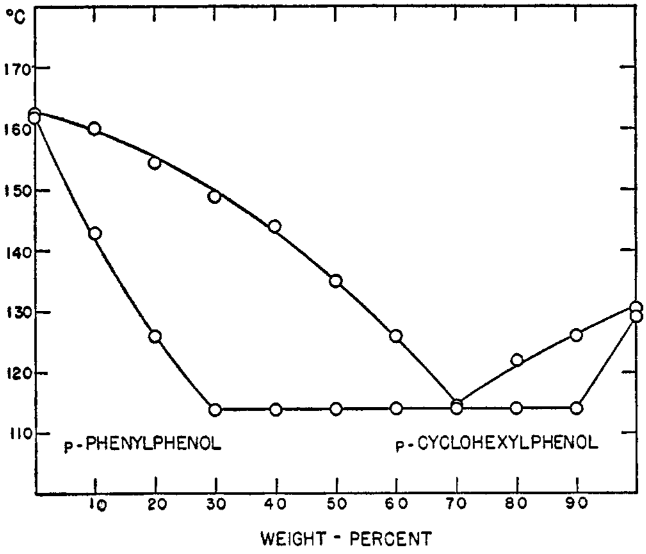

Fig. 5

Catalytic hydrogenation of the pure cyclohexanols. Both *cis*- and *trans*-4-phenylcyclohexanol (0.1 g. each) were hydrogenated at 26° under carefully controlled conditions in 20 cc. of acetic acid solution with 0.1 g. of Adams' catalyst (Fig. 2). The reaction was interrupted after absorption of the calculated amount of hydrogen and the products were isolated by dilution with water and extraction with benzene. The single product in each case was crystallized from ligroin. Neither *cis*- nor *trans*-4-cyclohexylcyclohexanol, m.p. 90.5-92° and 101-103°, depressed the melting point of an authentic specimen.

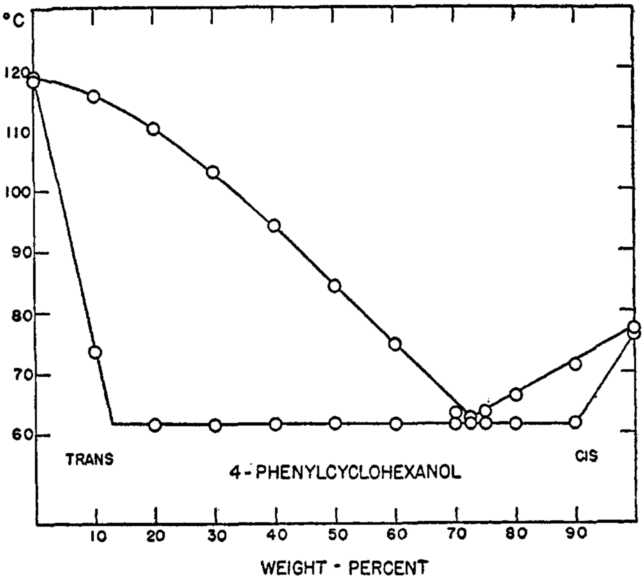

Fig. 6

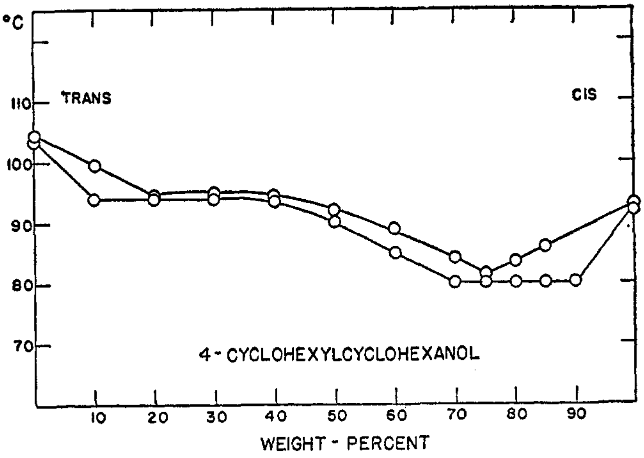

Fig. 7

The hydrogenation of *cis*- and *trans*-4-cyclohexylcyclohexanol (0.05 g. each) at 28° with platinum catalyst (0.1 g.) in 20 cc. of acetic acid (Fig. 3) stopped after absorption of one mole of hydrogen. The oily dicyclohexyl which was formed was not further investigated.

Molecular weights of the cyclohexanols. The molecular weights of the pure cyclohexanols were determined cryoscopically in pure ethylene bromide as a function of concentration (Fig. 4). Supercooling was held to 0.2° by seeding, and errors were eliminated by check runs with freshly prepared solutions.

Melting point diagrams. The melting point diagrams for mixtures of *p*-phenylphenol and *p*-cyclohexylphenol (Fig. 5) and the two pairs of *cis*, *trans*-isomers were obtained according to the procedure of Rheinboldt (21). Mixtures of *cis-* and *trans*-4-phenylcyclohexanol (Fig. 6) and the two phenols (Fig. 5) each gave a system with a single eutectic point. In the case of the cyclohexylcyclohexanol isomers, however, two eutectic points were obtained. The diagram (Fig. 7) is indicative of compound formation and some miscibility.

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SUMMARY

The pure *cis-* and *trans*-isomers of 4-phenyl- and 4-cyclohexyl-cyclohexanol have been prepared and characterized by derivatives. The configurations of the compounds have been established independently and by interconversion.

The hydrogenation of 4-phenylcyclohexanone and 4-cyclohexylcyclohexanone with Raney nickel at room temperature yields mixtures of isomers which correspond to eutectic points in the melting point-composition diagrams. *cis*-4-phenylcyclohexanol is more difficult to esterify than *cis*-4-cyclohexylcyclohexanol.

COLUMBIA, MO.

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