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The Infrared and Ultraviolet Spectra, Dipole Moments and Structures of Some New 2-(α-Hydroxy-p-halobenzyl)-cyclohexanones and Related Compounds[1]

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The chloro, bromo and iodo 2-(α-hydroxy-p-halobenzyl)-cyclohexanones, the bromo and iodo α-cyclohexyl-p-halobenzyl alcohols, the chloro and bromo 2-(p-halobenzyl)-cyclohexanones and the chloro, bromo and iodo 2-(p-halobenzylidene)-cyclohexanones have been made. The infrared spectra of the 2-(α-hydroxy-p-halobenzyl)-cyclohexanones, the α-cyclohexyl-p-halobenzyl alcohols, the 2-(p-halobenzyl)-cyclohexanones, the ultraviolet spectra and the dipole moments of the 2-(α-hydroxy-p-halobenzyl)-cyclohexanones have been measured. Two fractions were obtained for the bromo and iodo 2-(α-hydroxy-p-halobenzyl)-cyclohexanones. The higher melting fractions are shown to have the hydroxybenzyl groups in the equatorial position and it has been demonstrated that these compounds have an intramolecular hydrogen bond present both in dilute solution in carbon tetrachloride and in mulls. The hydrogen bonded OH in these compounds gives rise to a sharp narrow band of high extinction at 2.78 to 2.79 μ when measured in dilute solution. The band is shifted only 0.02 to 0.08 μ when measured in the solid. The evidence indicates the low melting fraction is a mixture of diastereoisomers having the hydroxybenzyl group also in an equatorial position. The 2-(α-hydroxy-p-halobenzyl)-cyclohexanones have a higher extinction at 290 mμ than does a simple ketone. The reason for the enhancement in this case appears not to be an interaction between the carbonyl and the phenyl, but an interaction between the carbonyl and the hydroxyl groups.

The synthesis of 2-(α-hydroxy-p-halobenzyl)-cyclohexanones by condensation of cyclohexanone with p-halobenzaldehydes in dilute alkali resulted in mixtures. In the case of the p-bromo compound, repeated recrystallizations gave a higher melting fraction with a sharp melting point 129.5–130.5° and a second fraction with a wide melting range 98–113°. Both fractions gave the correct bromine analysis and dehydration of both gave the same unsaturated product, m.p. 79–80°. The p-iodo compound behaved in a similar fashion. A mixture of stereoisomers is suggested.

The present evidence indicates that cyclohexane and a number of its derivatives exist in the chair form,[3-5] and although no direct evidence was found in the literature that conclusively proves that cyclohexanone has the chair form, some dipole moment measurements carried out in connection with the present work are consistent with cyclohexanone having the chair form.

Considering only the chair form, a substituted group on the number two carbon has the possibility of occupying either an equatorial or an axial[6] position. Examination of the Fisher–Hirschfelder–Taylor models of the 2-(α-hydroxy-p-halobenzyl)-cyclohexanones showed that when the α-hydroxybenzyl group was in the 2-equatorial position the hydroxyl is near enough to the carbonyl group to form a strong intramolecular hydrogen bond, but when it is in the 2-axial position the distances are too great and an intramolecular hydrogen bond is impossible. Figure 1 clearly illustrates the situation.

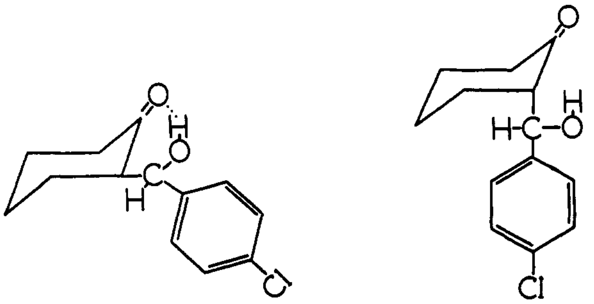

Fig. 1.—Left, 2-equatorial-(α-hydroxy-p-chlorobenzyl)-cyclohexanone; right, 2-axial-(α-hydroxy-p-chlorobenzyl)-cyclohexanone.

Infrared Spectra.—To decide which structure the sharp high melting compounds had, the infrared spectra of the high melting bromo and iodo and the sharp melting chloro compounds were obtained in dilute solution and in the solid as mulls, together with the spectra of corresponding compounds that contained only a hydroxyl and only a ketone group. The spectra were obtained on a Modified Beckmann I R 2 with a sodium chloride prism.[7] In Figs. 2, 3 and 4 are the infrared absorption curves for these compounds. From these it is clear that each of the compounds with a hydroxyl and no carbonyl has a sharp, narrow band in the region of 2.66 to 2.68 μ when measured in dilute solution. This band broadens considerably and moves to 3.01 to 3.04 μ amounting to a shift of 0.33 to 0.37 μ when these compounds are measured as mulls. On the other hand, the compounds having both a hydroxyl and a carbonyl, when measured in dilute solution, have a narrow band at 2.78 to 2.79 μ of almost twice the extinction of the band in the compounds without the carbonyl. When these compounds containing both hydroxyl and carbonyl are measured as mulls, the band is shifted only 0.02 to 0.08 μ compared with the above shift of 0.33 to 0.37 μ for those without the carbonyl.

The above observations may be interpreted as follows[8,9]: First, it is clear that in the compounds

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(1) From the Ph.D. Thesis in Pharmaceutical Chemistry of Alain C. Huitric, University of California (1954). Presented before the Organic Section at the Cincinnati Meeting of the American Chemical Society, April, 1955.

(2) Fellow of the Foundation for Pharmaceutical Education 1952–1954.

(3) D. A. Ramsay, G. B. B. M. Sutherland, *Proc. Roy. Soc.* (*London*), **A190**, 245 (1947).

(4) O. Hassel, *Quart. Rev.*, **7**, 221 (1953).

(5) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

(6) D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog, *Science*, **119**, 49 (1954).

(7) The spectra were measured by Mr. M. Hrenoff.

(8) L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 83–97 and 114–129.

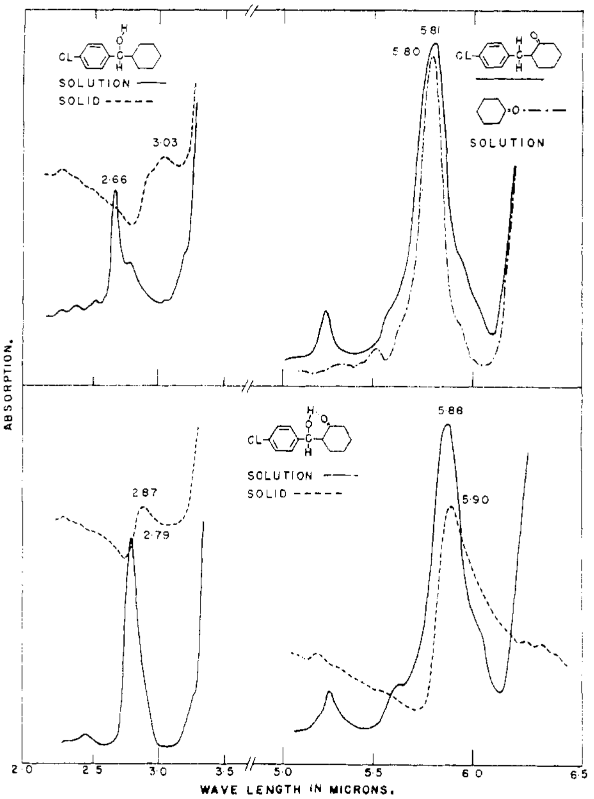

Fig. 2.—Infrared spectra of 2-(α-hydroxy-*p*-chlorobenzyl)-cyclohexanone and model compounds. The solids were measured as Nujol mulls and the solutions were 0.94% by weight in carbon tetrachloride.

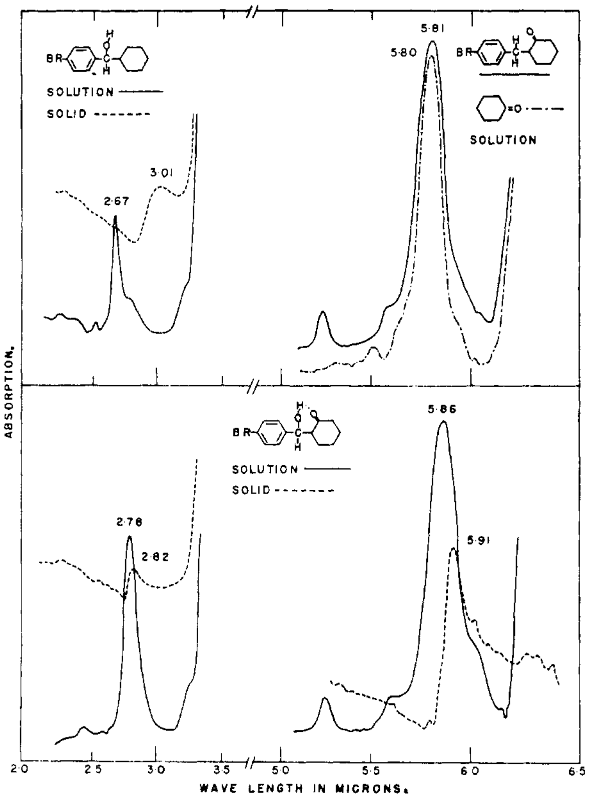

Fig. 3.—Infrared spectra of 2-(α-hydroxy-*p*-bromobenzyl)-cyclohexanone and model compounds. The solids were measured as Nujol mulls and the solutions were 0.94% by weight in carbon tetrachloride.

with hydroxyl and no carbonyl there is no possibility of an intramolecular hydrogen bond either in dilute solution or in mulls and when measured in dilute solution there is no possibility of an intermolecular hydrogen bond. The band at 2.66 to 2.68 μ therefore arises from the free hydroxyl, and the band at 3.01 to 3.04 μ is due to the OH when it is intermolecularly hydrogen bonded. The band at 2.78 to 2.79 μ for dilute solutions of the compounds containing both a carbonyl and a hydroxyl has been shifted 0.11 to 0.13 μ from the position of the free hydroxyl and has an extinction about twice that of the free hydroxyl, and therefore must be due to an intramolecular hydrogen bonded hydroxyl. The fact that these bands shift only the small amount of 0.02 to 0.08 μ when the measurements are made on mulls is further confirmation that they arise from intramolecularly bonded hydroxyl groups since such intramolecular hydrogen bonds would be retained and, therefore, little shift would be expected in going from dilute solution to mulls.

These findings that an intramolecular hydrogen bond can give rise to a narrow band of high extinction not far removed from the position of the free hydroxyl is in keeping with our previous observation[10] that intramolecular hydrogen bonds involving hydrogen attached to nitrogen give a narrow band of high extinction.

The evidence from the infrared spectra that these high melting compounds contain intramolecular hydrogen bonds indicates, in the light of the distances between the oxygen atoms as shown in Fig. 1, that the hydroxybenzyl group is in a 2-equatorial position and not a 2-axial position.

The carbonyl bands give evidence also of hydrogen bonding in the compounds containing both hydroxyl and carbonyl groups. Those compounds containing a carbonyl only have a band at 5.81 μ when measured in dilute solution, almost identical with the band for cyclohexanone at 5.80 μ. This band is shifted to 5.86–5.88 μ in the compounds having both a carbonyl and a hydroxyl, again giving evidence of an intramolecular hydrogen bond. Measured in the solid the band appears at 5.90–5.91 μ, thus like the hydroxyl band showing only a small shift in going from dilute solution to the solid.

The infrared spectra of the wide melting range fractions had bands at 2.77 and 2.85 μ in dilute solutions and in mulls for the bromo compound, and at 2.77 and 2.86 μ for the iodo compound, respectively. These bands for the wide melting range fractions consisted of a single peak that was almost identical in dilute solutions with those of the corresponding high melting compound. This is evidence that the wide melting fractions are not mixtures of axial and equatorial stereoisomers for if such were the case, there should be two peaks in this region in dilute solution, one for the associated hydroxyl in the equatorial compound, and one for the unassociated hydroxyl in the axial compound. The wide melting

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(10) W. D. Kumler, This Journal, **76**, 814 (1954).

fraction probably consists mainly of the diastereoisomers in which the substituted benzyl group is always in an equatorial position, and the hydroxyl and hydrogen have exchanged places as compared to where they were in the high melting fraction. Since each of these compounds would have a mirror image what we have is doubtless two enantiomorphic pairs. Assuming the cyclohexane ring is in the chair form, there would be two other possible enantiomorphic pairs with the hydroxybenzyl group in the polar position. This is a situation where a molecule with two asymmetric carbon atoms has the possibility of existing as four enantiomorphic pairs.

Dipole Moments.—The dipole moments of the sharp, high melting 2-(α-hydroxy-*p*-halobenzyl)-cyclohexanones have been measured in benzene and compared with the theoretical calculated moments to obtain further evidence on their structure. The method of Halverstadt and Kumler[11] was used in arriving at the measured moment values. The plots of ϵ_{12} *versus* ω_2 and ν_{12} *versus* ω_2 were straight lines within the limits of experimental error and the values of ϵ_1 and ν_1 were obtained by extrapolating the ϵ_{12} and ν_{12} values to zero weight fraction. The PE_2 values are the molar refractions calculated from electron group refractions. The results are given in Table I.

TABLE I

2-(α-HYDROXY-*p*-HALOBENZYL)-CYCLOHEXANONE

		Chloro	Bromo	Iodo
ϵ_1		2.2674	2.2689	2.2692
ν_1		1.14766	1.14769	1.14759
α		6.000	5.820	4.650
β		−0.3180	−0.4640	−0.5260
P_{20}		329.61	368.91	351.00
P_{E_2}		63.06	65.96	71.00
μ	Obsd.	3.64	3.88	3.73
	Theor.	3.78	3.76	3.69

The theoretical moments for the compounds here calculated for the 2-equatorial configuration in which the molecules were assumed to be fixed through hydrogen bonding as shown in Fig. 1.

Values of group moments used are the same as those in the previous paper. The COH group moment was taken as 1.70 and forming an angle of 62° with the direction of the C–O bond. The observed moments for these compounds are in good agreement with the calculated theoretical moments for the hydrogen bonded structure shown in Fig. 1. There is another configuration the molecule might have with the isomer shown in Fig. 1 and still retain its hydrogen bond. This can be formed by rotating the *p*-halobenzyl group around until the hydroxyl group hydrogen bonds with the carbonyl oxygen from the under side instead of from the top side as in Fig. 1. The benzene ring is then almost at right angles to the plane of the cyclohexane ring which is considered to pass through the equatorial hydrogen (not their centers) and to be above the centers of three of the carbons and below the centers of the other three carbons. The theoretical calculated moment for this configuration of approximately 5 in contrast to the observed moments of about 3.8 indicates the molecule is not in this form.

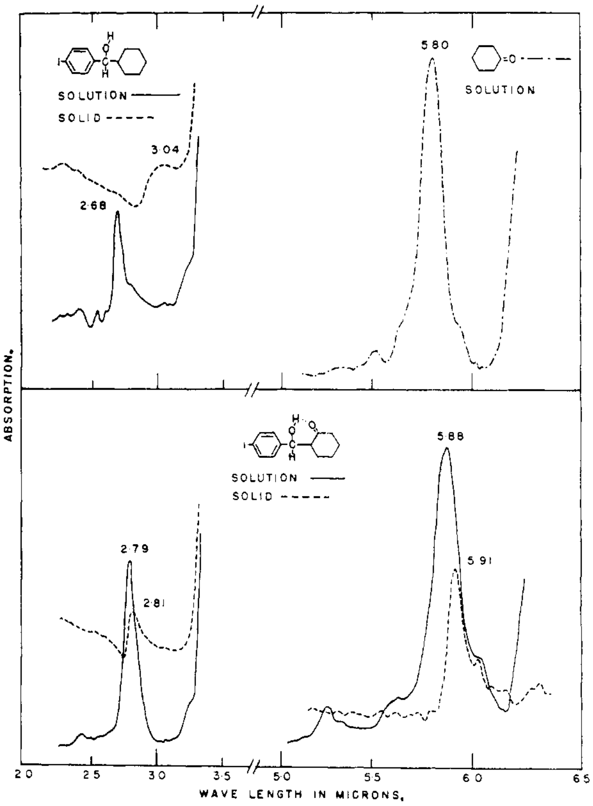

Fig. 4.—Infrared spectra of 2-(α-hydroxy-*p*-iodobenzyl)-cyclohexanone and model compounds. The solids were measured as Nujol mulls and the solutions were 0.94% by weight in carbon tetrachloride.

The possibility of free rotation is ruled out also because the theoretical dipole moment for free rotation would be appreciably higher than the observed moment. Also if there were free rotation the OH hydrogen would be free part of the time and so the infrared spectrum would show two bands, one at 2.67 and one at 2.79 μ while only one is observed at 2.79 μ.

Ultraviolet Spectra.—The ultraviolet spectra of some of the compounds were obtained in 95% ethanol using a Cary Recording Spectrophotometer, Model 11PMS with fused silica cells.

TABLE II

Compound	λmax, mμ	ε
2-(α-Hydroxy-*p*-chlorobenzyl)-cyclohexanone	260	247
	267	293
	275	232
	290	44
2-(α-Hydroxy-*p*-bromobenzyl)-cyclohexanone	254	243
	260	257
	267	280
	276	177
	290	44
2-(α-Hydroxy-*p*-iodobenzyl)-cyclohexanone	260[a]	990

[a] Hump in curve.

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[11] I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

The spectra of the 2-(α-hydroxy-*p*-halobenzyl)-cyclohexanones shown in Table II are of particular interest around 290 mμ for both the chloro and the bromo compound have a hump in the curve at 290 mμ with an extinction of 44 which is considerably higher than that for a simple carbonyl. In the iodo compound the band from the C–I bond overlaps and obscures this region and the 260 mμ region. The observation had been made by Kumler, Alpen and Strait[12,13] that in α-phenylcarbonyl compounds the carbonyl absorption peak is more intense than in simple aliphatic ketones and a direct interaction through space was suggested to account for the phenomenon. More specifically it appears the interaction involves the π-orbitals of the benzene ring and the *p*-orbitals of the carbonyl oxygen. It is apparent, however, that such an interaction through space is probably not the explanation in these compounds for the high extinctions at 290 mμ. It has already been shown that these compounds have an intramolecular hydrogen bond between the carbonyl oxygen and the α-hydroxyl group and while this can be formed in two ways the dipole moment shows that the molecule is in the form in which the phenyl group is away from the carbonyl oxygen so there is no likelihood of interaction between their π- and *p*-orbitals. The abnormal carbonyl absorption in this case probably results from the same cause that gives α- and β-hydroxy ketones a higher carbonyl absorption as has been observed by Lowry and Lishmund.[14] These compounds had no phenyl and consequently the abnormal carbonyl absorption could not be due to interaction of a phenyl with the carbonyl. It appears likely that it arises from the hydrogen bonding of the hydroxyl with the carbonyl.

Experimental

2-(α-Hydroxy-*p*-chlorobenzyl)-cyclohexanones.—A solution of 17.3 g. of sodium hydroxide in 500 ml. of water was added with stirring to a mixture of 43.5 g. (0.31 mole) of *p*-chlorobenzaldehyde (Heyden Chemical Corp.) and 121 g. (1.24 moles) of cyclohexanone in 3.5 liters of water at room temperature. The mixture was stirred at room temperature for 10 hours. The resulting precipitate was filtered with suction, washed thoroughly with water, and dried *in vacuo*, giving 65 g. (88%) of crude product, m.p. 77–82°. The product was recrystallized once from ethyl acetate and several times from isopropyl alcohol and from 95% ethanol, giving a colorless material, m.p. 86–87°.

Anal. Calcd. for $C_{13}H_{15}ClO_2$: Cl, 14.85. Found: Cl, 14.97.

The 2,4-dinitrophenylhydrazone was prepared according to the method of Birch[15] and recrystallized once from 95% ethanol, giving orange crystals, m.p. 205–206°.

Anal. Calcd. for $C_{19}H_{18}O_5N_4Cl$: Cl, 8.48. Found: Cl, 8.7.

Emerson, *et al.*,[16] obtained 2-benzylidenecyclohexanone from benzaldehyde and cyclohexanone by the above method. They isolated their product by distillation at reduced pressure and it is not clear whether dehydration had occurred prior to distillation.

2-(α-Hydroxy-*p*-bromobenzyl)-cyclohexanone.—When the reaction was carried out with a threefold excess of cyclohexanone under the same conditions as for the chloro analog, a small amount of disubstituted product was also formed. Dehydration of a small amount of product, by heating in 95% ethanol with a few drops of concentrated hydrochloric acid, gave a very small amount of bright yellow crystalline material, very slightly soluble in 95% ethanol, having a melting point of 166–167°; plus a much larger amount of yellow crystalline material, quite soluble in 95% ethanol and having a melting point of 79–80°. The two dehydration products were found to be 2,6-bis-(*p*-bromobenzylidene)-cyclohexanone and 2-(*p*-bromobenzylidene)-cyclohexanone, respectively.

The reaction was then carried out with a tenfold excess of cyclohexanone under conditions designed to favor maximum yield of the monosubstituted product. Seventy-three grams (0.745 mole) of cyclohexanone was added to a solution of 10 g. of sodium hydroxide in 2.5 liters of water. A solution of 20 g. (0.108 mole) of *p*-bromobenzaldehyde in 25 g. (0.255 mole) of cyclohexanone was then added dropwise, with stirring at room temperature, over a period of 4.5 hours. The mixture was stirred at room temperature for an additional 2 hours. The resulting precipitate was filtered with suction, washed with water, and dried *in vacuo*, giving 15.5 g. of colorless product. The aqueous filtrate was extracted with ether. The ether extracts were washed with water until neutral to litmus and the ether and the excess cyclohexanone were removed under vacuum, giving an additional 5.5 g. of dry, colorless product, making a total yield of 69%. Recrystallization from methanol gave a product with melting point of 95–103°. By repeated recrystallization from different solvents such as ethanol, ethyl acetate, *n*-hexane and benzene, two fractions were obtained: a high melting fraction, m.p. 129.5–130.5°, and a low melting fraction melting over a range of 98–113°. Dehydration of 0.5 g. of each of these fractions gave the same unsaturated product, m.p. 79–80°. The two fractions were analyzed for bromine and the percentage of bromine found in each fraction corresponds to the calculated amount of bromine in 2-(α-hydroxy-*p*-bromobenzyl)-cyclohexanone.

Anal. (Low m.p. fraction, 98–113°). Calcd. for $C_{13}H_{15}BrO_2$: Br, 28.22. Found: Br, 28.03.

Anal. (High m.p. fraction, 129.5–130.5°). Calcd. for $C_{13}H_{15}BrO_2$: Br, 28.22. Found: Br, 28.36.

2-(α-Hydroxy-*p*-iodobenzyl)-cyclohexanone.—Twenty-six g. (0.266 mole) of cyclohexanone was added to a solution of 8.6 g. of sodium hydroxide in 2 liters of water. Twenty grams (0.086 mole) of *p*-iodobenzaldehyde[17] was then added in small portions with stirring at room temperature over a period of one hour. The mixture was stirred for an additional 10 hours. The resulting precipitate was filtered with suction, washed thoroughly with water, dried *in vacuo* and recrystallized from isopropyl alcohol, giving 23.8 g. (84%) of colorless product, m.p. 116–135°. Repeated recrystallization from different solvents, methanol, isopropyl alcohol, *n*-hexane, ethyl acetate and benzene, yielded two fractions of colorless crystalline product: a high melting fraction, m.p. 147–148°, and a lower melting fraction, melting over a range of 115–121°. Dehydration of a small amount of these fractions yielded only the same unsaturated product, m.p. 86.5–87.5°. The two fractions were analyzed for iodine and the percentage of iodine found in each fraction corresponds to the calculated amount of iodine in 2-(α-hydroxy-*p*-iodobenzyl)-cyclohexanone.

Anal. (High m.p. fraction 147–148°). Calcd. for $C_{13}H_{15}IO_2$: I, 38.44. Found: I, 38.77.

Anal. (Low m.p. fraction 115–121°). Calcd. for $C_{13}H_{15}IO_2$: I, 38.44. Found: I, 38.70.

2-(*p*-Chlorobenzylidene)-cyclohexanone.—A solution of 3 g. (0.0126 mole) of 2-(α-hydroxy-*p*-chlorobenzyl)-cyclohexanone in 6 ml. of 95% ethanol was acidified with three drops of concentrated hydrochloric acid and heated at the boiling point for 5 minutes. Cooling in ice gave 2.5 g. (90%) of light yellow crystalline material which was recrystallized from isopropyl alcohol and from ethanol, m.p. 57–57.5°.

Anal. Calcd. for $C_{13}H_{13}ClO$: Cl, 16.07. Found: Cl, 16.15.

The 2,4-dinitrophenylhydrazone was prepared and recrystallized once from 95% ethanol; m.p. 173.5–174.5°.

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[12] W. D. Kumler, L. A. Strait and E. L. Alpen, This Journal, **72**, 1463 (1950).

[13] E. L. Alpen, W. D. Kumler and L. A. Strait, *ibid.*, **72**, 4558 (1950).

[14] T. M. Lowry and R. E. Lishmund, *J. Chem. Soc.*, 1313 (1935).

[15] A. J. Birch, *ibid.*, 593 (1946).

[16] W. S. Emerson, G. H. Birum and R. I. Longley, Jr., This Journal, **75**, 1312 (1953).

[17] This compound was prepared by the Sommelet Reaction. S. J. Angyal, P. J. Morris, R. C. Rassack and J. A. Watterer, *J. Chem. Soc.*, 2704 (1949).

Anal. Calcd. for $C_{19}H_{17}O_4N_4Cl$: Cl, 8.84. Found: Cl, 8.80.

2-(*p*-Bromobenzylidene)-cyclohexanone.—This compound was obtained in about quantitative yield from either fractions of 2-(α-hydroxy-*p*-bromobenzyl)-cyclohexanone by heating in 95% ethanol with a few drops of concentrated hydrochloric acid for about ten minutes. The product was recrystallized from 95% ethanol, giving a light yellow crystalline material, m.p. 79–80°.

Anal. Calcd. for $C_{13}H_{13}BrO$: Br, 30.14. Found: Br, 30.26.

2-(*p*-Iodobenzylidene)-cyclohexanone.—This compound was obtained in about quantitative yield from either fractions of 2-(α-hydroxy-*p*-iodobenzyl)-cyclohexanone by heating in 95% ethanol with a few drops of concentrated hydrochloric acid for about ten minutes, m.p. 82–86°. Recrystallization of the crude product from 95% ethanol gave a light yellow crystalline material, m.p 86.5–87.5°.

Anal. Calcd. for $C_{13}H_{13}IO$: I, 40.66. Found: I, 40.72.

2-(*p*-Chlorobenzyl)-cyclohexanone.—About one gram of Raney nickel W-2 was added to a solution of 4.3 g. of 2-(*p*-chlorobenzylidene)-cyclohexanone in a mixture of 75 ml. of thiophene-free benzene and 15 ml. of absolute ethanol, and hydrogenation carried out at 25 lb. pressure at room temperature. The calculated amount of hydrogen was taken up in 30 minutes. The catalyst was filtered off, leaving a colorless solution. Removal of the benzene and ethanol at room temperature under a stream of air gave a slightly yellow, oily substance which could not be crystallized. The semicarbazone was prepared and recrystallized from 80% ethanol; m.p. 194.5–195.5°. The semicarbazone was hydrolyzed by refluxing in a 15% aqueous solution of phosphoric acid for 2 hours. The cooled mixture was extracted with ether and the ether extracts were washed with 5% sodium bicarbonate solution followed by water. Evaporation of the ether gave a colorless crystalline product, m.p. 39–43°. Recrystallization from petroleum ether and from isopropyl alcohol–water mixture gave a melting point of 42.5–43.5°.

Anal. Calcd. for $C_{13}H_{15}ClO$: Cl, 15.92; C, 70.11; H, 6.79. Found: Cl, 16.02; C, 70.30; H, 6.89.

On a separate run the oily substance obtained from the hydrogenation of 4.3 g. of 2-(*p*-chlorobenzylidene)-cyclohexanone was allowed to stand at room temperature for eight or ten days and 0.7 g. of crystalline material separated out. Recrystallization from ethanol–water mixture gave a colorless crystalline material, m.p. 84–85.5°. This material was found to be insoluble in water but soluble in 5% sodium bicarbonate solution. It was not characterized. The remaining oily substance was treated through the semicarbazone, as above, giving a colorless crystalline product, m.p. 42.5–43.5°.

2-(*p*-Bromobenzyl)-cyclohexanone.—Two grams of 2-(*p*-bromobenzylidene) cyclohexanone in 100 ml. of thiophene-free benzene with about 0.6 g. of Raney nickel W-2 was hydrogenated at 30 lb. pressure at room temperature. The calculated amount of hydrogen was taken up in 30 minutes. The benzene was removed at room temperature under a stream of air, leaving a light yellow, oily substance which could not be crystallized. The semicarbazone was then prepared, giving 1.9 g. of colorless compound which was recrystallized from 95% ethanol, m.p. 194–195.5°. One and one-tenth g. of the purified semicarbazone was hydrolyzed by refluxing in a 15% aqueous solution of phosphoric acid for 2 hours. Extraction of the cooled mixture with ether and removal of the ether gave 0.9 g. of crystalline material which was treated with decolorizing carbon in ethanol, giving a colorless crystalline product, m.p. 54–55°.

Anal. Calcd. for $C_{13}H_{15}BrO$: Br, 29.91; C, 58.44; H, 5.66. Found: Br, 30.14; C, 58.68; H, 5.76.

α-Cyclohexyl-*p*-chlorobenzyl Alcohol.—This compound was obtained in 70% yield of crude material and 58% of purified product, m.p. 74–75°, by the method of Hamlin, *et al.*,[18] who reported a m.p. of 70–71°.

α-Cyclohexyl-*p*-bromobenzyl Alcohol.—A solution of 10 g. (0.054 mole) of *p*-bromobenzaldehyde in 50 ml. of anhydrous ether was cooled to 10° in an ice-bath. Thirty milliliters of ice-cold, 1.80 molar cyclohexylmagnesium bromide ethereal solution was then added with stirring at such a rate that the temperature was maintained below 20°. A white precipitate occurred at the beginning of the addition, but soon dissolved. When nearly all the Grignard reagent was added a red color developed which soon disappeared when the addition was stopped. The reaction mixture was worked up in the same manner as described for the chloro analog. The yield of the crude product was 11 g. (76%). Recrystallization from petroleum ether gave 9.5 g. (65.5%) of colorless product, m.p. 71.5–72.5°. A small amount was treated with decolorizing carbon in 95% ethanol and recrystallized from petroleum ether for analysis and infrared investigation, m.p. 71.5–72.5°.

Anal. Calcd. for $C_{13}H_{17}BrO$: Br, 29.69; C, 58.00; H, 6.37. Found: Br, 29.64; C, 57.98; H, 6.29.

α-Cyclohexyl-*p*-iodobenzyl Alcohol.—A solution of 16.2 g. (0.07 mole) of *p*-iodobenzaldehyde in 100 ml. of anhydrous ether was cooled to 10° in a bath. Thirty-nine milliliters of ice-cold, 1.80 molar cyclohexylmagnesium bromide ethereal solution was added with stirring, at such a rate that the temperature was maintained below 20°. A white precipitate developed at the beginning of the addition and partially dissolved as the addition proceeded. When the Grignard reagent was nearly all added, a red color developed which soon disappeared when the addition was stopped. The last two or so milliliters of Grignard reagent were discarded. The reaction mixture was worked up in the same manner as described for the chloro analog. The crude product was recrystallized from petroleum ether, giving 14.8 g. (67%) of colorless crystalline material; m.p. 65–70°. This product was found to give a positive test with 2,4-dinitrophenylhydrazine test solution. A portion of the compound was treated with decolorizing carbon in 95% ethanol and recrystallized several times from 95% ethanol and from petroleum ether for analysis and for spectroscopic investigation. The purified product gave a negative carbonyl test and had a melting point of 77–78°.

Anal. Calcd. for $C_{13}H_{17}IO$: I, 40.14; C, 49.38; H, 5.42. Found: I, 40.26; C, 49.53; H, 5.59.

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[18] K. E. Hamlin, A. W. Weston, F. E. Fischer and R. J. Michaels, Jr., THIS JOURNAL, **71**, 2731 (1949).