epoxide as colorless plates, m.p. 185.6–186.1°. The product exhibits infrared absorption[13] at 1725 cm.$^{-1}$ (unconj. C=O) with an ultraviolet maximum[12] at 291 mμ (ε 27,800).

Anal. Calcd. for $C_{40}H_{36}O_3$: C, 85.07; H, 6.43. Found: C, 84.96; H, 6.52.

Catalytic hydrogenation of the dimer. A solution of 5.97 g. (0.0108 mole) of the dimer in 200 ml. of ethyl acetate was hydrogenated at room temperature and atmospheric pressure over the catalyst obtained from 0.315 g. of platinum oxide. The reaction was stopped after the absorption of 354 ml. (1.58 equiv.) of hydrogen. After the catalyst had been removed by filtration, the filtrate was concentrated under reduced pressure. A combination of fractional recrystallization from ethanol and chromatography on Merck acid-washed alumina separated 0.8872 g. (14.8% recovery) of the unchanged dimer, 1.4615 g. (24.5%) of one crystalline modification of the dihydrodimer A, m.p. 159–162°, 0.3796 g. (6.4%) of a second crystalline modification of the dihydrodimer A, m.p. 171–172.5°, and 0.2914 g. (4.9%) of the dihydrodimer B, m.p. 208–211°.

One pure crystalline modification of the dihydrodimer A was obtained as white needles, m.p. 161.5–163°, by recrystallization from an ethanol-ethyl acetate mixture. The product exhibits infrared absorption[13] at 1720 cm.$^{-1}$ (unconj. C=O) with no absorption in the 3 μ region attributable to a hydroxyl function; the ultraviolet spectrum[12] exhibits a maximum at 293 mμ (ε 28,500).

Anal. Calcd. for $C_{40}H_{38}O_2$: C, 87.23; H, 6.96. Found: C, 86.91; H, 6.87.

The dihydrodimer A occasionally separated in a second crystalline modification as white prisms, m.p. 173.5–175°, which exhibit the same infrared and ultraviolet absorption as the crystalline form melting at 161.5–163°.

Anal. Calcd. for $C_{40}H_{38}O_2$: C, 87.23; H, 6.96. Found: C, 86.96; H, 6.98.

The pure dihydrodimer B crystallized from an ethanol-ethyl acetate mixture as colorless prisms, m.p. 212.5–214° dec., which exhibit infrared[13] absorption at 1718 cm.$^{-1}$ (unconj. C=O) with no absorption in the 3 μ region attributable in a hydroxyl function and an ultraviolet maximum[12] at 292 mμ (ε 23,600).

Anal. Calcd. for $C_{40}H_{38}O_2$: C, 87.23; H, 6.96. Found: C, 87.16; H, 6.84.

Treatment of the dihydrodimer **13** *with zinc and acetic acid.* A mixture of 0.8292 g. (0.0015 mole) of the dihydrodimer A, m.p. 161–163°, and 1.078 g. (0.019 g.-atom) of zinc dust in 20 ml. of acetic acid was refluxed with stirring for 1 hr. and then poured into cold water and filtered. Fractional crystallization of the residue from ethanol–ethyl acetate mixtures separated 0.6225 g. (75% recovery) of unchanged dihydrodimer A and 0.0557 g. (6.7%) of dihydrodimer B, m.p. 211–213° dec., identified by a mixed melting-point determination.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Asymmetric Induction

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Received September 6, 1960

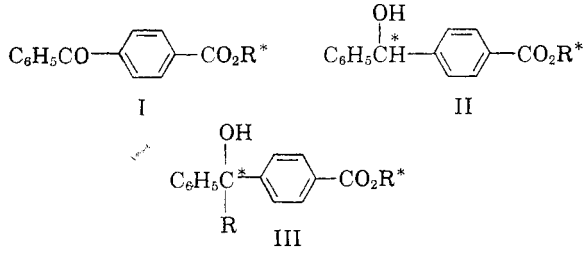
(−)-Menthyl *p*-benzoylbenzoate, a vinylog of an optically active α-keto ester has been subjected to the action of reducing agents and Grignard reagents to see if optical activity appears at the new asymmetric center produced at the benzoyl group after subsequent removal of the (−)-menthyl moiety. If asymmetric induction operates as do ordinary inductive forces through an aromatic nucleus, the ultimate products of such reactions should be optically active. If purely steric effects are responsible for asymmetric synthesis the products of such reactions should be optically inactive. In none of our experiments were we able to detect optical activity in the final reaction products, indicating that asymmetric induction if it exists is incapable of transmission through an aromatic nucleus.

Two distinct concepts of the mechanism of asymmetric synthesis are to be found in the literature. The first, that of "Asymmetric Induction," based on early suggestions of LeBel[1] and Erlenmeyer,[2] was developed in the hands of Kortum,[3] Lowry,[4] Ritchie,[5] Turner,[6] and Phillips[7] to explain not only McKenzie's classic asymmetric syntheses in the α-keto ester series[8,9] but also certain mutarotation[8,10] and anomalous rotatory dispersion[5,7] phenomena. This concept, in brief, postulates the asymmetric polarization of a symmetrical center in a molecule, under the influence of a nearby preexisting center of asymmetry. Such polarization is assumed to produce differing quantities of two diastereomeric "activated species," which ultimately react chemically to yield unequal amounts of diastereomeric products, and which are also responsible for anomalous mutarotation or rotatory dispersion properties. The second and more recent mechanism rationalizing asymmetric synthesis is one in which purely steric interactions between the symmetrical and asymmetric reactants lead to a stereochemically favored reaction path and to the ultimate production of unequal amounts

(1) J. A. LeBel, *Bull. soc. chim.* (iii), **8**, 613 (1892).
(2) E. Erlenmeyer, Jr., *Biochem. Z.*, **35**, 149 (1911).
(3) G. Kortum, *Samml. chem. u. chem.-tech. Vortrage*, 10 (1932).
(4) T. M. Lowry and co-workers, *Nature*, **113**, 565 (1924); *Bull. soc. chim.* (iv), **39**, 203 (1926).
(5) P. D. Ritchie, *Asymmetric Synthesis and Asymmetric Induction*, Oxford University Press, London, 1933. *Cf.* also J. Kenyon and S. M. Partridge, *J. Chem. Soc.*, 1313 (1936).
(6) E. E. Turner and M. M. Harris, *Organic Chemistry*, p. 653, Longmans, Green and Co., London, 1952.
(7) H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).
(8) A. McKenzie and co-workers, *J. Chem. Soc.*, **85**, 1249 (1904); **95**, 544 (1909); *Biochem. Z.*, **208**, 456 (1929); **231**, 412 (1931); **237**, 1 (1931); **250**, 376 (1932).
(9) E. E. Turner and co-workers, *J. Chem. Soc.*, 3219, 3223, 3227 (1951).
(10) E. E. Turner and co-workers, *J. Chem. Soc.*, 538 (1941); S-169 (1949).

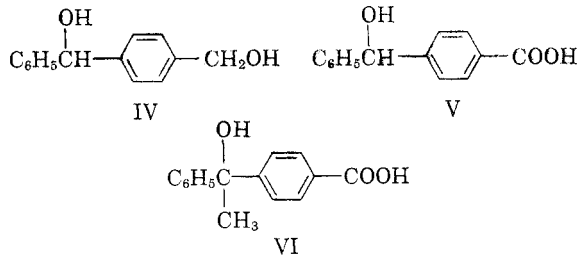
of diastereomeric products.[11-17] While the latter steric rationalization appears now generally accepted, there has been little experimental basis for a decision as to which of the two conflicting hypotheses is correct. We have attempted to design a series of semicritical experiments which might provide the basis for such a decision.

(−)- Menthyl *p*-benzoylbenzoate (I,R = (−)-menthyl) constitutes a vinylog of the optically active α-keto ester system used by McKenzie in his studies on asymmetric synthesis. Reduction of I to produce the secondary alcohol II, as well as reaction of RMgX with I to give the tertiary alcohol



III involve the introduction of a new asymmetric center at the formerly symmetrical benzoyl function in I. A true induced asymmetry by the (−)- menthyl moiety of I might, like other inductive effects, be reasonably supposed capable of transmission through the aromatic nucleus to the *p*-keto group, thus affording unequal quantities of the diastereomers of II and III. If, on the other hand, such asymmetric syntheses are due to steric interactions alone, the separation of the preexisting asymmetric center and the reacting keto function of I, as well as the linear structure of I, should preclude the unequal production of the diastereomers of II and III and the appearance of optical activity in the products resulting on removal of the (−)-menthyl moiety from II and III.

(−)-menthyl *p*-benzoylbenzoate (I), prepared either by direct esterification or *via* the corresponding chloride, proved to be an oil, and was accordingly characterized through its crystalline oxime. The action of excess lithium aluminum hydride upon I led ultimately to a sample of crystalline *p*-(α-hydroxybenzyl)benzyl alcohol (IV) which



proved to be optically inactive, indicating the failure of "asymmetric induction" to be transmitted through the phenyl nucleus of I. Reduction of I with sodium borohydride led smoothly to high yields of crystalline (−)-menthyl *p*-(α-hydroxybenzyl)benzoate (II). Alkaline or acidic hydrolysis of II yielded optically inactive, crystalline *p*-(α-hydroxybenzyl)benzoic acid (V). Since direct reduction of II with lithium aluminum hydride was incomplete due to the formation of an insoluble complex, the ester II was converted to its acetate and the latter smoothly reduced with lithium aluminum hydride to produce crystalline *p*-(α-hydroxybenzyl)benzyl alcohol (IV). The optical inactivity of the latter again indicated that no asymmetric induction had been transmitted through the phenyl nucleus of ester I during reduction of I.

In order to parallel McKenzie's successful asymmetric syntheses using Grignard reagents on α-keto esters, methylmagnesium iodide was allowed to react in benzene solvent with ester I. An excellent yield of crystalline (−)-menthyl *p*-(α-hydroxy-α-methylbenzyl)benzoate (III. R = CH_3, R* = (−)-menthyl) resulted, which on alkaline hydrolysis produced optically inactive *p*-(α-hydroxy-α-methylbenzyl)benzoic acid (VI). Reduction of ester III with lithium aluminum hydride yielded a sirupy product, presumably *p*-(α-hydroxy-α-methylbenzyl)benzyl alcohol which, though uncharacterized, proved to be optically inactive. These data again indicate the failure of asymmetric induction to be transmitted through the aromatic ring of ester I on reaction of its keto group.

As a control to the above experiments we have repeated some of the classical asymmetric syntheses of McKenzie[8] under our reaction conditions. The action of methylmagnesium iodide on (−)-menthyl phenylglyoxylate led to results comparable to those described by earlier workers,[8,9,11] while the reduction of this ester with lithium aluminum hydride or with sodium borohydride gave asymmetric synthesis to the extent of 4 to 12% preponderance of one enantiomer.[18]

The above experimental evidence clearly indicates that asymmetric induction of the sort postulated by Ritchie and others, if it indeed exists, is incapable of being transmitted across the *para* positions in an aromatic nucleus, and strongly

(11) V. Prelog and co-workers, *Helv. Chim. Acta*, **36**, 308, 320, 325, 1178 (1953); **38**, 303 (1955); **39**, 1086 (1956); *Bull. soc. chim.*, 987 (1956).

(12) W. Klyne, *Progress in Stereochemistry*, Butterworths Scientific Publications, London, 1954, p. 198 ff.

(13) D. J. Cram and co workers, *J. Am. Chem. Soc.*, **74**, 5829 (1952); **75**, 2293, 6007 (1953); **76**, 22 (1954).

(14) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J Am. Chem. Soc.*, **79**, 6160 (1957).

(15) H. S. Mosher and E. La Combe, *J. Am. Chem. Soc.*, **72**, 3994, 4991 (1950).

(16) W. von E. Doering and R. W. Young, *J. Am. Chem. Soc.*, **72**, 631 (1950).

(17) *Cf.* also L. M. Jackson, J. A. Mills, and J. S. Shannan, *J. Am. Chem. Soc.*, **72**, 4814 (1950); A. Streitwieser and co-workers, *J. Am. Chem. Soc.*, **75**, 5014 (1953); **77**, 1117 (1955); **78**, 5597 (1956); **79**, 903 (1957).

(18) V. Prelog, M. Wilhelm, and D. B. Bright, *Helv. Chim. Acta*, **37**, 221 (1954).

confirms the current assignment of asymmetric bias to purely steric interactions.

EXPERIMENTAL

(−)-*Menthyl phenylglyoxylate* was prepared from phenylglyoxylic acid[19] according to the general procedure of McKenzie,[8] m.p. 72–73°, $[\alpha]_D^{26}$ − 45.7° (*c*, 4.85; ethanol). Its 2,4-dinitrophenylhydrazone, shining, golden platelets, had m.p. 161–162°.

Anal. Calcd. for $C_{24}H_{28}O_6N_4$: C, 61.53; H, 6.02. Found: C, 61.57; H, 6.29.

Reaction of methylmagnesium iodide with (−)-menthyl phenylglyoxylate. The Grignard solution, prepared from magnesium turnings (0.58 g.) and excess methyl iodide in anhydrous ether (55 ml.), was added dropwise over a period of 45 min. to a stirred solution of (−)-menthyl phenylglyoxylate (2.88 g.) in ether (4 ml.). The mixture was stirred for an additional 45 min. and allowed to stand overnight, then decomposed with dilute sulfuric acid containing crushed ice. The ether layer was washed twice with sodium bisulfite solution and with water, then evaporated to yield a yellow oil. This was dissolved in 6% alcoholic potassium hydroxide solution (30 ml.) and heated under reflux for 1 hr., whereupon the alcohol was distilled and water was added to the oily residue. The menthol so precipitated was filtered and the filtrated was clarified with Norit, then heated on the steam bath to remove the last traces of menthol. The filtered solution was treated with hydrochloric acid (20 ml.) and extracted with ether. The extracts were clarified with Norit and stripped of solvent, affording 0.5 g. (30%) of atrolactic acid, m.p. 83–85, $[\alpha]_D^{22}$ − 11.1° (*c*, 5.02; ethanol). After one recrystallization the acid had m.p. 90–91.5° and $[\alpha]_D^{22}$ − 11.6°. McKenzie[8] reports a yield of 79% of an acid having $[\alpha]_D^{18}$ −9.5°.

Reduction of (−)-menthyl phenylglyoxylate with lithium aluminum hydride. The above menthyl ester (5.0 g.) in anhydrous ether (50 ml.) was added dropwise with stirring to a slurry of lithium aluminum hydride (1.47 g.) in ether (50 ml.). The reaction mixture was stirred for an additional hour and the complex was decomposed by the cautious addition of saturated ammonium chloride solution. The ether layer was stripped of solvent and the residue subjected to steam distillation, yielding the theoretical amount of menthol. The residue was saturated with sodium chloride and extracted four times with ether. The extract was dried and stripped of solvent to yield 73% of phenylglycol, m.p. 57–64°, $[\alpha]_D^{27}$ − 3.2° (*c*, 6.03; ethanol). The dibenzoate derivative of this product had m.p. 93.5–95° in good agreement with the value recorded in the literature.[20] Prelog[18] obtained from the same reaction an 85% yield of phenylglycol having $[\alpha]_D$ − 2.95°.

Reduction of (−)-menthyl phenylglyoxylate with sodium borohydride. Finely powdered sodium borohydride (0.42 g.) was added slowly with cooling to a solution of (−)-menthyl phenylglyoxylate (6 g.) in methanol (100 ml.). The solution was allowed to stand at room temperature for 2.5 hr. then poured into cold water (250 ml.). The milky mixture was extracted four times with ether, and the extracts were dried and stripped of solvent *in vacuo*, affording 5.54 g. (91.7%) of white solid having m.p. 82.5–84° and $[\alpha]_D^{26}$ − 75.8° (*c*, 6.04; ethanol). The physical properties reported[8,11] for (−)-menthyl (±)-mandelate (XVI) are m.p. 85–86° and $[\alpha]_D$ −74°.

Since acid hydrolysis of the above (−)-menthyl mandelate preceded with unsatisfactory results, the above product was subjected to further reduction with lithium aluminum hydride. The product (4.94 g.) from the above sodium borohydride reduction in anhydrous ether (50 ml.) was added dropwise to a stirred, slurry of lithium aluminum hydride (0.6 g.) in ether (50 ml.). After completion of the addition the mixture was stirred for 15 min., then processed as above, affording ultimately a pale yellow liquid which crystallized on standing in a desiccator, 1.52 g. (64.7%), $[\alpha]_D^{19}$ − 2.64° (*c*, 6.07; ethanol). This sample of phenylglycol afforded a dibenzoate having m.p. 93.5–94° after one recrystallization. In a duplication of the above experiment a sample of phenylglycol having $[\alpha]_D^{30}$ − 3.44° was obtained in 81% yield.

(−)-*Menthyl p-benzoylbenzoate.* *p*-Benzoylbenzoic acid (27.48 g.), (−)-menthol (74.39 g.) and *p*-toluenesulfonic acid (*ca.* 1 g.) were heated on the steam bath for 2.5 days. The crude product was dissolved in a 1:1 mixture of ether and benzene and the solution was washed well with a saturated solution of sodium carbonate, then with water. The solution was steam distilled for 3.5 hr., after which time the odor of menthol was substantially removed. The aqueous residue was extracted with benzene and the extracts were dried and passed through a column of alumina. The effluate was evaporated *in vacuo* to yield 23.5 g. (53%) of pale yellow sirup, b.p. 203–204° (1 mm.), $[\alpha]_D^{28}$ − 54.1° (*c*, 2.24; ethanol). No attempts to crystallize this ester were successful and it was accordingly characterized through its oxime. The latter crystallized from ethanol as feathery, colorless needles having m.p. 160–161° and $[\alpha]_D^{30}$ − 49.2° (*c*, 2.13; chloroform).

Anal. Calcd. for $C_{24}H_{29}O_3N$: C, 75.96; H, 7.70; N, 3.69. Found: C, 75.98, 76.04; H, 7.61. 7.72; N, 3.48, 3.53.

Reduction of (−)-menthyl p-benzoylbenzoate with lithium aluminum hydride. (−)-Menthyl *p*-benzoylbenzoate (5 g.) in anhydrous ether (60 ml.) was added dropwise over a 15-min. period to a slurry of lithium aluminum hydride (1.17 g.) in ether (60 ml.). The mixture was stirred for an additional 30 min., then decomposed by the cautious addition of excess 15% hydrochloric acid. The aqueous layer was salted and extracted with ether and the combined ether solution was evaporated and subjected to steam distillation. When the odor of menthol was no longer apparent the mixture was cooled, treated with sodium chloride, and extracted four times with ether. The ethereal extract was dried and evaporated under reduced pressure leaving 3.39 g. (117.7%) of yellow sirup. This high yield as well as the low yield of recovered menthol (67.3%) suggested that reduction of the starting material had been incomplete. Accordingly the sirupy product was dissolved again in ether and its solution added dropwise to a slurry of lithium aluminum hydride (1.17 g.) over a 1.3-hr. period. The mixture was stirred under reflux for an additional 2 hr. then processed as before, affording a yellow, viscous oil which was optically inactive in chloroform. Crystallization from ethanol followed by three recrystallizations from benzene yielded pure *p*-(α-hydroxybenzyl)benzyl alcohol, m.p. 103–105°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 79.16; H, 6.86.

Reduction of (−)-menthyl p-benzoylbenzoate with sodium borohydride. The ester (5 g.) in ethanol (50 ml.) was added to sodium borohydride (0.13 g.) in methanol (50 ml.). The latter solution had been treated with 10% sodium hydroxide solution until approximately *p*H 9 to prevent effervescence. After 3 hr. the mixture was poured into 10% hydrochloric acid (200 ml.) and the milky mixture was extracted with ether. The extracts were washed with water, dried, and evaporated *in vacuo* to yield 4.57 g. (91%) of solid having m.p. 103–125° $[\alpha]_D^{25}$ − 58.6° (*c*, 2.27; ethanol). Five recrystallizations of the product from methanol gave pure (−)-menthyl *p*-(α-hydroxybenzyl)benzoate, m.p. 144–145°, $[\alpha]_D^{27}$ − 43.3° (*c*, 2.7; ethanol).

Anal. Calcd. for $C_{24}H_{30}O_3$: C, 78.65; H, 8.25. Found: C, 78.39, 78.22; H, 7.89, 7.87.

p-(α-Hydroxybenzyl)benzoic acid. The above crude ester (3.42 g.) was treated with ethanol (25 ml.) and 2.5*M* potassium hydroxide solution (20 ml.). The solution was heated under reflux for 4 hr., whereupon the ethanol was

(19) D. B. Corson, R. A. Dodge, S. A. Harris, and R. K. Hazen, *Org. Syntheses*, Coll. Vol. I, 241 (1944).

(20) A. Perret and R. Perrot, *Helv. Chim. Acta*, **28**, 558 (1945).

removed by distillation and the residue was extracted six times with 20-ml. portions of ether. The last extract was optically inactive, indicating complete removal of the menthol. The alkaline solution was acidified and the abundant precipitate was extracted into ether. The extracts were dried and stripped of solvent to yield 1.80 g. (84.5%) of white solid, m.p. 153–161°. The crude acid was optically inactive. Recrystallization from dilute methanol raised the m.p. to 164–165.5°, unchanged by further crystallization.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.39, 73.44; H, 5.13, 5.23.

When an attempt was made to hydrolyze the above (−)-menthyl *p*-(α-hydroxybenzyl)benzoate in dilute acetic acid containing sulfuric acid, the crude acidic product was obtained in 43.5% yield and proved to be optically inactive in ethanol.

Acetylation and lithium aluminum hydride reduction of (−)-menthyl p-(α-hydroxybenzyl)benzoate. Crude (−)-menthyl *p*-(α-hydroxybenzyl)benzoate (2 g.) was dissolved in pyridine (20 ml.). Acetic anhydride (4 ml.) was added and the solution was heated under reflux for 8 min., then poured onto chopped ice. The oily product was extracted into ether, and the extract was washed thoroughly with 6*N* hydrochloric acid, water, and sodium carbonate solution. Drying and solvent removal yielded 1.87 g. (83.9%) of cream-colored sirup. The crude sirupy acetate was dissolved in anhydrous ether (30 ml.) and the solution was added dropwise with stirring to a slurry of lithium aluminum hydride (0.51 g.) in ether (30 ml.). After 2 hr. of reflux, the mixture was hydrolyzed and processed in the usual way, yielding 0.94 g. (95.9%) of *p*-(α-hydroxybenzyl)benzyl alcohol which crystallized spontaneously. The sample was optically inactive in chloroform (*c*, 6.37) and showed no mixed melting point depression with the *p*-(α-hydroxybenzyl)benzyl alcohol obtained by the above lithium aluminum hydride reduction of (−)-menthyl *p*-benzoylbenzoate.

The reaction of methylmagnesium iodide with (−)-menthyl p-benzoylbenzoate. Methylmagnesium iodide from magnesium turnings (0.83 g.) and methyl iodide (4.87 g.) in anhydrous ether (50 ml.) was added dropwise during 1 hr. to a stirred solution of (−)-menthyl *p*-benzoylbenzoate (10 g.) in anhydrous benzene (100 ml.), causing gentle refluxing. After addition the ether component was distilled and the remaining benzene solution was stirred under reflux for 5 hr., chilled in ice, and treated gradually with 6*N* hydrochloric acid (50 ml.). Customary processing yielded 10.6 g. (101%) of an amber sirup which solidified in a vacuum desiccator.

A sample of this crude (−)-menthyl *p*-(α-hydroxy-α-methylbenzyl)benzoate (5 g.) was dissolved in anhydrous ether and the solution was added dropwise to a slurry of lithium aluminum hydride (1.11 g.) in anhydrous ether over a 30-min. period. Glass beads were then introduced into the mixture, stirring under reflux was continued for an additional 5 hr. and the excess hydride was destroyed by cautious addition of water and 6*N* hydrochloric acid. Customary work-up, including steam distillation for menthol removal yielded 2.72 g. (90.7%) calculated as *p*-(α-hydroxy-α-methylbenzyl)benzyl alcohol) of yellow sirup which proved to be optically inactive in ethanol solution.

The above crude (−)-menthyl *p*-(α-hydroxy-α-methylbenzyl)benzoate (4.95 g.) was dissolved in ethanol (40 ml.) containing 2.5*N* aqueous potassium hydroxide (20 ml.). The mixture was refluxed for 4 hr., the ethanol was distilled and the residue was cooled and extracted thoroughly with ether until the extracts were optically inactive, indicating menthol removal. The alkaline layer was acidified, at which point a heavy amber oil separated. This was extracted into ether and the dried extracts were evaporated *in vacuo*, yielding 2.59 g. (82.2%) of cream-colored solid which proved optically inactive in ethanol. The latter was recrystallized four times from benzene to yield pure *p*-(α-hydroxy-α-methylbenzyl)benzoic acid, m.p. 135–139°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.22, 74.16; H, 5.71, 5.60.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Conformational Studies. I. The Relative Stabilities of the *cis*-2-Decalols[1]

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Received September 22, 1960

Equilibration of the isomeric *cis*-2-decalols in refluxing decalin in the presence of approximately 5 mole per cent of sodium showed that their free energies are about equal. A reinvestigation of the equilibration in the presence of excess sodium showed that the *cis-cis* isomer is present in 66 ± 2% in an equilibrated mixture rather than the previously reported 80%. The equilibria were approached from both sides and the isomer ratios determined by infrared intensity measurements and by the binary melting point diagram method. The results are briefly discussed in the light of conformational analysis concepts.

The flexibility of the *cis*-decalin system permits the existence of two interconvertible chair-chair conformations, so that in passing from one to the other an axial substituent becomes equatorial and *vice versa*. Thus, the situation is similar to that existing with cyclohexane derivatives except that the *cis*-decalins would be expected to have additional non-bonded interactions imposed by the second ring. Present conformational concepts as applied to *cis*-decalins seem to hold quite well and have aided greatly in stereochemical studies.[3]

It is possible for the *cis*-2-decalols to exist in four conformations having the most stable double-chair ring system. These are shown in Fig. 1 where Ia and Ib represent the two possible conformations of *cis-cis*-2-decalol, and IIa and IIb those for the *cis-trans*-isomer.[4]

(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society in Richmond, Va., November, 1959.

(2) Taken in part from a dissertation submitted by L. C. Ellis in partial fulfillment of the requirements of the degree of Doctor of Philosophy, University of Virginia, 1961.

(3) For example, see (a) W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954); (*b*) J. A. Mills, *J. Chem. Soc.*, 260 (1953).