dimethylsuccinic acid (3.8 g.), adipic acid (5.2 g.), succinic acid (4.5 g.), residue (15 g.). The acids were all identified by mixed-melting points with authentic samples of the corresponding acids.

Since chromatography of the residual acids indicated only a trace of C_4-dicarboxylic acid, it appeared that no methylmalonic acid, a product of carboxylation at the α-carbon atom, was formed.

Carboxylation of 1-Hydroxycyclohexyl Hydroperoxide.—A 3-l. flask, similar to that used in the carboxylation of *t*-butyl alcohol, was charged with 750 ml. of methanol and 750 ml. of water and was chilled to 10°. Two solutions, one consisting of 139 g. (0.5 mole) of ferrous sulfate heptahydrate and 28 ml. (0.5 mole) of concd. sulfuric acid in 288 ml. of water and the other solution containing 66 g. (0.5 mole) of 1-hydroxycyclohexyl hydroperoxide in sufficient methanol to make 375 ml., were added at equivalent rates to the vigorously stirred reactor during 0.3 hr. The temperature was maintained at 10–20°, and carbon monoxide was bubbled through the reaction mixture at the rate of 1.5 l./min.

The product was saturated with anhydrous sodium sulfate and extracted continuously with ether. The ether solution was extracted with aqueous alkali to recover organic acids. Methanol was distilled from the alkaline extract which was then acidified and steam distilled to remove volatile monocarboxylic acid. The procedure for separation of pimelic (carboxylation product) and dodecanedioic (coupled product) acids[18] in the steam distillation residue was based on their distribution ratios between ether and water (approximately 1 for pimelic acid and 1000 for dodecanedioic acid). The acids were extracted from the residue with ether, and the ether solution was extracted four times with an equal volume of water to obtain an ether-soluble acid fraction (19 g.), mainly dodecanedioic acid, and a water-soluble acid fraction (9 g.) believed to be mostly pimelic acid.

Samples of the fractions were separated on a silica gel column. The ether-soluble fraction contained 95% dodecanedioic acid. The water-soluble fraction contained four acids of which the two principal components appeared to be pimelic acid (50%) and dodecanedioic acid (35%).

A 2-g. sample of the water-soluble acids was separated into ten fractions by counter-current extraction using five 100-ml. portions of water and of ether. A comparison of a calculated distribution of pimelic acid among the various fractions with the actual acid content as determined by titration indicated that the four middle fractions (two ether and two water) contained nearly pure pimelic acid. The crude acid from these fractions weighed 0.5 g. After recrystallization, the acid melted at 94–96° (compared with 103° reported for pimelic acid); the melting point was not depressed by mixing with authentic pimelic acid. *Anal.* Calcd. for $C_7H_{12}O_4$: C, 52.5; H, 7.5; neut. equiv., 80. Found: C, 53.1; H, 7.67; neut. equiv., 82.

The yield of pimelic acid calculated from the chromatographic separation of the water-soluble acid fraction was 2.8 g. (0.02 mole) from 0.5 mole of 1-hydroxycyclohexyl hydroperoxide.

WILMINGTON, DELAWARE

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[18] W. Cooper and W. H. T. Davison, *J. Chem. Soc.*, 1180 (1952); N. Brown, M. J. Hartig, M. J. Roedel, A. W. Anderson and C. E. Schweitzer, THIS JOURNAL, **77**, 1756 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Base-catalyzed Isomerization of 5,8-Dihydro-1-naphthol and Its Methyl Ether

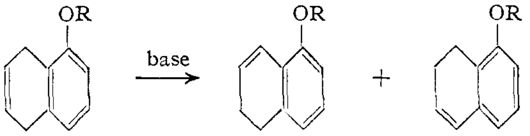
BY JEROME F. EASTHAM AND DONALD R. LARKIN

RECEIVED JULY 22, 1957

5,8-Dihydro-1-naphthol (I) is isomerized by base to produce primarily 5,6-dihydro-1-naphthol and some 7,8-dihydro-1-naphthol. Isomerization of the methyl ether of I proceeds in a similar manner. The structure of 5,6-dihydro-1-naphthol has been shown by degradation and of 7,8-dihydro-1-naphthol by degradation and synthesis. The rates of these base-catalyzed isomerizations of I and its methyl ether have been compared. The ultraviolet spectra of isomeric pairs such as 5,6- and 7,8-dihydro-1-naphthol are discussed.

The base-catalyzed isomerization of an allylphenol to a propenylphenol is a well known reaction.[1] In connection with other work[2] it was necessary to prepare a quantity of 5,8-dihydro-1-naphthol (I), a cyclic analog of an allylphenol. The present paper reports our findings on the course and the rate of base-catalyzed isomerization of I.

Potassium and alcohol in liquid ammonia efficiently reduce 1-naphthol to 5,8-dihydro-1-naphthol (I).[3] The unconjugated dihydronaphthol (I) produced is isomerized (equation 1) by alkali to a conjugated isomer[4] whose structure had never been determined. Isomerization of the methyl ether[5] II of the reduction product proceeds in a similar manner. It has now been shown that the base-catalyzed isomerization of 5,8-dihydro-1-naphthol or its methyl ether yields predominantly the 5,6-dihydroisomer (III or IV) along with some of the 7,8-dihydroisomer (V or VI). The chemical evidence for the position of the double bond in 5,6-dihydro-1-naphthol is shown in Chart I.



(1)

I, R = H
II, R = CH_3

III, R = H
IV, R = CH_3

V, R = H
VI, R = CH_3

The crystalline product from alkali-isomerization of 5,8-dihydro-1-naphthol was methylated[6] and

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[1] As leading references see D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 19; and A. R. Bader, THIS JOURNAL, **78**, 1708 (1956).

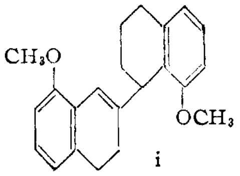
[2] J. F. Eastham and D. R. Larkin, Abstracts, 7th Annual Southeastern Regional Meeting of the American Chemical Society, Columbia, S. C., 1955. Details of this work, which concerned the effect of variables on the rate of the reduction in ref. 3, will be reported later.

[3] A. J. Birch, *J. Chem. Soc.*, 430 (1944).

[4] F. M. Rowe and E. Levin, *ibid.*, **119**, 2021 (1921).

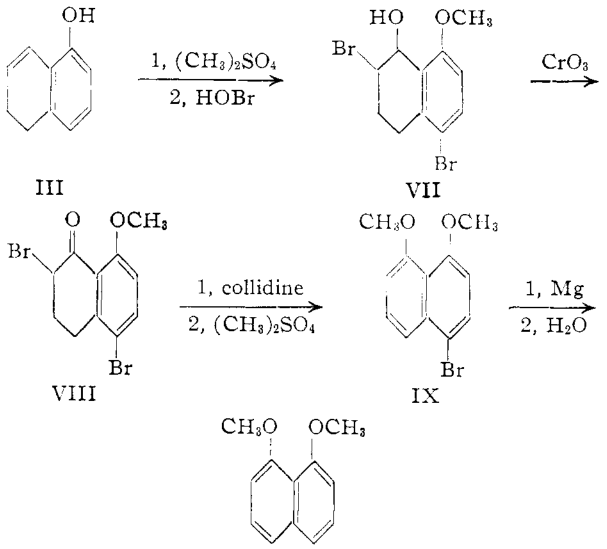
[5] The 5,8-dihydro ether II, a liquid, did not form a crystalline adduct with mercuric acetate as does the parent hydrocarbon, 1,4-dihydronaphthalene (J. Sand and O. Grenssler, *Ber.*, **36**, 3699 (1903)). An acetate, also a liquid, could be prepared from the dihydronaphthol I by treatment with acetic anhydride.

[6] Initially some attempts were made to show the position of the double bond in III through a crystalline acetate prepared from it. However, work with the methyl ether IV proved more fruitful. Purification by distillation of the ether IV always left a dimer, $C_{22}H_{24}O_2$, m.p. 148°, probably with the structure indicated by i.



i

CHART I

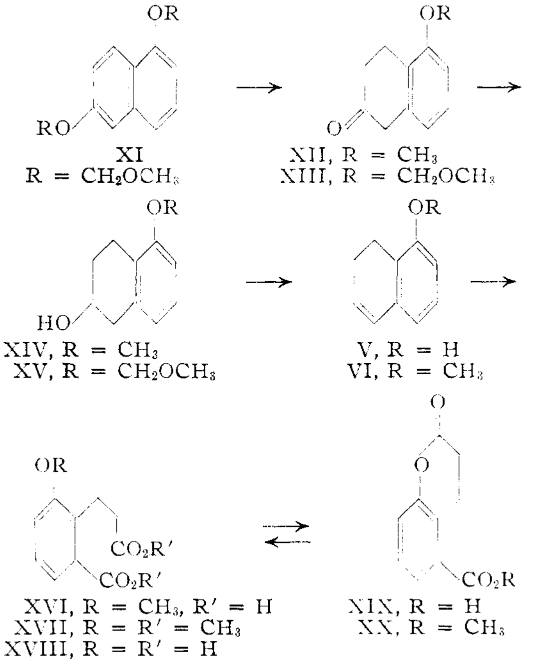


treated with aqueous hypobromite to yield crystalline 1-hydroxy-2,5-dibromo-8-methoxytetralin (VII). The same dibromohydrin could be obtained by methylating 5,8-dihydro-1-naphthol and then isomerizing with base and treating with hypobromite. Upon oxidation with chromium trioxide the dibromohydrin VII[7] yielded a dibromoketone VIII which after dehydrobromination and methylation gave 1,8-dimethoxy-4-bromonaphthalene (IX).[8] Bromine was reduced from IX through its Grignard reagent to produce the known 1,8-dimethoxynaphthalene (X). The synthesis by this sequence (Chart I) of the 1,8-derivative X, rather than 1,5-dimethoxynaphthalene, shows the starting compound to be the 5,6-dihydroisomer III, rather than 7,8-dihydro-1-naphthol (V).

This 7,8-dihydro-1-naphthol (V) and its methyl ether VI have now been synthesized as shown in Chart II. Base-catalyzed dehydration of the carbinol XIV obtained by reduction of 5-methoxy-2-tetralone (XII) yielded the methyl ether VI of 7,8-dihydro-1-naphthol. That the double bond in VI is in the 5,6-position was shown by characterizing (Chart II) the dibasic acid XVI obtained by oxidation of VI. This dibasic acid, 3-(2-methoxy-6-carboxyphenyl)-propanoic acid (XVI), yielded a dimethyl ester XVII when treated with diazomethane and a lactone-acid XIX when treated with hot pyridinium chloride. The lactone acid, 5-carboxy-3,4-dihydrocoumarin (XIX), gave a monomethyl ester XX with diazomethane but neither this lactone-ester XX nor the lactone-acid XIX could be cleaved by saponification followed by acidifying to obtain the phenol-dibasic acid XVIII. This was true because of the facile lactonization of an acid with the expected structure, 3-(2-hydroxy-6-carboxyphenyl)-propanoic acid (XVIII). The lactone ring could be kept open, however, by saponification followed by treatment of the basic reaction solution with excess dimethyl sulfate to obtain the previously characterized methyl ether XVI of the phenol-dibasic acid XVIII.[9]

Because the methyl ether VI of 7,8-dihydro-1-naphthol (V) could not be cleaved to the free naphthol,[10] this compound was prepared through use of a more easily cleaved ether, 1,6-bis-(methoxymethoxy)-naphthalene (XI). Reduction of XI by potassium and ammonium chloride in liquid ammonia followed by an acid hydrolysis of the crude product yielded 5-methoxymethoxy-2-tetralone (XIII). Lithium aluminum hydride reduction of XIII gave 5-methoxymethoxy-2-tetralol (XV) Hydrolysis of this ether XV yielded the correspond ing diol which was dehydrated with alkali to crystal line 7,8-dihydro-1-naphthol (V). Methylation of V gave the previously prepared 1-methoxy-7,8 dihydronaphthalene.

CHART II



The ultraviolet absorption spectra of the isomeric pairs III-V and IV-VI corroborate the chemical evidence for their structure. The chromophores in these compounds are, respectively, those

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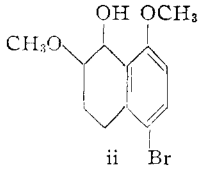
(7) Treatment of the dibromohydrin VII with methanolic silver nitrate did not yield any rearrangement product. The only isolable product, $C_{12}H_{15}O_3$, m.p. 141.5°, obtained from such treatment is probably 1-hydroxy-2,8-dimethoxy-5-bromotetralin (ii).

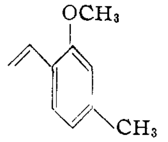


(8) The position of bromine in IX is assumed and has not been proved.

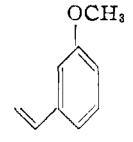
(9) The ultraviolet and infrared spectra of the lactone-methyl ester XX are in accord with the structure given. In the ultraviolet region XX has an absorption maximum at 295 mμ. In its infrared spectrum there are maxima at 1788 cm.$^{-1}$ (lactone carbonyl) and 1730 cm.$^{-1}$ (methyl ester carbonyl).

(10) Methods which were tried for cleavage of the ether VI included heating with pyridinium chloride and with dry methylmagnesium iodide. The chief difficulty encountered was undoubtedly polymerization through the styrene-type double bond of VI. Another reaction which failed with VI was the addition of HOBr. Under conditions which yielded up to 60% of dibromohydrin VII from 5,6-dihydro-1-methoxynaphthalene (III), nothing could be isolated from the 7,8-dihydro-isomer VI.

of phenol and anisole pairs with a styrene-type double bond first in the *ortho* and then in the *meta* position. In Table I the spectra of these pairs are compared with those of a known methoxystyrene pair, with a similar chromophore. The absorption maximum is the same for both members of a given pair in Table I and in every case is in the region 250–270 mμ.[11] However, in each pair the member whose double bond is *ortho* to the oxygen function absorbs more strongly than does the member whose double bond is *meta* to the oxygen function. This decrease in absorption intensity in going from an *ortho* to a *meta* disubstituted benzene derivative seems to be rather general and could be useful in distinguishing between members of such pairs. Doub and Vandenbelt list the ultraviolet absorption characteristics of twenty-five pairs of *o*- and *m*-disubstituted benzene derivatives.[11] In all but two[12] of these the first primary band of the *o*-compound is more intense than that of its *m*-isomer.



XXI



XXII

TABLE I

Compound	λ_{max}, mμ	log ε
III[a]	267	3.83
V[a]	267	3.65
IV[a]	265	3.94
VI[a]	265	3.89
XXI[b]	250	4.06
XXII[a]	250	3.93

[a] Spectrum determined in this work. [b] Spectrum reported by H. A. Laitinen, F. A. Miller and T. D. Parks, THIS JOURNAL, 69, 2707 (1947).

The isomerization of 5,8-dihydro-1-naphthol shown in equation 3 does not produce exclusively the 5,6-dihydro isomer. The crude product from the treatment with alkali requires extensive recrystallization for purification. If the crude product is methylated, then the presence of the 7,8-dihydro isomer can be shown by oxidation. From treatment of the crude methylated product with permanganate one can isolate in low yield 3-(2-methoxy-6-carboxyphenyl)-propanoic acid (XVI), the dibasic acid from the 7,8-dihydromethyl ether VI. The yield of dibasic acid XVI is about the same whether the sequence of reactions from 5,8-dihydro-1-naphthol is isomerization–methylation–oxidation, or is methylation–isomerization–oxidation. That is, the course of the isomerization of the methyl ether II is the same as for the free naphthol I. The pure 5,6-dihydromethyl ether (IV) can be prepared by methylation of the purified 5,6-dihydro-1-naphthol. When the pure 7,8-dihydromethyl ether had been prepared as in Chart II, it was of interest to compare the infrared spectra of the isomeric ethers (II, IV, VI). By infrared spectroscopy it was then possible to estimate that the isomerization of the 5,8-dihydro isomer, equation 3, produced a ratio of about 4:1 of the 5,6-dihydro and 7,8-dihydro isomers.

The kinetics of the isomerization of 5,8-dihydro-1-naphthol (I) and its methyl ether II have been measured, Fig. 1. For these measurements a spectrophotometric method of analysis was used. In the presence of excess potassium *t*-amylate in *t*-amyl alcohol at 100° the kinetics were first order during the first 30% of the reaction. The first-order rate constant of the methyl ether II, 3.49 × 10^{-3} min.$^{-1}$, was not much larger that that of the free naphthol I, 2.93 × 10^{-3} min.$^{-1}$. It is rather surprising that the two rates are so close. Whatever the mechanistic details of this base-catalyzed isomerization, an intermediary carbanion is probably required, as in equation 2. It was expected that the rate of formation of the necessary carbanion Ib from the free naphthol would be reduced (and thereby the rate of isomerization of the free naphthol would be less than that of its methyl ether) by effective removal of this free naphthol as its conjugate base Ia in the basic isomerization

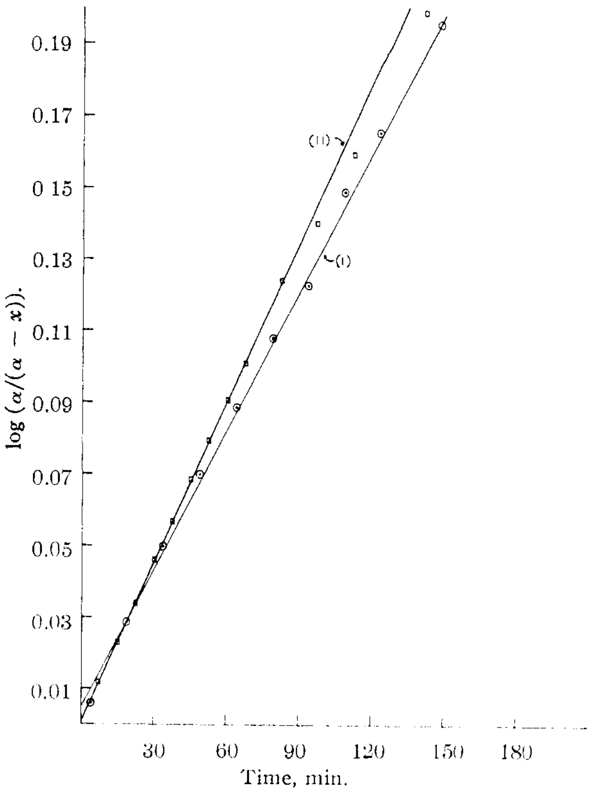
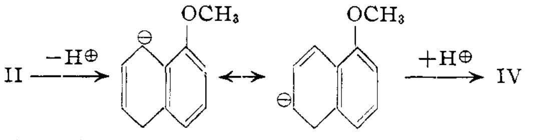


Fig. 1.—First-order plots for the isomerization of 5,8-dihydro-1-naphthol (I) and its methyl ether (II) at 100° in *t*-amyl alcohol solutions 0.13 *M* in the potassium salt of this alcohol. The slopes of these lines show k_I to be 2.97 × 10^{-3} min.$^{-1}$ and k_{II} to be 3.44 × 10^{-3} min.$^{-1}$.



(2)

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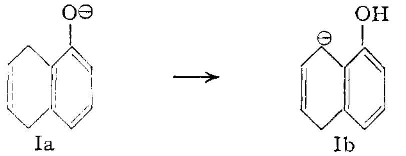
[11] According to nomenclature employed by L. Doub and J. M. Vandenbelt (THIS JOURNAL, **71**, 2414 (1949)) this is the "first primary band."

[12] These two are chlorobenzoic acid and the potassium salt of this acid.

medium. Possibly this effect is offset by Ia effecting an internal proton transfer to give Ib, equation 3.



Ia Ib (3)

Experimental[13]

5,8-Dihydro-1-naphthol (I).—To a solution of 110 ml. of absolute ethanol in 600 ml. of liquid ammonia 23 g. of potassium metal was added in small portions and allowed to react, after which 85 g. of powdered 1-naphthol was added to give a solution of potassium 1-naphthoxide. There was then added in small portions sufficient potassium metal, about 50 g., to impart a blue color to the solution for one minute.

The mouths of the flask were loosely covered with glassine paper and the liquid ammonia was allowed to evaporate at room temperature. Ice was added to the residue and the resulting solution diluted to 3 l. with water and acidified with hydrochloric acid. The cream-colored precipitate was collected, washed with water, dried, vacuum distilled (b.p. 120° (1 mm.)) and recrystallized from hexane. The yield of colorless prisms was 67 g. (80%), m.p. 72–73.5° cor.[14] The ultraviolet spectrum of the product shows maxima at 273 and 279 mμ with molar extinction coefficients of 1700 and 1600, respectively. **1-Acetoxy-5,8-dihydronaphthalene** was prepared by refluxing together 0.1 g. of *p*-toluenesulfonic acid and 5 g. of the 5,8-dihydro-1-naphthol in 10 ml. of isopropenyl acetate. The excess isopropenyl acetate and the acetone produced were distilled and the residue was fractionated to give 4.1 g. (64%) of the acetate as a colorless liquid, b.p. 170–171° (23 mm.), n^{25}_{Hg} 1.5367.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.75; H, 6.57.

Reduction of 1-Naphthol and Isomerization of the Product.—The reduction exactly as described in the first paragraph above was repeated, after which 250 ml. of xylene was added to the cold reaction solution and the liquid ammonia was allowed to evaporate overnight; 150 ml. of ethanol was added to the xylene solution which was then refluxed for eight hours. This solution was worked up by the two alternate methods described in the sections following which describe the preparation of 5,6-dihydro-1-naphthol (III) and of 1-methoxy-5,6-dihydronaphthalene (IV).

5,6-Dihydro-1-naphthol (III).—The 5,6-dihydro-1-naphthoxide ion was extracted from the above reaction mixture with 2 l. of water. The water extract was cooled by the addition of ice and acidified with concentrated hydrochloric acid. The cream-colored precipitate was collected, washed with water, dried and distilled, to give colorless needles, m.p. 64–67°. After several recrystallizations from benzene and hexane the product melted 69.2–70.7° cor.[4] A mixed melting point of the product with 5,8-dihydro-1-naphthol was depressed only slightly; however, the two compounds have very different ultraviolet spectra. 5,6-Dihydro-1-naphthol has maxima at 267, 298 and 308 mμ with molar extinction coefficients of 8010, 2850 and 2550, respectively. **1-Acetoxy-5,6-dihydronaphthalene** prepared with isopropenyl acetate and III and purified by distillation, b.p. 280° (745 mm.), is a wax-like solid, m.p. 72–75°; ultraviolet λ_{max} 265 and 300 mμ, ϵ 7000 and 1800.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.28; H, 6.63.

1-Methoxy-5,6-dihydronaphthalene (IV).—Concentrated hydrochloric acid (110 ml.) was added slowly to the ethanol-xylene solution of isomerized dihydronaphthol; 150 ml. of methyl sulfate was added to the mixture dropwise and potassium hydroxide solution was added as needed to keep the reaction mixture basic. After addition of the methyl sulfate was complete, the mixture was refluxed for two hours. Sufficient concentrated ammonium hydroxide was added to decompose the excess methyl sulfate and the reaction mixture was diluted with 1 l. of water. The xylene layer was separated and the water layer was extracted with benzene, which then was combined with the xylene layer. The combined extracts were washed with dilute hydrochloric acid and with aqueous sodium bicarbonate and dried. The solvent was removed under reduced pressure and the product fractionally distilled, b.p. 130–131° (15 mm.). The yield was 94–100 g. (85–90%) of a colorless oil, n^{25}_{D} 1.5882; ultraviolet λ_{max} 265, 296 and 307 mμ, ϵ 8550, 2400 and 200, respectively.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.54; H, 7.70.

The tar left in the pot after the vacuum distillation of the above 1-methoxy-5,6-dihydronaphthalene (IV) was triturated with acetone to leave a white crystalline material. After two recrystallizations from methanol this product melted 147.5–148.5°; ultraviolet λ_{max} 280, 300 and 325 mμ, ϵ 3700, 850 and 570, respectively. The product probably has the structure of **the dimer i.**[6]

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55; mol. wt., 320. Found: C, 82.48, 82.38; H, 7.56, 7.44; mol. wt. (Rast), 304.

1-Methoxy-5,8-dihydronaphthalene (II).—A solution of 60 g. of 5,8-dihydro-1-naphthol and 23 g. of potassium hydroxide in 200 ml. of water was treated alternately with methyl sulfate (about 57 ml. total employed) and potassium hydroxide (enough to keep the solution basic) in the usual manner. Sufficient ammonium hydroxide was added to decompose the excess methyl sulfate and the reaction mixture was poured into 500 ml. of water and extracted with ether. The ether extract was dried, the ether removed under reduced pressure, and the product purified by vacuum distillation to give 55 g. (84%) of a colorless oil, b.p. 123–124° (11 mm.), n^{25}_{D} 1.5735; ultraviolet λ_{max} 269 and 277 mμ, ϵ 2100 and 1910, respectively.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.40; H, 7.65.

Isomerization of 1-Methoxy-5,8-dihydronaphthalene.—After 50 g. of potassium metal had been dissolved in 250 ml. of refluxing absolute ethanol, 250 ml. of xylene and 100 g. of 1-methoxy-5,8-dihydronaphthalene were added and the resulting solution refluxed for eight hours. The reaction mixture was poured into ice-water and the xylene layer separated. The water layer was extracted with benzene which was then combined with the xylene layer. The combined extracts were washed with dilute hydrochloric acid and with aqueous sodium bicarbonate and dried. The solvent was removed under reduced pressure and the product vacuum distilled to give 93 g. of 1-methoxy-5,8-dihydronaphthalene as a colorless oil, identical with the compound produced by methylation of isomerized 5,8-dihydro-1-naphthol.

1-Hydroxy-2,5-dibromo-8-methoxytetralin (VII).—An emulsion was formed from 10 g. of 1-methoxy-5,6-dihydronaphthalene, 250 ml. of water and 2 g. of Tide. The emulsion was stirred vigorously and heated to 70° while 1300 ml. of aqueous 5% sodium bromide solution containing 15 g. of bromine was added dropwise. When the addition was complete, air was bubbled through the reaction mixture to remove excess bromine. The organic material was allowed to settle and the supernatant aqueous solution decanted. The white solid obtained was recrystallized twice from methanol to give 11.6 g. (56%) of 1-hydroxy-2,5-dibromo-8-methoxytetralin, m.p. 157.5–159°; ultraviolet λ_{max} 282 and 290 mμ, ϵ 2000 and 1850, respectively.

Anal. Calcd. for $C_{11}H_{12}O_2Br_2$: C, 39.31; H, 3.60; Br, 47.56. Found: C, 39.19; H, 3.72; Br, 47.52.

2,8-Dimethoxy-1-hydroxy-5-bromotetraline (ii).—To a solution of 6 g. of 1-hydroxy-2,5-dibromo-8-methoxytetralin and 2.6 g. of sodium carbonate in 60 ml. of methanol was added dropwise 5 g. of silver nitrate dissolved in 120 ml. of methanol and 10 ml. of water. The reaction mixture was stirred for one hour at room temperature and then for one hour on the steam-bath. It was concentrated to half its volume and poured into water and the water solution extracted with benzene. The benzene was evaporated to leave 2.3 g. of a semi-crystalline mass, m.p. 93–97°, which was recrystallized from methanol and then from benzene–

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[13] Melting points are reported uncorrected unless otherwise noted. Ultraviolet absorption spectra were determined in ethyl alcohol solution.

[14] This procedure is modified from that of Birch,[3] who reports a m.p. for the final product of 74°.

petroleum ether to give colorless crystals, m.p. 140.5–141.5°; ultraviolet λ_{max} 283 mμ, ϵ 1750.

Anal. Calcd. for $C_{12}H_{15}O_3Br$: C, 50.19; H, 5.27; Br, 27.83. Found: C, 50.19, 50.33; H, 5.33, 5.27; Br, 26.92, 26.77.

2,5-Dibromo-8-methoxy-1-tetralone (VIII).—Seven and one-half grams of chromium trioxide in 10 ml. of water and 430 ml. of glacial acetic acid was added to 25 g. of 1-hydroxy-2,5-dibromo-8-methoxytetralin in 430 ml. of glacial acetic acid. The resulting reaction mixture was stirred for three hours at room temperature and was then allowed to stand overnight. It was diluted with 3.5 l. of water and allowed to stand for an additional three days at 5°. The yellow powder which precipitated was collected, washed with water and dried. The crude product, 20.2 g., m.p. 110–113°, was recrystallized from methanol to give VIII as yellow cubes, m.p. 118.2–120°; ultraviolet λ_{max} 263 and 335 mμ, ϵ 7350 and 3700, respectively.

Anal. Calcd. for $C_{11}H_{10}O_2Br_2$: C, 39.55; H, 3.02; Br, 47.85. Found: C, 39.83, 39.92; H, 3.22, 3.15; Br, 47.49, 47.33.

Dehydrobromination of 2,5-Dibromo-8-methoxy-1-tetralone.—To find the optimum temperature for dehydrobromination preliminary tests were run using 0.5 g. of 2,5-dibromo-8-methoxy-1-tetralone (VIII) in 20 ml. of collidine. The ultraviolet spectra of the crude products were examined to see if dehydrobromination occurred. No reaction took place at 100 or 125°. At 170° dehydrobromination occurred, but no product could be isolated from the viscous tars produced in the reaction. A temperature of 150° was chosen as the best reaction temperature. A solution of 18.5 g. of VIII in 250 ml. of collidine which had been freshly distilled under nitrogen was placed under a nitrogen atmosphere and heated to 150–155° for 45 minutes. It was then cooled, filtered to remove carbonaceous material and poured onto a cracked ice–hydrochloric acid mixture which was then extracted three times with chloroform. Evaporation of the chloroform gave 6 g. of a viscous residue. The crude product was distilled in a molecular still at a pot temperature of 240–250° and a pressure of 0.2 mm. to yield approximately 3.5 g. of a white sticky semi-solid. This product was oxidized so rapidly in air that no further attempt at purification was made; it was used immediately as described in the following experiment.

1,8-Dimethoxy-4-bromonaphthalene (IX).—Five grams of the crude material produced as in the last paragraph was dissolved in 30 ml. of methanol and made basic with 1.2 g. (0.021 mole) of potassium hydroxide. While the reaction mixture was stirred and heated on the steam-bath an alternate addition of 1.95 ml. of methyl sulfate and 1.2 g. of potassium hydroxide was repeated four times. The excess methyl sulfate was destroyed with ammonium hydroxide and the reaction mixture extracted with chloroform. The chloroform extract was filtered, dried and evaporated to leave a residue which was sublimed at a pot temperature of 160–170° at 0.2 mm. The sublimate was recrystallized from methanol to give 1.4 g. of 1,8-dimethoxy-4-bromonaphthalene, m.p. 93–94.5°; ultraviolet λ_{max} 308.5, 323 and 336.5 mμ; ϵ 9350, 8200 and 6700, respectively.

Anal. Calcd. for $C_{12}H_{11}O_2Br$: C, 53.95; H, 4.15; Br, 29.92. Found: C, 53.78; H, 4.34; Br, 30.05.

1,8-Dimethoxynaphthalene (X).—To 0.6 g. of magnesium turnings in a flask filled with nitrogen was added a drop of methyl iodide in 2 ml. of ether. When reaction had begun 1.1 g. of 1,8-dimethoxy-4-bromonaphthalene and 0.6 g. of methyl iodide dissolved in 20 ml. of ether was added dropwise just fast enough to keep the reaction mixture refluxing. After complete addition the reaction mixture was refluxed for 40 minutes. On cooling, a black liquid separated from the ether and settled to the bottom of the reaction flask. An ethereal solution of alcohol was added slowly to the stirred reaction mixture. When the vigorous reaction had subsided, dilute hydrochloric acid was added and the mixture was filtered and extracted with benzene. Evaporation of the benzene extract gave a residue which was sublimed at 100–110° and 0.3 mm. and then recrystallized from methanol to give colorless plates, m.p. 159–159.5° cor.; ultraviolet λ_{max} 298.5, 315.5 and 330 mμ; ϵ 7700, 6650 and 6900. A mixed melting point with an authentic sample of 1,8-dimethoxynaphthalene showed no depression.[15]

5-Methoxy-2-hydroxytetralin (XIV).—To 1.70 g. of lithium aluminum hydride in 150 ml. of ether was added slowly 27.5 g. of 5-methoxy-2-tetralone dissolved in 100 ml. of ether. The reaction mixture was refluxed on the steam-bath for one hour. Excess lithium aluminum hydride was decomposed with a dilute ethereal solution of alcohol and the reaction mixture was diluted with water, acidified with hydrochloric acid and extracted with ether. The ether was removed under reduced pressure and the product was vacuum distilled, b.p. 126–129° (0.3 mm.), and then recrystallized from ligroin and benzene to give 21.2 g. (77%) of 5-methoxy-2-hydroxytetralin, m.p. 73–74°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.27; H, 7.79.

Five grams of 5-methoxy-2-hydroxytetralin was mixed with 15 g. of benzoyl chloride and heated for 15 minutes on the steam-bath. The reaction was worked up in the usual manner to give an essentially quantitative yield, 7.6 g., of the **benzoate of 5-methoxy-2-hydroxytetralin**, m.p. 111–112°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.41; H, 6.49.

1-Methoxy-7,8-dihydronaphthalene (VI).—Attempts to prepare 1-methoxy-7,8-dihydronaphthalene by pyrolysis of the benzoate of 5-methoxy-2-hydroxytetralin failed. This compound distilled unchanged at 240° (760 mm.) from a pot temperature of 360°. The 5-methoxy-2-hydroxytetralin (XIV) was dehydrated in a mixture of molten potassium hydroxide and sodium hydroxide.

Seven and one-half grams of XIV was mixed with 12.5 g. of potassium hydroxide and 12.5 g. of sodium hydroxide and heated to 260–300°. After 30 minutes the reaction mixture was poured onto ice which was then diluted with water and extracted with ether. The ether was evaporated and the residue distilled to give 6.15 g. of 1-methoxy-7,8-dihydronaphthalene, b.p. 145° (23 mm.), $n^{27}D$ 1.5828; ultraviolet λ_{max} 265 and 298 mμ; ϵ 7800 and 2130.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.37; H, 7.52.

3-(2-Methoxy-6-carboxyphenyl)-propanoic Acid (XVI).—A stirred slurry of 1 g. of 1-methoxy-7,8-dihydronaphthalene in 10 ml. of acetone and 10 ml. of water was maintained at or below 5° while 2.7 g. of potassium permanganate in 40 ml. of water was added to it dropwise. After two hours the reaction mixture was diluted to 200 ml. with water, filtered to remove manganese dioxide, acidified with hydrochloric acid and placed in the refrigerator overnight. The precipitated acid was collected, washed with water and air-dried to yield 0.42 g. of 3-(2-methoxy-6-carboxyphenyl)-propanoic acid (XVI), m.p. 218–220°. Recrystallization of the acid from methanol gave an analytical sample, m.p. 221–222°.

Anal. Calcd. for $C_{11}H_{12}O_5$: C, 58.92; H, 5.40. Found: C, 58.81; H, 5.42.

Methyl 3-(2-Methoxy-6-carbomethoxyphenyl)-propanoate (XVIII).—To a solution of 5 g. of 3-(2-methoxy-6-carboxyphenyl)-propanoic acid in 150 ml. of tetrahydrofuran was added 120 ml. of ether containing approximately 3.3 g. of diazomethane. After a few minutes the excess diazomethane in the reaction mixture was destroyed with acetic acid. The ether–tetrahydrofuran reaction mixture was washed with aqueous sodium bicarbonate and with water, dried, and evaporated under reduced pressure to leave 5.60 g. of crude ester, m.p. 65°. After recrystallization from methanol the methyl 3-(2-methoxy-6-carbomethoxyphenyl)-propanoate melted 75–76°.

Anal. Calcd. for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.96; H, 6.57.

No particular difficulty was encountered in repetition of their methylation reactions for the preparation of authentic X. It was therefore surprising to find the recent statement by Ng. Ph. Buu-Hoï and D. Lavit, *J. Chem. Soc.*, 2912 (1956), that ". . . even the structure of [1,8-dihydroxynaphthalene's] methylation products has not yet been elucidated." Although this statement does not seem justified, a comparison of the melting points of 1,8-dihydroxynaphthalene, its monomethylation product, and its dimethylation product is arresting. For this diol, hydroxy-ether and diether the melting points are, respectively, 146°, 56° and 160°. For the bromination product IX of the latter, in a similar irrational vein, the m.p. drops to 95°.

(15) H. Schmid, A. Ebnother and M. Burger, *Helv. Chim. Acta*, **33**, 609 (1950), were the first to prepare 1,8-dimethoxynaphthalene (X).

The Lactone XIX of 3-(2-Hydroxy-6-carboxyphenyl)-propanoic Acid.—Fifteen grams of pyridinium chloride and 4.8 g. of 3-(2-methoxy-6-carboxyphenyl)-propanoic acid were heated at 210° for 3.5 hours. Hydrogen chloride gas was bubbled through the mixture during this time. The reaction mixture was poured into 100 ml. of dilute hydrochloric acid and the precipitated product was collected, redissolved in aqueous sodium bicarbonate and reprecipitated from the filtered solution with hydrochloric acid. The product was recrystallized from tetrahydrofuran–benzene to give 3.1 g. of the lactone XIX, m.p. 173–175°; ultraviolet λ_{max} 295 mμ; ϵ 2650.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 62.08, 62.10; H, 4.04, 4.14.

The Lactone XX of 3-(2-Hydroxy-6-carbomethoxyphenyl)-propanoic Acid.—An ethereal solution of excess diazomethane was added to a solution of 0.1 g. of the lactone of 3-(2-hydroxy-6-carboxyphenyl)-propanoic acid in 2 ml. of dimethylformamide. After a few minutes the excess diazomethane was destroyed with acetic acid. The ether solution was extracted with aqueous sodium bicarbonate, dried and distilled under reduced pressure to leave 0.1 g. of crude ester. After vacuum distillation and recrystallization from methanol the lactone of 3-(2-hydroxy-6-carbomethoxyphenyl)-propanoic acid melted 101–102°; infrared maxima, 1788, 1730 cm.$^{-1}$; ultraviolet λ_{max} 295 mμ, ϵ 2600.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.07; H, 3.89. Found: C, 64.03; H, 4.74.

Conversion of the Lactone XIX of 3-(2-Hydroxy-6-carboxyphenyl)-propanoic Acid into 3-(2-Methoxy-6-carboxyphenyl)-propanoic Acid (XVI).—A solution of 0.7 g. of the lactone XIX and 9 g. of potassium hydroxide in 15 ml. of water was heated on the steam-bath for one hour. Then 3 ml. of methyl sulfate in 10 ml. of methanol was added dropwise to the hot reaction mixture. Additional potassium hydroxide was added as needed to keep the reaction mixture basic. When the basic reaction mixture became clear it was extracted with chloroform and acidified, whereupon crystallization occurred. The yield of product was 0.8 g. (95%), m.p. 221–222°. A mixed melting point with previously prepared 3-(2-methoxy-6-carboxyphenyl)-propanoic acid showed no depression.

1,6-Bis-(methoxymethoxy)-naphthalene (XI).—In 350 ml. of absolute methanol there was dissolved in turn 7.2 g. of sodium, 50 g. of 1,6-dihydroxynaphthalene and (dropwise) 25 g. of chloromethyl methyl ether. When this reaction solution had been stirred for two hours there was added to it an additional amount of sodium methoxide solution made from 7.2 g. of sodium and 100 ml. of methanol. After this another 25 g. of the chloromethyl ether was added dropwise to the reaction solution. After two more hours there was added in turn a final sodium methoxide solution made from 3.6 g. of sodium and 50 ml. of methanol and (dropwise) 12.5 g. of the chloromethyl ether. The reaction mixture was allowed to stand overnight at room temperature and then poured into 1 l. of water. The water solution was extracted with ether and the ether extracts evaporated under reduced pressure. The residue was distilled to give 47 g. (60%) of 1,6-bis-(methoxymethoxy)-naphthalene, b.p. 147–148° (0.3 mm.), n^{29}D 1.5812; ultraviolet λ_{max} 235 (broad), 283, 315 and 330 mμ; ϵ 18200, 5300, 2250 and 2100, respectively.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.83, 67.61; H, 6.40, 6.65.

Reduction of 1,6-Bis-(methoxymethoxy)-naphthalene (XI).—To 1200 ml. of liquid ammonia was added in turn 60 g. of 1,6-bis-(methoxymethoxy)-naphthalene in 100 ml. of dry ethyl ether, 13 g. of ammonium chloride and 9.7 g. of potassium metal in small pieces. The alternate addition of ammonium chloride and potassium metal was repeated four more times. In all 65 g. of ammonium chloride and 48.5 g. of potassium metal were added. The ammonia was allowed to evaporate overnight at room temperature. The residue was dissolved in water and extracted three times with ether. Evaporation of the dried ether gave 57 g. of dark oil. No attempt was made to purify this oil. However, an ultraviolet spectrum of the crude oil showed that reduction had taken place. The spectrum was similar to that of a simple anisole with a maximum at 267 mμ and a molar extinction coefficient of 1650. The very intense maximum at 235 mμ of 1,6-bis-(methoxymethoxy)-naphthalene had disappeared completely.

Thirty-six grams of the crude reduction product was dissolved in 150 ml. of water and 400 ml. of alcohol and heated to boiling; 5 ml. of concentrated hydrochloric acid was added and the solution was refluxed for five minutes. It was then poured onto ice, diluted with water and extracted with chloroform. This chloroform solution yielded both 5-hydroxy-2-tetralone and its methoxymethyl ether XIII as described in the following section.

5-Hydroxy-2-tetralone and Its Methoxymethyl Ether XIII.—The chloroform solution from the last paragraph was extracted with aqueous potassium hydroxide (see next paragraph for work-up of this extract) and evaporated to leave a viscous brown liquid. This liquid was poured into a solution of 100 g. of sodium bisulfite in 250 ml. of water and 65 ml. of ethanol. The sodium bisulfite addition product, which formed after about ten minutes, was collected, washed with ether and decomposed by mixing with 200 ml. of aqueous sodium carbonate. The 5-methoxymethoxy-2-tetralone (XIII) was extracted into ether, the ether evaporated and the compound distilled, b.p. 155–160° (1 mm.). The yield of XIII, a colorless liquid, was 7.2 g. Satisfactory analytical values could not be obtained for this compound. Its characterization depends on the facts that it could be hydrolyzed to 5-hydroxy-2-tetralone and reduced to 5-methoxymethoxy-2-hydroxytetralin (see XV below).

The above potassium hydroxide extract was acidified and extracted with chloroform. Evaporation of this chloroform gave a black phenolic-smelling tar. Sublimation, bath temperature 180° (10.5 mm.), of the tar gave 2 g. of 5-hydroxy-2-tetralone, m.p. 155–162° dec.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.06, 74.19; H, 6.17, 6.44.

5-Methoxymethoxy-2-hydroxytetralin (XV).—To 0.80 g. of lithium aluminum hydride in 10 ml. of ether was added 5 g. of 5-methoxymethoxy-2-tetralone dissolved in 50 ml. of ether. After being stirred for one hour at room temperature the reaction mixture was refluxed for 30 minutes on the steam-bath. The excess lithium aluminum hydride was decomposed with a methanol–ether solution, after which the reaction mixture was diluted with an aqueous solution of sodium potassium tartrate. The ether layer was dried and evaporated to leave a residue which was distilled to give 3.5 g. of 5-methoxymethoxy-2-hydroxytetralin as a viscous colorless liquid, b.p. 158–160° (1.75 mm.), n^{32}D 1.5428.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.45, 69.26; H, 7.72, 7.71.

2,5-Dihydroxytetralin.—One gram of 5-methoxymethoxy-2-hydroxytetralin was dissolved in 10 ml. of ethanol and 4 ml. of water and heated to reflux temperature. To the hot solution was added 0.12 ml. of concentrated hydrochloric acid and the solution was refluxed for one hour. The solution was then poured over ice, diluted with water and extracted with ether. The ether was dried and evaporated to leave 0.57 g. of crude product. Sublimation at a bath temperature of 180° (3 mm.) and recrystallization from benzene gave 2,5-dihyroxytetralin as white disks, m.p. 127–128°.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 72.95, 73.25; H, 7.05, 7.05.

7,8-Dihydro-1-naphthol (V).—A mixture of 0.5 g. of 2,5-dihydroxytetralin, 1 g. of potassium hydroxide and 1 g. of sodium hydroxide was placed in a copper test-tube under a nitrogen atmosphere and heated to 290° for ten minutes. The cooled mixture was dissolved in cold water, acidified, extracted with ether and the ether evaporated. The semi-solid residue was sublimed and then recrystallized from hexane to give 7,8-dihydro-1-naphthol as colorless plates, m.p. 73.5–74.5°; ultraviolet λ_{max} 267, 299 and 309 mμ; ϵ 4500, 1750 and 1500. A mixed melting point with 5,6-dihydro-1-naphthol (produced by the isomerization of 5,8-dihydro-1-naphthol) showed no depression.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.83, 81.73; H, 6.77, 6.61.

3-Methoxystyrene.—From a mixture of 10 g. of 3-methoxycinnamic acid, 40 ml. of quinoline, 1 g. of anhydrous copper sulfate and 0.6 g. of hydroquinone, 3-methoxystyrene was distilled at a pot temperature of 260°. The product was washed with dilute sulfuric acid, dried and fractionally distilled. The yield of 3-methoxystyrene as a colorless liquid, b.p. 94–95° (17 mm.), n^{25}D 1.5590,[16] was 2.4 g.; ultraviolet λ_{max} 250 and 293 mμ, ϵ 8600 and 2150.

The Oxidation of 1-Methoxy-5,6-dihydronaphthalene.[17]—To a slurry of 10 g. of 1-methoxy-5,6-dihydronaphthalene[17] in 100 ml. of acetone and 100 ml. of water cooled to 0°, 16 g. of potassium permanganate dissolved in 400 ml. of water was added dropwise. The reaction mixture was stirred while chipped ice was added regularly to the flask throughout the reaction to keep the temperature below 5°. After three hours the manganese dioxide formed in the reaction was removed by filtration and washed with aqueous sodium bicarbonate which was then added to the filtrate. The clear yellow filtrate was extracted twice with chloroform. The manganese dioxide was washed with chloroform and this washing added to the chloroform extract. Evaporation of the chloroform extracts and crystallization of the residue from methyl alcohol gave 0.5 g. of a glycol, probably *cis*-1,2-dihydroxy-5-methoxytetralin, m.p. 150–151°.[18]

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.08; H, 7.41.

The filtrate from the permanganate oxidation described above, after being extracted with chloroform, was acidified and cooled overnight in a cold-room. The precipitate of cream colored needles was collected, washed with water, dried, and recrystallized from methanol to give 1.3 g. of an acid which melted 221–222° without depression by 3-(2-methoxy-6-carboxyphenyl)-propanoic acid.

Kinetics of the Base-catalyzed Isomerization of 1-Methoxy-5,8-dihydronaphthalene and of Potassium 5,8-dihydro-1-naphthoxide.—In 500 ml. of dry, oxygen-free *t*-amyl alcohol there was dissolved 5.35 g. of potassium metal. The solution was maintained at 100° under a nitrogen atmosphere and 6 g. of 5,8-dihydro-1-naphthol was added to the reaction flask at time zero. At 15-minute intervals 5-ml. aliquots were removed from the reaction flask and added to 65 ml. of chilled 0.0274 *N* ethanolic hydrochloric acid in 100-ml. volumetric flasks. Each aliquot was diluted to 100 ml. with ethanol and the precipitated potassium chloride allowed to settle. A portion of each diluted aliquot was then further diluted 10:1 with ethanol. The concentration of product in each aliquot was determined spectroscopically. The spectrum of the product has a maximum at 299 mμ while the starting material absorbs negligibly at this wave length. The rate constant was determined graphically (Fig. 1). After the final aliquot had been removed, the concentration of potassium *t*-amylate in the residual reaction mixture was determined by titration with standard ethanolic hydrochloric acid, using phenolphthalein as indicator.

The kinetics of the isomerization of 1-methoxy-5,8-dihydronaphthalene were determined in the same manner except that aliquots were taken at 7.5-minute intervals. Only 4.0 g. (0.103 mole) of potassium metal was used while 6.57 g. (0.0411 mole) of 1-methoxy-5,8-dihydronaphthalene was added.

The isomerization of each compound followed first-order kinetics for the first 30% of reaction and then began to deviate slightly, Fig. 1. The rate constant for potassium 5,7-dihydro-1-naphthoxide was 0.00297 min.$^{-1}$ at the base concentration of 0.133 *N*. The rate constant for 1-methoxy-5,8-dihydronaphthalene was 0.00344 min.$^{-1}$ in 0.135 *N* base.

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[16] M. Sulzbacher, *J. Appl. Chem.*, **1**, 95 (1951).

[17] The 1-methoxy-5,6-dihydronaphthalene employed in this experiment was that prepared by methylation of the crude isomerization product of 5,8-dihydro-1-naphthol.

[18] The isomeric glycol *cis*-1,2-dihydroxy-8-methoxytetralin which could have been obtained from 1-methoxy-5,6-dihydronaphthalene melts at 125°. We are indebted to Dr. R. Pappo for furnishing us a sample of this lower melting isomeric glycol.

[Contribution from the Chemistry Department of Northwestern University]

The Stereochemistry of Ketonization. VI. Decarboxylation of 2-Phenylcyclohexane-1,1-dicarboxylic Acid[1]

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The decarboxylation of 2-phenylcyclohexane-1,1-dicarboxylic acid has been found to afford preferentially the *cis* isomer of 2-phenylcyclohexanecarboxylic acid, the exact isomer distribution depending on the nature of the proton donor. The stereoselectivity of ketonization of exocyclic cyclohexane enols as a function of molecular structure is discussed.

As a part of an investigation[2–5] of the relation between molecular structure and the direction and degree of stereoselectivity of the ketonization reaction of enols, it was of interest to determine the stereochemical course of decarboxylation of 2-phenylcyclohexane-1,1-dicarboxylic acid.

Previously this compound had been reported by Kipping and Perkin[6] as an unanalyzed oil obtained by saponification of the base-catalyzed condensation product of 1,5-dibromo-1-phenylpentane and diethyl malonate. The diacid was stated to afford on decarboxylation and extensive purification an unspecified yield of 2-phenylcyclohexanecarboxylic acid, m.p. 104–105°. Both *cis*- and *trans*-2-phenylcyclohexanecarboxylic acids have been synthesized unambiguously by Gutsche[7]; the *cis* isomer was reported as melting at 76–77° while the melting point of the *trans* acid was 108°. Thus the work of Kipping and Perkin seemed to suggest preferential formation of *trans*-2-phenylcyclohexanecarboxylic acid in the decarboxylation of 2-phenylcyclohexane-1,1-dicarboxylic acid. On the other hand, by analogy to the stereochemistry of decarboxylation of the 4-phenyl analog[4] and in view of the factors controlling ketonization of the enolic reaction intermediate,[2] the *cis* product would have been predicted to predominate.

In the present investigation a simple synthetic approach to the 2-phenylcyclohexanecarboxylic acid system was found in the Diels–Alder reaction of 1-phenylbutadiene with diethyl methylenemalonate. The product, diethyl 2-phenylcyclohex-3-ene-1,1-dicarboxylate (I), m.p. 78°, was converted to the desired 2-phenylcyclohexane-1,1-dicarboxylic acid (IV) in two ways. Saponification of I afforded 2-phenylcyclohex-3-ene-1,1-dicarboxylic acid (II),

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[1] For Paper V of this series see H. E. Zimmerman and T. E. Nevins, This Journal, **79**, 6559 (1957).

[2] H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

[3] H. E. Zimmerman, This Journal, **78**, 1168 (1956).

[4] H. E. Zimmerman and H. J. Giallombardo, *ibid.*, **78**, 6259 (1956).

[5] H. E. Zimmerman, *ibid.*, **79**, 6554 (1957).

[6] F. S. Kipping and W. H. Perkin, Jr., *J. Chem. Soc.*, 315 (1890).

[7] C. D. Gutsche, This Journal, **70**, 4150 (1948).