by a new empirically-standardized micro procedure[15] involving determination of ultraviolet absorption of dilute acidified sugar solution heated for fixed periods of time. Since the rate of furfural formation from arabinose is much greater than that of hydroxymethylfurfural from mannose, a high degree of sensitivity is achieved. The presence of fructose accompanying mannose was indicated by polarographic examination,[16] but the sensitivity of the procedure permitted only the definition of an upper limit for the amount of fructose possibly present.

In Table IV are shown the proportions of the several sugars found present in the sulfite waste liquor sample derived from about 85% Western Hemlock (*Tsuga heterophylla*) and 15% White Fir (*Abies grandis*) woods.[7] This sulfite waste liquor contains relatively less glucose and more galactose than a sulfite waste liquor from a spruce which was examined by Hägglund[6] with results also included in Table IV. Total reducing value recoveries in present chromatographic experiments were 95 and 101%.

SEATTLE, WASHINGTON RECEIVED AUGUST 30, 1950

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[15] Q. P. Peniston and H. D. Agar, unpublished work.

[16] J. Heyrovsky and I. Smöler, *Collection Czechoslov. Chem. Commun.*, **4**, 521 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

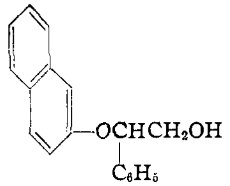
The Acid-Catalyzed Reaction of Styrene Oxide with Phenol and with 2-Naphthol

BY CYRUS O. GUSS,[1] HOMER R. WILLIAMS[2a] AND LEONARD H. JULES[2b]

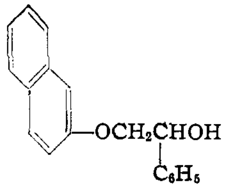
The acid-catalyzed reaction of styrene oxide with phenol formed, in addition to ether-alcohols, two types of products: those expected from the isomerization of the oxide to phenylacetaldehyde, which then reacted with phenol; and those that are postulated to result from a unimolecular ring opening accompanied by nuclear attack on the phenol to give isomeric phenol-alcohols. With 2-naphthol a similar course was indicated by the products isolated; the phenol-alcohol initially formed here, however, cyclized to a dihydrofuran so that the latter was found among the reaction products.

Ether-alcohols are the expected products from the reaction of olefin oxides with hydroxylic compounds. The observation[3] that a mixture of alkali-soluble materials, not identified, resulted from the acid-catalyzed reaction of styrene oxide with phenol suggested the present investigation.

In this study of the acid-catalyzed reaction of styrene oxide with phenols, 2-naphthol was utilized initially in order to reduce the formation of isomers, which would complicate the isolation of pure products. Unexpectedly, however, the products isolated from the reaction of styrene oxide with excess 2-naphthol at 140–145°, in the presence of *p*-toluenesulfonic acid, were alkali-insoluble. This result was in apparent contradiction to the phenol–styrene oxide reaction mentioned. That the formation of ether-alcohols was not an explanation was shown when 2-(2-naphthoxy)-2-phenylethanol (I), m. p. 107–108°, and 2-(2-naphthoxy)-1-phenylethanol (II), m. p. 87–88°, were prepared[4] and found to be unlike any of the alkali-insoluble products at hand from the acid-catalyzed experiment. Neither were I nor II converted into any of the products isolated from the acid-catalyzed run under the same experimental conditions.

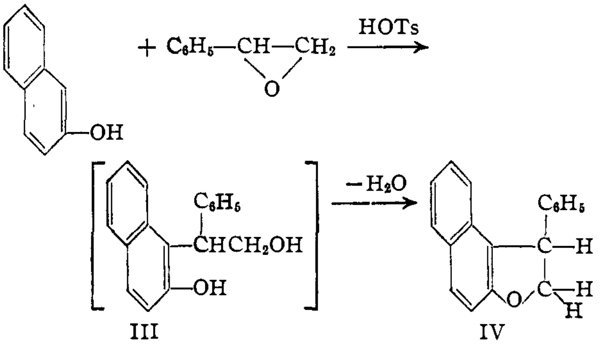


I



II

One of the alkali-insoluble compounds, m.p. 95–96°, isolated from the acid-catalyzed interaction of styrene oxide with 2-naphthol in 43% yield, gave analytical values for carbon and hydrogen that corresponded to either I or II less a molecule of water. It was presumed, therefore, that nuclear attack had occurred, followed by intramolecular loss of water to form a furan. The preparation[5] of III and its cyclization[5] by acid catalysis to 1-phenyl-1,2-dihydronaphtho(2,1-b)furan (IV), m.p. 95–96°, identical with that obtained from styrene oxide and 2-naphthol, was considered to validate this view. Later it was shown[4] that the base-catalyzed reaction of styrene oxide with 2-naphthol could be made to give III as the major product as well as some of I.



III IV

Another alkali-insoluble product, m.p. 81–82°, obtained in small amount once from the acid-catalyzed reaction had the correct analysis for an isomer of IV. Its structure was not elucidated.

A third component, m.p. 178–178.5°, was isolated from the alkali-insoluble fraction in 21.5% yield. This compound had the correct analysis for

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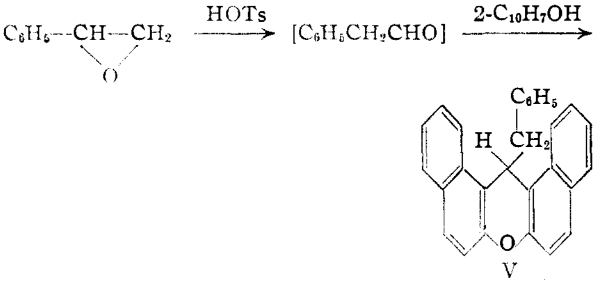
[2] (a) The experiments with phenol are from a portion of the M.S. thesis (August, 1950) of Homer R. Williams, Department of Chemistry, Stanford University, Palo Alto, California. (b) The work with 2-naphthol is based on a portion of the M.S. thesis (August, 1949) of Leonard H. Jules, Sahyun Laboratories, 316 Castillo St., Santa Barbara, California.

[3] C. O. Guss, THIS JOURNAL, **71**, 3460 (1949).

[4] C. O. Guss and L. H. Jules, *ibid.*, **72**, 3878 (1950).

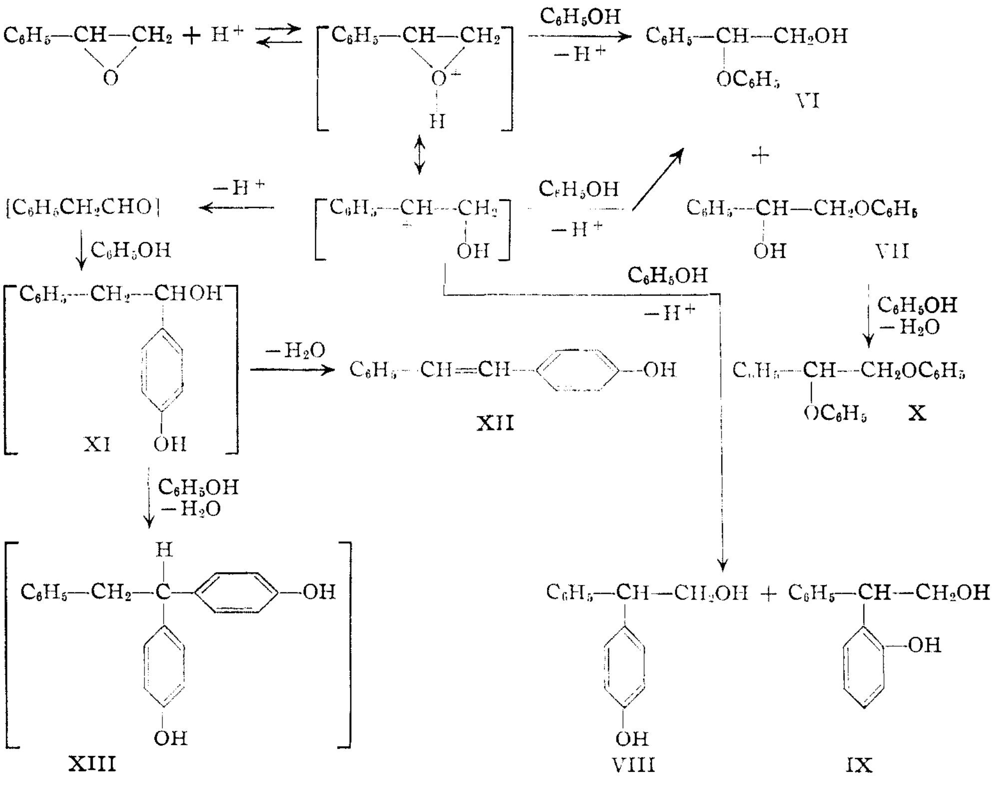
[5] C. O. Guss and L. H. Jules, *ibid.*, **72**, 3462 (1950).

$C_{28}H_{20}O$. The isomerization of styrene oxide to phenylacetaldehyde was known[6] to occur under conditions similar to those employed in this work, and Dilthey and Giebert[7] had shown that phenylacetaldehyde and 2-naphthol gave 1,2,7,8-dibenzo-9-benzylxanthene (V), m.p. 177–178°. The xanthene (V) was prepared as by Dilthey and Giebert[7]; it did not depress the melting point of the compound, m.p. 178–178.5°, obtained from styrene oxide and 2-naphthol according to the equation shown.



V

With the preceding as a background, the acid-catalyzed reaction of styrene oxide with excess phenol was then investigated. At 70° these reactants rapidly produced a rather complex mixture from which six solid compounds were isolated in a combined yield of about 47%, and, with one exception, identified. The isolated compounds are numbered and unbracketed in the following scheme, which is designed to suggest certain mechanistic aspects.



The ether-alcohols (VI and VII) were separated by distillation as a mixture whose composition as predominantly VI was determined by the use of a phase diagram.[3] The other alkali-insoluble compound (X) was obtained from a high boiling fraction of the alkali-insoluble portion of the reaction mixture. Its structure and indicated mode of formation are conjectural.

Distillation of the alkali-soluble products, followed by recrystallization of the several fractions so obtained, gave the phenol-alcohols (VIII and IX) and 1-(4-hydroxyphenyl)-2-phenylethylene (XII). The identity of VIII and IX was demonstrated by mixed melting point determinations with authentic compounds synthesized for this purpose. The melting point of XII obtained here corresponded to the literature value, and the tetrabromo derivative and the methyl ether served further to substantiate its identity. Apparently XII was not present in the reaction mixture but was formed during the fractional distillation of the alkali-soluble products. The precursor (XI) indicated seems to be a reasonable choice.

Although 1,1-bis-(4-hydroxyphenyl)-2-phenylethane (XIII) was never isolated from the acid-catalyzed reaction of styrene oxide with phenol, it was found in the products from the acid-catalyzed reaction of phenylacetaldehyde with phenol and of VI with phenol. Distillation of the residue after the removal of XIII from the reaction of phenylacetaldehyde with phenol gave XII.

The ether-alcohol (VI) was found to interact with phenol to give VIII, IX, XII and XIII, but the rate of this reaction was shown to be too slow to account entirely for the formation of these compounds in the acid-catalyzed reaction of styrene oxide with phenol. The alkylation of phenol by VI was not unexpected, since the conditions used were similar to those known[8] to give this type of reaction. The presence of XII and XIII can also be explained by a cleavage of VI at the ether linkage, followed by rearrangement to phenylacetaldehyde. The isomeric ether-alcohol (VII) gave alkali-soluble products when warmed with phenol and *p*-toluenesulfonic acid, but the attempt to isolate pure products from the mixture was unsuccessful.

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(6) C. O. Guss and L. Herzog, unpublished data.

(7) W. Dilthey and H. Giebert, *Ber.*, **76**, 1084 (1943).

(8) E. F. Pratt, R. K. Preston and J. D. Draper, THIS JOURNAL, **72**, 1367 (1950).

When the acid-catalyzed reaction of styrene oxide with phenol was conducted in toluene, a 51% yield of a mixture of VI and VII was obtained, the ratio of the two isomers being the same as that found in the absence of this solvent. A small amount of X was also isolated.

Kadesch and others[9] have discussed the acid-catalyzed unimolecular ring opening of olefin oxides. With some olefin oxides, such as styrene oxide and 3,4-epoxy-1-butene, the resonance stabilization of a transitory state is thought to favor the formation of one of the two possible isomers. In the present work, not only the direction of ring opening but also the incidence of nuclear attack to form phenol-alcohols is in harmony with this viewpoint. Nuclear attack in the acid-catalyzed reaction of olefin oxides with phenols is a rather uncommon result as far as previous knowledge[10] is concerned, and it is not yet possible to designate those oxides that will give nuclear attack. It is clear, however, that the base-catalyzed reaction of styrene oxide with 2-naphthol[4] may give a considerable amount of a phenol-alcohol, while the analogous reaction of ethylene oxide[11] or propylene oxide[11] does not give a phenol-alcohol at all, or very little at most.

Experimental[12]

The Acid-Catalyzed Reaction of Styrene Oxide with 2-Naphthol.—In a flask equipped with stirrer, reflux condenser and dropping funnel were placed 2-napthol (21.6 g., 0.15 mole) and *p*-toluenesulfonic acid monohydrate (0.1 g.). To the stirred molten mixture, at a bath temperature of 140–145°, was added styrene oxide (6.0 g., 0.05 mole, n^{20}_D 1.5338) over a 20-minute period. The dark red solution was heated and stirred an additional 40 minutes, then cooled, dissolved in benzene (150 cc.) and extracted with 4% sodium hydroxide (150 cc.). This alkaline solution was extracted with benzene (100 cc.), and the combined benzene solutions, dark orange in color, were first dried over anhydrous sodium sulfate and then over silica gel. The dried solution was passed through a 1 × 90 cm. column of activated alumina and the benzene then evaporated to leave a yellow solid. The latter was digested with boiling 80% ethanol, filtered hot, and the remaining solid washed with boiling 80% ethanol. This solid was then recrystallized and obtained as white leaves from glacial acetic acid to give 4.0 g. (21.5%) of 1,2,7,8-dibenzo-9-benzylxanthene (V), m.p. 178–178.5°.

Anal. Calcd. for $C_{28}H_{20}O$: C, 90.29; H, 5.41. Found: C, 90.31; H, 5.75.

This same compound, prepared by the method of Dilthey and Giebert,[7] melted at 178–178.5° alone and when mixed with V obtained from styrene oxide and 2-naphthol as described.

When the 80%-ethanol filtrate from the separation of V was cooled to room temperature, a white solid appeared. This solid was recrystallized from ethanol to give 3.5 g. of 1-phenyl-1,2-dihydronaphtho(2,1-b)furan (IV), m.p. 94–95°. An additional 1.8 g. (43% total yield) of IV, m.p. 93–94°, was isolated from the glacial acetic acid liquor from the recrystallization of the xanthene (V). Purification by recrystallization from ethanol raised the melting point to 95–96°, which was not depressed when this material was mixed with authentic IV.[5]

The ethanol filtrates from the isolation and purification of IV were diluted with excess water until no more solid separated. Fractional crystallization of this solid from dilute ethanol gave white needles, m.p. 81–82°. It was not always possible to isolate a solid at this point.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.95; H, 5.94.

This compound was isomeric with IV, but no structure proof was undertaken.

When the preceding acid-catalyzed reaction of styrene oxide with 2-naphthol was repeated in benzene (25 cc.) as a solvent at the reflux temperature, it was possible, by a similar sequence of operations, to isolate a 1.5% yield of the xanthene (V) and a 48.8% yield of the furan (IV). A duplication of this run in benzene, but in the absence of any *p*-toluenesulfonic acid, resulted in a 92% recovery of 2-naphthol and the isolation of a small quantity of the ether-alcohol (I).

After a solution of 2-naphthol (1.1 g.), 2-(2-naphthoxy)-2-phenylethanol[4] (I) (1.0 g.) and *p*-toluenesulfonic acid (0.1 g.) in benzene (50 cc.) was refluxed for 1 hour, a quantitative recovery of the 2-naphthol was realized. The ether-alcohol (I) that was isolated was contaminated by a small amount of a solid material, m.p. 165–170°, soluble in heptane. There was no evidence for the rearrangement of I to III.

The only alkali-insoluble material that was isolated after refluxing a solution of 2-naphthol (0.2 g.), 2-(2-naphthoxy)-1-phenylethanol (II) (0.2 g.) and *p*-toluenesulfonic acid (0.05 g.) in benzene (15 cc.) for 1 hour was a solid, m.p. 155–165°, from dilute ethanol.

The Acid-Catalyzed Reaction of Styrene Oxide with Phenol.—Styrene oxide (12.0 g., 0.1 mole, n^{20}_D 1.5353) was added over a period of 7 minutes to a solution of phenol (56.4 g., 0.6 mole) and *p*-toluenesulfonic acid monohydrate (0.4 g.) contained in a flask at 70°. The rate of addition was that sufficient to maintain the temperature at 69–72° without external heating. The reaction mixture was then poured immediately into a cold solution of 14% sodium hydroxide (200 cc.).

The alkali-insoluble products were taken up in ether (four 25-cc. portions) and dried over anhydrous potassium carbonate. The ether was then removed and the residue distilled in the manner previously described.[3] This procedure gave 3.44 g. (16.1%) of a mixture of 2-phenoxy-2-phenylethanol (VI) and 2-phenoxy-1-phenylethanol (VII). Analysis of the mixture, m.p. 78°, by the use of a phase diagram,[3] indicated that VI comprised 94% of the total, assuming no contamination by X. A fraction, b.p. 165–230° (1 mm.), taken off after the distillation of the foregoing ether-alcohols (VI and VII), existed as a viscous oil, 0.85 g., until crystallized from isopropyl alcohol, whereupon 0.08 g. of a crystalline product, m.p. 123–124°, was obtained. Purifying recrystallizations raised the melting point of the fine, white needles to 127–127.5°. The analysis approximated that for $C_{20}H_{18}O_2$ which is the empirical formula for 1,2-bis-(phenoxy)-1-phenylethane (X), one of the likely alkali-insoluble compounds that might be present.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 83.27; H, 6.23.

The alkaline solution remaining after the removal of the alkali-insoluble products was acidified with concd. hydrochloric acid. After separation of the phenolic layer, the aqueous layer was extracted with ether (two 25-cc. portions). The ether solution and the phenolic material were combined and the ether and phenol removed under reduced pressure. Distillation of the residue through a modified Claisen flask having 2″ of 1/8 glass helices gave 12.1 g., b.p. 120–230° (1 mm.). This mixture was redistilled over the same range and separated into five fractions totalling 11.47 g. The individual fractions were dissolved in toluene to give saturated solutions at room temperature.

The solutions of the three highest boiling fractions, after cooling to 0° for 15 hours, yielded 2.68 g. (12.5%) of 2-(4-hydroxyphenyl)-2-phenylethanol (VIII), m.p. 87–89.5°, identified by a mixed melting point determination with pure, authentic VIII, m.p. 93–94°.

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(9) R. G. Kadesch, THIS JOURNAL, **68**, 41 (1946); A. R. Day, "Electronic Mechanisms of Organic Reactions," American Book Co., New York, N. Y., 1950, p. 102; E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 218; S. Winstein and R. B. Henderson in R. C. Elderfield's "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., Vol. I, Chapter I, p. 32.

(10) C. C. Price and G. P. Müller, THIS JOURNAL, **66**, 628 (1944), have observed nuclear attack with the boron trifluoride-catalyzed reaction of cyclohexene oxide with phenol and with ansiole.

(11) See, *e.g.*, D. R. Boyd and E. R. Marle, *J. Chem. Soc.*, **105**, 2117 (1914), and A. R. Sexton and E. C. Britton, THIS JOURNAL, **70**, 3606 (1948).

(12) All melting points are uncorrected. Microanalyses are by Mr. Joseph Pirie of this Department and by the Elek Micro Analytical Laboratories, Los Angeles 16, California.

The second and third fractions, in toluene at 0°, deposited 0.71 g. (3.6%) of 1-(4-hydroxyphenyl)-2-phenylethylene (XII), m.p. 180–182.5°, which, after several recrystallizations from toluene, melted at 186–187.5° (lit. 184.5°[13] and 189°[14]) and analyzed correctly for carbon and hydrogen. Material designated as XII in this work was converted into 1,2-dibromo-1-(3,5-dibromo-4-hydroxyphenyl)-2-phenylethane, m.p. 196–198°, by the method of Zincke and Geibel,[14] who reported a melting point of 201°. The methyl ether, prepared in quantitative yield from XII and dimethyl sulfate, melted at 135–135.5° as reported by others.[13]

The portions of the product that had not crystallized during the foregoing procedure were combined and, after removal of the solvent, redistilled at 145–220° (1 mm.) to yield 5.24 g. as three fractions. When these three fractions were dissolved in warm toluene, the highest boiling fraction yielded 0.12 g. (0.5%) of crude XII, m.p. 179–182°. The toluene solutions were then cooled to 0° and seeded with a small crystal of IX. Over a period of one week 2.99 g. (13.9%) of 2-(2-hydroxyphenyl)-2-phenylethanol (IX) crystallized out, m.p. 70–73°. Identification of IX was achieved by a mixed melting point determination with the authentic compound, m.p. 76.5–77.5°.

The acid-catalyzed reaction of styrene oxide with phenol was repeated, using the same amounts of reactants and the same temperature as in the preceding experiment, but in the presence of toluene (100 cc.). The styrene oxide was added in 7 minutes, and the mixture was maintained at 70° for an additional 8 minutes. From this reaction a 51% yield of VI + VII and 0.98 g. of X was isolated. The isomeric mixture of VI + VII was 94% VI. The alkali-soluble fraction, 7.65 g., was not worked up.

The Acid-Catalyzed Reaction of Phenylacetaldehyde with Phenol.—Phenol (22.6 g., 0.24 mole) and *p*-toluenesulfonic acid monohydrate (0.2 g.) were heated to 70°, and phenylacetaldehyde (6.0 g., 0.05 mole, $n^{20}\text{D}$ 1.5366) was added over a 5-minute period. After 1 hour at 70° the reaction mixture was dissolved in ether (50 cc.) and washed with saturated sodium bicarbonate (10 cc.) and water, respectively. All the material that boiled up to 100° (2 mm.) was distilled off, then the residue was crystallized from toluene to yield 3.0 g. (20.7%) of crude 2,2-bis(4-hydroxy phenyl)-1-phenylethane (XIII), m.p. 115–126°. Several recrystallizations from toluene raised the melting point to 139–140°. Campbell[15] reported 140° as the melting point for XIII.

From the toluene solution that remained after the separation of the crude XIII it was possible, but only by distillation, to obtain 3.8 g. of a product which, after recrystallization from toluene, gave 0.6 g. (6.1%) of XII, m.p. 186.5–187.5°.

The Acid-Catalyzed Reaction of 2-Phenoxy-2-phenylethanol (VI) and of 2-Phenoxy-1-phenylethanol (VII) with Phenol.—To a solution of 2-phenoxy-2-phenylethanol (VI) (8.0 g., 0.037 mole) and phenol (20 g., 0.213 mole) at 70° was added *p*-toluenesulfonic acid (0.14 g.). After 1 hour at this temperature the mixture was poured into cold 18% sodium hydroxide (100 cc.). By the procedure used in working up the products from the acid-catalyzed reaction of styrene oxide with phenol, there was obtained 1.22 g. of alkali-insoluble material, which was not identified, and 7.65 g. of alkali-soluble product. The latter was separated into 1.48 g. (18.5%) of VIII, m.p. 71–74°; 1.17 g. (14.6%) of IX, m.p. 88–90°; 0.31 g. (4.2%) of XII, m.p. 179–182°; and 0.08 g. (0.74%) of XIII, m.p. 132–134°. When this reaction was repeated with the time of reaction reduced to 7 minutes, a 78% recovery of VI was realized.

The substitution of the isomer (VII) for VI in this acid-catalyzed reaction with phenol gave, after 22 hours at 70°, 3.3 g. of alkali-insoluble, viscous oil, of which 1.39 g. distilled at 180–220° (1 mm.). The alkali-soluble portion of the reaction mixture, after distillation at 210–275° (1 mm.), weighed 1.75 g. No crystalline products could be isolated from either distillate.

Preparation of 2-(4-Hydroxyphenyl)-2-phenylethanol (VIII).—The reduction of α-(4-hydroxyphenyl)-phenylacetic acid (2.18 g., 0.0096 mole, m.p. 171–173°), prepared by the method of Bistrzycki and Flatau,[16] with lithium aluminum hydride (0.54 g., 0.0142 mole) in ether gave 0.9 g. (44%) of crude 2-(4-hydroxyphenyl-2-phenylethanol (VIII), m.p. 85–88°. Recrystallization from toluene produced fine, white needles, m.p. 93–94°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.50; H, 6.57.

Preparation of 2-(2-Hydroxyphenyl)-2-phenylethanol (IX).—The lactone of α-(2-hydroxyphenyl)-phenylacetic acid[16] (20.1 g., 0.096 mole, m.p. 111–112°) in ether (150 cc.) was reduced with lithium aluminum hydride (4.75 g., 0.125 mole) in ether (150 cc.). The crude product, 19.23 g. (93%) melted at 70–72°, and after recrystallization from toluene the fine, granular crystals melted at 76.5–77.5°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.44; H, 6.43.

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[13] J. J. Hewitt, W. Lewcock and F. G. Pope, *J. Chem. Soc.*, **101**, 604 (1912).

[14] T. Zincke and K. Geibel, *Ann.*, **349**, 111 (1906).

[15] N. R. Campbell, *Proc. Roy. Soc.* (*London*), **129B**, 528 (1940).

[16] A. Bistrzycki and J. Flatau, *Ber.*, **28**, 989 (1895); *ibid.*, **30**, 124 (1897).