4-Acetoxy-2-acetylthiomethylphenol (7).—Compound **7**, m.p. 121–123°, could be isolated in 84% yield at this point by washing the solids with 500 ml. of water and recrystallizing the residual crystals from 80% aqueous ethanol.

Anal. Calcd. for $C_{11}H_{12}O_4S$: C, 55.0; H, 5.0; S, 13.3. Found: C, 54.7; H, 5.1; S, 13.0.

Phenol intermediates such as **7**, however, were not usually isolated, but, instead, were acetylated by refluxing the crude mixture of phenol and amine hydrobromide for 1 hr. in 500 ml. of acetic anhydride. The clear solution was concentrated to a syrup which was triturated in 1 l. of cold water. After standing for 1 hr. the crystals were collected, dried, and recrystallized from 80% aqueous ethanol.

When this thiolation procedure was applied to 2,6-bis(bromomethyl)hydroquinone diacetate (**13**), a difficultly separable mixture (m.p. 88–130°) containing **14** (by v.p.c.) was obtained. Authentic **14** was prepared by adding a solution of thiolacetic acid (60.8 g., 0.8 mole) and potassium hydroxide (39 g., 85% pure, 0.59 mole) in 300 ml. of ethanol to **13** (91 g., 0.24 mole) in 300 ml. of warm dimethylformamide. After standing for 30 min., the mixture was poured into 5 l. of cold water. The product crystallized over a 2-hr. period and was collected (76 g., 86%) and recrystallized as yellow plates from benzene–ligroin (b.p. 60–90°), m.p. 91–94°. Repeated recrystallizations from a variety of solvents as well as use of column chromatography failed to rid this material of a small amount of yellow impurity.

Anal. Calcd. for $C_{16}H_{18}O_6S_2$: C, 51.9; H, 4.9; S, 17.3. Found: C, 51.6; H, 5.1; S, 17.3.

Mercaptomethyl Derivatives (See Table II).—A mixture of 0.5 mole of a thiolacetate of Table I and 500 ml. of 1% methanolic hydrogen chloride was heated on a steam bath for 2 hr. With the exception of **20** the crystalline residue obtained after removal of the solvent was dissolved in 1 l. of ether and washed until neutral with 5% aqueous sodium bicarbonate. Concentration of the dried (sodium sulfate) ether layer to *ca.* 200 ml., followed by dilution with ligroin (b.p. 30–60°), yielded the desired crystalline product. Thiol **20** was purified by short-path distillation after the sodium bicarbonate neutralization step.

2,3-Dihydroxybenzyl Sulfide (22).—3-Mercaptomethylcatechol (**20**, 5.0 g., 0.032 mole) was heated in the presence of two crystals of sodium bicarbonate for 5 hr. at 130° under 5-mm. pressure. Sulfide **22** (4.5 g., 100%), m.p. 147–149°, crystallized from the hot melt. A recrystallization from ether–ligroin (b.p. 30–60°) did not change the melting point.

Anal. Calcd. for $C_{14}H_{14}O_4S$: C, 60.5; H, 5.0; S, 11.5. Found: C, 60.4; H, 5.3; S, 11.7.

Authentic **22** was prepared by allowing 3-bromomethylcatechol diacetate (14.35 g., 0.05 mole), **20** (7.8 g., 0.05 mole), and ethyl diisopropylamine (6.3 g., 0.05 mole) in 200 ml. of acetone to react at room temperature for 15 min. The mixture was concentrated to a syrup which, in turn, was placed in 400 ml. of ether and washed with 400 ml. of water. The ether layer was dried over sodium sulfate and concentrated to a syrup which was dissolved in 500 ml. of 1% methanolic hydrogen chloride. The syrup obtained after refluxing the solution for 4 hr., followed by removing the solvent, was dissolved in 500 ml. of ether and washed until neutral with 5% aqueous sodium bicarbonate solution. The desired product (**22**) crystallized after the ether solution was concentrated to 100 ml., followed by dilution with ligroin (b.p. 30–60°), and was identical in every respect with the product from the pyrolysis of **20**.

Disulfides.—Disulfides **23**, **24**, and **25** were prepared by a general procedure involving the iodometric titration (0.1 *N* iodine solution) of the thiol (5.0 g.) dissolved in 200 ml. of ether containing the stoichiometric quantity of pyridine to act as a hydrogen iodide scavenger. The ether layer was separated, washed with 100 ml. of water, and then concentrated to a crystalline residue.

Disulfide **23** was recrystallized from ethanol–ligroin (b.p. 30–60°) and had m.p. 195–197°.

Anal. Calcd. for $C_{14}H_{14}O_4S_2$: C, 54.2; H, 4.5; S, 20.7. Found: C, 54.3; H, 5.0; S, 20.3.

Disulfide **24** from ethyl acetate–ligroin had m.p. 115–119°.

Anal. Calcd. for $C_{14}H_{14}O_4S_2$: C, 54.2; H, 4.5; S, 20.7. Found: C, 54.0; H, 4.7; S, 20.7.

Disulfide **25**, m.p. 171–173°, was recrystallized twice from ether–ligroin

Anal. Calcd. for $C_8H_8O_2S_2$: C, 48.0; H, 4.0. Found: C, 48.7; H, 4.4.

The diacetate of **25** had m.p. 152–156° (ethanol).

Anal. Calcd. for $C_{12}H_{12}O_4S_2$: C, 50.7; H, 4.2; S, 22.5. Found: C, 50.7; H, 4.4; S, 22.5.

Quinone Methides. Base-Catalyzed Condensation Reactions of Hydroxybenzyl Alcohols and Ethers

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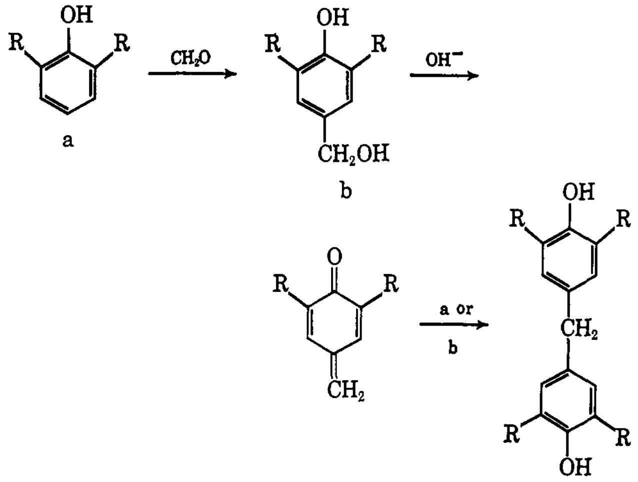
Of the products observed from the reaction of phenols with formaldehyde in basic medium, perhaps the most common are the diarylmethanes.[1-4] It is known that a hydroxybenzyl alcohol is initially formed and generally accepted that the symmetrical diarylmethane results from an intermediate quinone methide, *viz.*



Although this industrially important reaction is quite general, only a few attempts to utilize the intermediate quinone methide in rational syntheses have been reported. These include the use of phenol Mannich bases[5,6] and their methiodides and oxides[7] and sulfur analogs of these bases.[8]

We describe here the use of easily accessible hydroxybenzyl alcohols and their ethers as quinone methide precursors in syntheses which have proven to be very useful.

The reaction of 1-methoxymethyl-2-naphthol (I) (prepared from the methiodide of 1-dimethylaminomethyl-2-naphthol and sodium methoxide) with 2,6-

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[1a] Note Added in Proof.—To whom correspondence should be addressed: Department of Chemistry, University of Utah, Salt Lake City, Utah.

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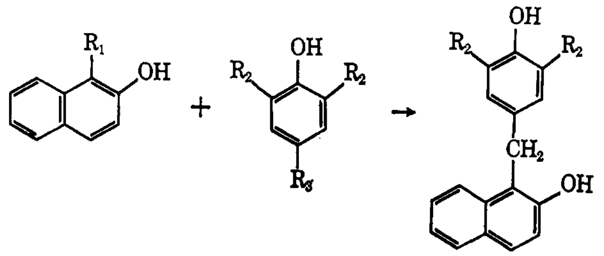
dimethylphenol (II) in methanolic potassium hydroxide afforded 1-(3,5-dimethyl-4-hydroxybenzyl)-2-naphthol (III). The same product resulted from the similar reaction between 2-naphthol (IV) and 2,6-dimethyl-4-methoxymethylphenol (V). Although V was chosen in preference to VI in early experiments, to minimize self-condensation, the reaction between IV and VI was subsequently found to afford VII in good yield.

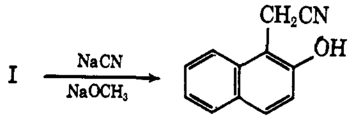


I, R_1 = CH_2OCH_3
IV, R_1 = H

II, R_2 = CH_3; R_3 = H
V, R_2 = CH_3; R_3 = CH_2OCH_3
VI, R_2 = H; R_3 = CH_2OH

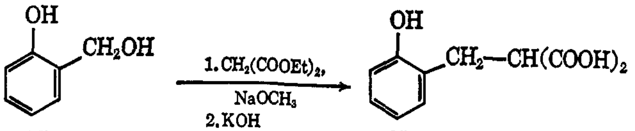
III, R_2 = CH_3
VII, R_2 = H

The reaction between I and sodium cyanide in basic medium gave the expected 1-cyanomethyl-2-naphthol (VIII).



VIII

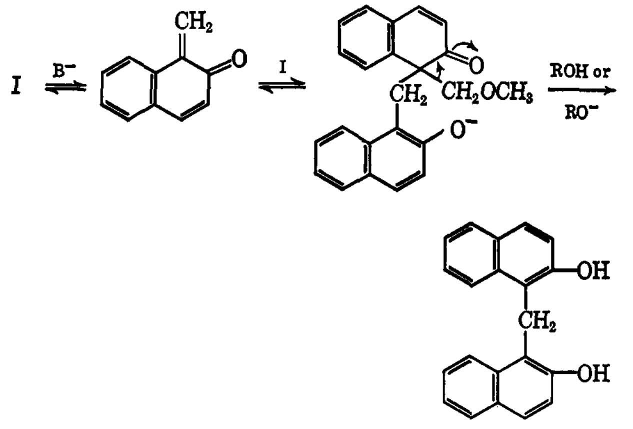
A still more useful type of synthesis is illustrated in the reaction between *o*-hydroxymethylphenol (saligenin, IX) and malonic ester. The principle product, after hydrolysis of the ester functions, was X.



IX

X

A point of some significance in phenol–formaldehyde chemistry is the mechanism of formation of diarylmethanes.[8] Although the apparent route is through reaction of a quinone methide molecule with the starting phenol, evidence has been presented suggesting that it also occurs by the reaction between two molecules of the hydroxymethylphenol.[9] A possible criticism of this postulate is that the formation of hydroxymethylphenols in basic media is almost certainly reversible and that the parent phenol might therefore still be a low-concentration intermediate. To shed light on this problem, the behavior of I, which cannot undergo this retrograde reaction, was examined in basic solution. The fact that the only isolable product was the diarylmethane XI lends support to the proposal that the free phenol is not a required intermediate in the formation of products such as XI. The mechanism can be formalized as follows.



XI

Experimental Section

1-Methoxymethyl-2-naphthol (I).—To a solution prepared by dissolving 14.0 g. of sodium in 750 ml. of dry methanol was added 68.6 g. of the methiodide of 1-dimethylaminomethyl-2-naphthol.[7] The mixture was heated under reflux for *exactly* 35 min. and then poured into 2.5 l. of an ice–water mixture to which had been added 110 ml. of concentrated hydrochloric acid. The mixture was extracted with two portions of ether and the combined extract was washed with water and 10% sodium bicarbonate solution. Thorough drying of the solution (magnesium sulfate) followed by evaporation of solvent at an aspirator at 30° afforded a viscous oil. The oil was dissolved in 100 ml. of carbon tetrachloride and cooled to 0° for 2 hr. Suction filtration afforded 2.5 g. of XI, m.p. and m.m.p. 189–191°. The filtrate was concentrated to dryness under reduced pressure, the residue was dissolved in 25 ml. of ethyl acetate, and the solution was diluted with 150 ml. of petroleum ether (b.p. 30–60°). Cooling at 0° for 24 hr. gave 17.5 g. (47%) of pale yellow crystals (I), m.p. 79–80°. Further recrystallization from the same solvent system afforded colorless prisms, m.p. 80–81°.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.41; H, 6.55.

The yield of I in this experiment is not a measure of the efficiency of the reaction but of the difficulty in separating remaining I from residual XI by crystallization. Chromatography on Magnesol–Celite afforded yields of I as high as 67%.

Reaction of 1-Methoxymethyl-2-naphthol (I) with 2,6-Dimethylphenol.—1-Methoxymethyl-2-naphthol (5.0 g.) and 3.2 g. of 2,6-dimethylphenol were dissolved in a solution of 3.0 g. of potassium hydroxide in 60 ml. of methanol. The mixture was heated under reflux for 4.5 hr.[10] and cooled. The volume was decreased by about one-half by evaporation under reduced pressure and the concentrate was poured into cold, dilute hydrochloric acid. Collection of the resulting solid by suction filtration and recrystallization from ethyl acetate and petroleum ether gave 3.7 g. (51%) of 1-(3,5-dimethyl-4-hydroxybenzyl)-2-naphthol (III). Further purification by recrystallization afforded material having m.p. 153.5–154.0°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.51. Found: C, 82.00; H, 6.38.

Reaction of 2,6-Dimethyl-4-methoxymethylphenol (V) with 2-Naphthol.—A mixture of 1.36 g. of 2,6-dimethyl-4-methoxymethylphenol (V) and 1.18 g. of 2-naphthol was dissolved in 30 ml. of a solution of 0.94 g. of potassium hydroxide in methanol. The resulting solution was heated under reflux for 3.5 hr.,[10] cooled, and poured into cold dilute hydrochloric acid. Processing as described in the preceding experiment, including recrystallization from ethyl acetate–petroleum ether, afforded 1.0 g. (44%) of III which was identical in all respects with material obtained by the other route.

Reaction of *p*-Hydroxybenzyl Alcohol (VI) with 2-Naphthol.—*p*-Hydroxybenzyl alcohol (6.0 g.) and 6.9 g. of 2-naphthol were dissolved in a solution of 5.6 g. of potassium hydroxide in 60 ml. of methanol. The mixture was stirred under reflux for 4 hr., cooled, and poured into cold dilute hydrochloric acid. The resulting solid was separated by suction filtration, washed well

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(9) J. H. Freeman and C. W. Lewis, *J. Am. Chem. Soc.*, **76**, 2080 (1954).

(10) This reaction time is undoubtedly excessive. No effort was made to determine optimum reaction time or temperature.

with water, and dried. Recrystallization from ethyl acetate and benzene gave 9.0 g. (75%) of 1-(4-hydroxybenzyl)-2-naphthol (VII), m.p. 198–200°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.57; H, 5.63. Found: C, 81.24; H, 5.67.

Reaction of 1-Methoxymethyl-2-naphthol (I) with Cyanide Ion.—A mixture of 5.8 g. of 1-methoxymethyl-2-naphthol, 2.6 g. of sodium methoxide, and 3.1 g. of sodium cyanide was dissolved in 100 ml. of dry methanol and heated under reflux for 12 hr.[10] The solution was cooled and poured into cold dilute hydrochloric acid (hood). The resulting solid was separated by suction filtration and washed repeatedly with cold water. Recrystallization of the dried product from ethyl acetate–benzene gave 4.3 g. (78%) of 1-cyanomethyl-2-naphthol (VIII), m.p. 184–185° (lit.[8] m.p. 177°). This substance exhibits strong infrared absorption at 4.45 μ.

Anal. Calcd. for $C_{12}H_9NO$: C, 78.66; H, 4.95. Found: C, 78.41; H, 4.99.

Reaction of *o*-Hydroxymethylphenol (IX) with Diethyl Malonate.—To a solution prepared by dissolving 9.3 g. of sodium in 200 ml. of absolute ethanol were added 16.5 g. of *o*-hydroxymethylphenol and 53.0 g. of diethyl malonate. The solution was heated under reflux for 3 hr., cooled, and poured, with stirring, into cold dilute hydrochloric acid. The resulting mixture was extracted with three portions of ether and the combined extracts were processed in the usual way. Removal of ether at an aspirator and distillation of the residue afforded 16.0 g. (46%) of diethyl *o*-hydroxybenzylmalonate, b.p. 131–140°. The substance was identified by base hydrolysis to the corresponding diacid which, after crystallization from water, weighed 8.5 g. (31%), m.p. 139° dec.

Anal. Calcd. for $C_{10}H_{10}O_5$: C, 57.14; H, 4.79. Found: C, 57.13; H, 4.88.

Self-Condensation of 1-Methoxymethyl-2-naphthol (I).—1-Methoxymethyl-2-naphthol (6.0 g.) was dissolved in a solution of 2.0 g. of potassium hydroxide in 35 ml. of methanol and heated under reflux for 4 hr. The solution was concentrated essentially to dryness under reduced pressure and the residue was dissolved in water. Acidification gave a solid which was then dissolved in ethyl acetate and treated with activated charcoal. Addition of petroleum ether and cooling afforded 1.5 g. (31%) of 1-(2-hydroxy-1-naphthylmethyl)-2-naphthol (XI), m.p. 193–196°. A mixture melting point with authentic material was undepressed.

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Reduction of Organomercury Compounds with Chromium(II)

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The synthetic utility of chromous ion in organic chemistry has been reinvestigated in recent years.[1] Applications of this versatile reducing agent were described early in this century[2] and date back to Berthelot.[3] We report here a rapid quantitative reduction of organomercuric salts by chromous ion. A general method for the formation of symmetrical disubstituted mercury compounds has been devised. By suitable modifications of the method it should be possible to (1) produce mixed disubstituted mercury compounds; (2) provide new approaches to organochromium compounds; and (3) produce symmetrical disubstituted mercury compounds directly from alkyl halides.

All of the reactions described in this note were carried out on a 0.105 molar scale. Reference will be made only to the relative equivalents of each reactant. The disubstituted organomercury compounds produced were shown to be stable to the reaction conditions.

Injection of 1 equiv. of aqueous chromous ion into a solution of 1 equiv. of benzylmercuric perchlorate in 100 ml. of dimethylformamide produced immediately upon contact a fine dispersion of free mercury and a green solution. The mercury was isolated by centrifugation and analyzed using standard analytical techniques. Dibenzylmercury was isolated quantitatively by flooding the reaction mixture with water.[4] The stoichiometry of the reaction is given in eq. 1.

$$2PhCH_2Hg^+ + 2Cr^{+2} \longrightarrow (PhCH_2)_2Hg + Hg + 2Cr^{+3} \qquad (1)$$

The most reasonable mechanism for the reaction is outlined in equations 1a–d.[5,6]

$$PhCH_2Hg^+ + Cr^{+2} \longrightarrow PhCH_2Hg\cdot + Cr^{+3} \qquad (1a)$$

$$PhCH_2Hg\cdot \longrightarrow PhCH_2\cdot + Hg \qquad (1b)$$

$$PhCH_2\cdot + Cr^{+2} \longrightarrow PhCH_2Cr^{+2} \qquad (1c)$$

$$PhCH_2Cr^{+2} + PhCH_2Hg^+ \longrightarrow (PhCH_2)_2Hg + Cr^{+3} \qquad (1d)$$

Step 1a must have a favorable potential as the oxidation potential of chromous ion is 0.41 v.[7] Steps 1b and 1a may occur simultaneously as the second bond dissociation of dialkylmercury compounds is thought to be very low. The bond dissociation energy of the methylmercury radical is approximately 7 kcal./mole.[8] The average bond dissociation energy of dialkylmercury compounds decreases with increasing stability of the alkyl radical.[9] The facile formation of nitrosochromic ion from the reaction of chromous ion with nitric oxide,[10] and more directly, the hydroperoxide experiments of Kochi[11] illustrate the effectiveness of chromous ion as a free-radical trap. Step 1c is rapid and quantitative with benzyl radicals. Step 1d has been shown

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(1) (a) P. L. Julian, W. Cole, A. Magnani, and E. W. Meyer, *J. Am. Chem. Soc.*, **67**, 1728 (1945); (b) G. Rosenkranz, O. Mancera, J. Gatica, and C. Djerassi, *ibid.*, **72**, 4077 (1950); (c) W. Cole and P. L. Julian, *J. Org. Chem.*, **19**, 131 (1954); (d) P. L. Julian, W. Cole, E. W. Meyer, and B. M. Regan, *J. Am. Chem. Soc.*, **77**, 4601 (1955); (e) F. A. L. Anet, *Can. J. Chem.*, **37**, 58 (1959); (f) C. W. L. Bevan, T. Halsall, M. N. Nwaji, and D. A. H. Taylor, *J. Chem. Soc.*, 768 (1962); (g) K. O. Kopple, *J. Am. Chem. Soc.*, **84**, 1586 (1962); (h) D. H. R. Barton and J. T. Pinhey, *Proc. Chem. Soc.*, 279 (1960); 280 (1962); (i) G. Büchi and H. J. E. Loewenthal, *ibid.*, 280 (1962); (j) C. E. Castro and W. C. Kroy, Jr., *J. Am. Chem. Soc.*, **85**, 2769 (1963); (k) L. Slaugh and J. H. Raley, *Tetrahedron*, **20**, 1005 (1964).

(2) (a) W. Traube and W. Passman, *Ber.*, **49**, 1692 (1916); (b) J. B. Conant and H. B. Cutler, *J. Am. Chem. Soc.*, **48**, 1023 (1926); (c) R. Graf, *J. prakt. Chem.*, **140**, 34 (1934); **146**, 90 (1936).

(3) M. Berthelot, *Ann. Chim.*, **49**, 401 (1866).

(4) Disubstituted mercury compounds are stable to both Cr^{+2} and Cr^{+3} under the reaction conditions and the reduction of these compounds must involve a higher potential than available from Cr^{+2}.

(5) An alternate mechanism utilizing Cr(IV) as an intermediate is less likely. Two electron changes in the reaction of Cr^{+2} with various metal

$$R\text{–}Hg^+ + Cr^{+2} \longrightarrow R\text{–}Cr^{+3} + Hg$$
$$R\text{–}Cr^{+3} + Cr^{+2} \longrightarrow R\text{–}Cr^{+2} + Cr^{+3}$$

salts have been discounted on the basis of stability of products with respect to the alternate one-electron change mechanism. See ref. 6.

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