phenylphenyl-*p*-tolylsilane in 50 ml. of toluene was added dropwise to a suspension of 3.5 g. (0.15 g.-atom) of molten sodium in 100 ml. of refluxing toluene. The reaction mixture was heated at reflux for 4 hr. and, after cooling to room temperature, cautiously treated with 100 ml. of 95% ethanol. The reaction mixture was then poured upon crushed ice containing sulfuric acid, and subsequently worked up in the usual manner. Chromatography of the reaction products over alumina with petroleum ether (b.p. 60–70°) gave 3.87 g. of colorless solid, m.p. 190–214°. This material was fractionally recrystallized, with much effort, from a mixture of absolute ethanol and benzene to give two substances. The more insoluble material was recrystallized many times from absolute ethanol-benzene mixtures to give ultimately 0.39 g. (2.2%) of colorless crystals, m.p. 221–222.5°, of *trans*(?)-5,10-diphenyl-5,10-di-*p*-tolyl-5,10-dihydrosilanthrene.

Anal. Calcd. for $C_{38}H_{32}Si_2$: C, 83.8; H, 5.92; Si, 10.30. Found: C, 83.9; H, 5.82; Si, 10.21.

The more soluble material was likewise recrystallized many times from absolute ethanol-benzene mixtures to give 1.02 g. (5.7%) of colorless crystals, m.p. 215–217°, of *cis*(?)-5,10-diphenyl-5,10-di-*p*-tolyl-5,10-dihydrosilanthrene.

Anal. Calcd. for $C_{38}H_{32}Si_2$: C, 83.8; H, 5.92; Si, 10.30. Found: C, 84.2; H, 5.91; Si, 10.13.

An admixture of this compound with the above material melted over the range 214–222°. The infrared spectra of the compounds as carbon disulfide solutions were nearly superimposable. Absorption bands, indicative of C—H aromatic and aliphatic groups, and aromatic *para*-disubstitution, *ortho*-disubstitution, and monosubstitution, were present at 3.3, 3.45, 12.5, 13.3, and 13.7 μ, respectively. A doublet was also present at 8.95–9.05 μ, possibly indicative of the types of silicon-phenyl linkages. Both isomers volatilized at 530–540° with decomposition, turning light brown at 480°.

Acknowledgment.—This research was supported in part by the United States Air Force under Contract AF 33(616)-627 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State University, with special acknowledgment to Dr. V. A. Fassel, Mr. R. Knisely, and Miss E. Conrad for the spectra.

Syntheses of Polymethylphenols and Their Derivatives. I

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Received September 29, 1961

Simple methods of syntheses of prehentenol and durenol have been studied. Reactions of prehentenol, durenol, hemimelletenol, and isopseudocumenol with formaldehyde have been studied qualitatively in order to isolate various phenol methylols and dihydroxydiphenylmethanes. All the new phenolmethylols isolated have also been prepared by alternate routes, not involving addition of formaldehyde.

In order to study the general nature and kinetics of phenol–formaldehyde reactions and the effect of methyl and methylol substituents on reactions rates, it was convenient to choose phenols with only one reactive position, since the reactions are less complex and are expected to lead to the formation of one monomethylol only. Results with 2,4- and 2,6-xylenols are not useful because of their low reactivities towards formaldehyde. Further, there is no conclusive evidence with regard to reactivities of free *meta* positions in phenols towards formaldehyde. Edell[1] claims to have isolated 2,3′-dihydroxydiphenylmethane from the acid condensation of phenol and formaldehyde which is interesting as a first reported case of *meta* substitution. Megson,[2] Finn and co-workers,[3,4] and Martin[5] have reported evidence for the condensation between formaldehyde and the *meta*-hydrogen of phenol under certain conditions. Nickerson,[6] Lilley,[7] and Imoto[8] also think that reaction in the *meta* position should not be excluded, particularly with phenols with a methyl group in the *para* position which might activate *meta* position. More recently Wegler and Regel[9] reported condensation of formaldehyde with the *meta* positions of phenols substituted in both *ortho* and *para* positions. On the other hand *meta* substitution may be obviated by using 3,5-dimethyl-phenols for rate studies. The use of the latter brings the added advantage of the *ortho-para* directing methyl groups located *meta* to the phenolic hydroxyl group, enhancing the reactivity of the phenol.[10] As examples of such substituted phenols, the monofunctional phenols prehentenol and durenol, and the difunctional phenols, hemimelletenol and isopseudocumenol, have been chosen for our studies. Simple methods of synthesis of these phenols have been evolved starting from 3,5-xylenol, and a qualitative study

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(1) G. M. Edell, dissertation, Columbia University, May 1932.

(2) N. J. L. Megson, *J. Soc. Chem. Ind.* (London), **52**, 420 T (1933); *Kunststoffe*, **38**, 76 (1948); *Brit. Plastics*, **19**, 70 (1947).

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(6) H. Nickerson, *Brit. Plastics*, **19**, 345 (1947).

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(9) R. Wegler and E. Regel, *Makromol. Chem.*, **9**, 1–24 (1952).

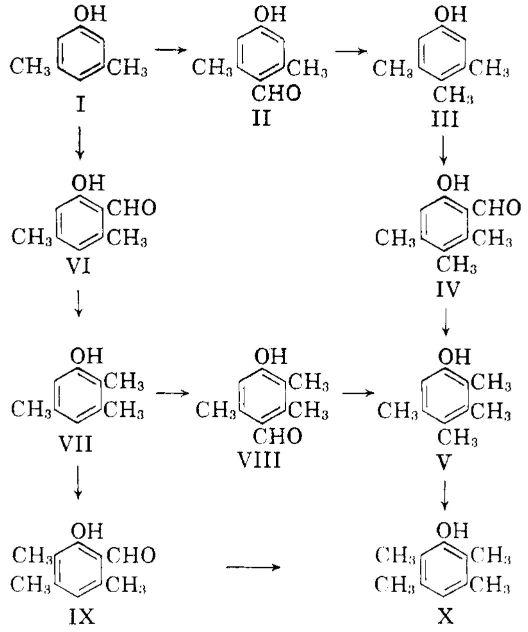
(10) M. M. Sprung, *J. Am. Chem. Soc.*, **63**, 334 (1941).

of the reactions between these phenols and formaldehyde, *viz.* isolation of corresponding phenol methylols and dihydroxydiphenylmethanes has been made. The identities of the phenol methylols have been confirmed by employing alternative methods of synthesis.

The tetramethylphenols are usually prepared by methylation of xylene, separation of the polymethylbenzenes formed, followed by sulfonation and alkali fusion.[11,12a] Fitzgerald's[12b] synthesis of prehentenol starting with 2-chloro-3,5-xylenol and formaldehyde, involved isolation of the corresponding phenolmethylols which were heat sensitive, thereby lowering the yield at each stage. Buu Hoï[13] has reported synthesis of prehentenol by formylating the methyl ether of 3,5-xylenol with dimethylformamide and phosphorus oxychloride. The aldehyde group *para* to the methoxy group has been reduced to methyl with hydrazine hydrate and alkali. A similar treatment for introduction of the methyl group in the *ortho* position, followed by demethylation has yielded prehentenol. On repetition of this synthesis, we observed that formylation with dimethylformamide and phosphorus oxychloride resulted in the formation of not only the *p*-methoxyaldehyde but also the *o*-methoxyaldehyde in appreciable amount. Further, it has been reported that the product of formylation of the methyl ether of 3,5-xylenol melts at 18°, while 4-methoxy-2,6-dimethylbenzaldehyde and 2-methoxy-4,6-dimethylbenzaldehyde are reported in literature[14–16] as melting at 47° and 48°, respectively.

An alternative method for the syntheses of tri- and tetramethylphenols has been adopted.

The Gattermann reaction on 3,5-xylenol (I) and the Clemmensen reduction of the isomeric hydroxyaldehydes II and VI to give III and VII, respectively, have been reported by Auwers[14a] and Finn.[14b] Conversion of III to IV and subsequently to V has now been carried out. Auwers[17a] has described the formation of IX, while Fitzgerald[12b] reported VIII, both from VII. It has now been observed that the Gattermann reaction on VII leads to VIII and IX. The aldehydes are separable by steam distillation. The precursor IX for X has been best prepared in 50% yield by formylation of VII with hexamine and glacial acetic acid.



Experimental

Formylation of the Methyl Ether of 3,5-Xylenol.—The methyl ether of 3,5-xylenol has been formylated with dimethylformamide and phosphorus oxychloride.[13] The product b.p. 130–134° (13 mm.) solidified in the ice chest to a pale yellow solid m.p. 18°. That the product is a mixture of the *o*- and *p*-methoxyaldehydes and is not the *p*-methoxyaldehyde alone has been concluded as follows: (i) The pale yellow solid (2 g.) suspended in 10% sodium hydroxide solution (8 cc.) was shaken with potassium permanganate (0.6 g. in 20 cc. water) for 4 hr. Sulfur dioxide was passed in and the methoxy acid which separated was recrystallized from hot water, m.p. 122–123°, which did not correspond to either the *p*-methoxy acid (lit.,[14b] m.p. 144°) or the *o*-methoxy acid (lit.,[14a,b] m.p. 167°). (ii) A second portion of the pale yellow solid was reduced with hydrazine hydrate and potassium hydroxide. The product could not be identified as the methyl ether of hemimelletenol. (iii) A third portion of the aldehyde mixture was demethylated using hydroiodic acid and steam distilled. The steam volatile product, m.p. 48°, corresponded to the *o*-hydroxyaldehyde of 3,5-xylenol, while the nonvolatile product, m.p. 190°, corresponded to the *p*-hydroxyaldehyde.[14–16]

Gattermann Reaction on 3,5-Xylenol (I).—To a mixture of anhydrous hydrocyanic acid (80 g., 3 moles) and 3,5-xylenol (122 g., 1 mole) dissolved in dry benzene (500 cc.), and cooled in an ice bath was added powdered anhydrous aluminum chloride (100 g., 1.5 moles). Dry hydrogen chloride was passed through for 4 hr. at 30°, the mass was then hydrolyzed, the benzene removed, and the product steam distilled. The steam volatile product was the *o*-hydroxyaldehyde (VI) m.p. 48°, yield 35%. The nonvolatile product was the *p*-hydroxyaldehyde (II) m.p. 190°, yield 65%.

Clemmensen Reduction of Aldehydes II and VI to III and VII.—A mixture of the *p*-hydroxyaldehyde from 3,5-xylenol (II, 50 g.), amalgamated zinc (200 g.), water (150 cc.) and concd. hydrochloric acid (200 cc.) was refluxed for 4 hr. and steam distilled. Hemimelletenol (III) was recovered from the steam distillate, m.p. 107°, yield 85% (lit.,[12b,14a,b] m.p. 107°). The *o*-hydroxyaldehyde (VI) was similarly reduced to isopseudocumenol (VII) m.p. 94°, yield 62% (lit.,[12,14a] m.p. 95°).

Gattermann Reaction on Hemimelletenol (III).—Using a procedure similar to the Gattermann reaction described

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(11) Tohl, *Ber.*, **21**, 645, 907 (1888).

(12)(a) J. S. Fitzgerald and R. J. L. Martin, *Australian J. Chem.*, **8**, No. 2, 194 (1955); (b) J. S. Fitzgerald, *J. Appl. Chem.* (London), **5**, 289 (1955).

(13)(a) Ng Ph Buu Hoï, Guy Lejeune, and Michel Sydney, *Compt. rend.*, **240**, 2241 (1955); (b) Ng Ph Buu Hoï, Guy Lejeune, Michel Sydeny, and Andree Chewtin, *Bull. soc. chim. France*, 1073 (1957).

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(15) Carl Djerassi and A. L. Wilds, *J. Am. Chem. Soc.*, **68**, 1862 (1946).

(16) K. V. Auwers and Borsche, *Ber.*, **48**, 1713 (1915).

(17)(a) K. V. Auwers, H. Bundesmann, and F. Wieners, *Ann.*, **447**, 183 (1926); (b) K. V. Auwers, and K. Ziegler, *Ann.*, **425**, 217 (1921).

earlier, the steam volatile *o*-hydroxyaldehyde (IV), which is the only product of the Gattermann reaction on hemimelletenol, was obtained in quantitative yield. Pale yellow shining needles from alcohol m.p. 78°.[17b]

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.18; H, 7.46. Found: C, 73.23; H, 7.9.

Oxime: m.p. 205°; semicarbazone: m.p. 318–320° (with dec.).; phenylhydrazone: m.p. 119°; 2,4-dinitrophenylhydrazone: m.p. 279° (with dec.).; benzoate: m.p. 119–120°; acetate: m.p. 131°.

Gattermann Reaction on Isopseudocumenol (VII).—The procedure was described earlier. *o*-Hydroxyaldehyde (IX) was recovered from the steam distillate as yellow needles from alcohol, m.p. 78°, yield 25% (lit.[13b,17a,c] m.p. 78–79°). The *p*-hydroxyaldehyde (VIII) was recovered from the nonvolatile product as white shining prisms from alcohol water, m.p. 150°, yield 65% (lit.,[12b] m.p. 147°). Acetate: m.p. 103°.

Hexamine Method of Formylation of Isopseudocumenol (VII).—A mixture of VII (10 g.) and hexamethylenetetramine (30 g.) in glacial acetic acid (80 cc.) was refluxed on a water bath for 4 hr. Hydrochloric acid (120 cc. 1:1) was added, the mixture was heated to boiling and was steam distilled to yield product (IX), m.p. 78°, yield 50%, mixed melting point with previous sample was not depressed.

Prehentenol (V) was obtained by Clemmensen reduction of IV or VIII followed by steam distillation. Shining white needles from alcohol–water, m.p. 85°, yield 65% (lit.,[12b,13] m.p. 84–86°). Acetate: m.p. 56°; phenylurethane, m.p. 145°.

Durenol (X) was obtained by Clemmensen reduction of IX followed by steam distillation, as white shining needles from petroleum ether, m.p. 118°, yield 60% (lit.[12b] m.p. 118°). The 4-bromo derivative melted at 118° (lit.,[12b] m.p. 118°); phenylurethane, m.p. 212°.

Prehentenolmethylol.—When a mixture of prehentenol (1.5 g.), formalin (1 cc. of 36% soln.) and sodium hydroxide (0.1 g.) in 10% dioxane–water (100 cc.) was warmed for 2 hr., a white crystalline compound separated which was identified as dihydroxydiphenylmethane. Prehentenolmethylol could be prepared employing Leighton Holmes' method.[18] A mixture of prehentenol (15 g., 0.1 mole), paraformaldehyde (9 g., 0.3 mole), and sodium ethoxide (6.8 g., 0.1 mole) dissolved in absolute ethanol (50 cc.) was left in a refrigerator at 5° for 3 days. The white solid which separated was filtered, washed with 10 cc. of absolute ethanol, dissolved in water (100 cc.), cooled in ice, and neutralized with dilute acetic acid. The product was recrystallized from petroleum ether, m.p. 112°, yield 68%.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.35; H, 8.88. Found: C, 74.8; H, 8.80.

On diluting the alcoholic mother liquor with water a solid separated which was identified as 3,4,5,6,3′,4′,5′,6′-octamethyl-2,2′-dihydroxydiphenylmethane, m.p. 225–226°, yield 1.3 g. (lit.,[12a] m.p. 225–227°).

Anal. Calcd. for $C_{21}H_{28}O_2$: C, 80.80; H, 9.00. Found: C, 80.20; H, 8.86.

Prehentenolmethylol forms a green colored complex with ferric chloride, a color test common to all *ortho*-methylolphenols. The number of hydroxyl groups in a molecule of the methylol was estimated by a combined determination of its molecular weight (Rast method) and the acetyl value (Shutter and Berkman[19] method. A hydroxyl value of 1.98 per mole was obtained. Diacetate: white shining needles, m.p. 59–60°.

(i) **Prehentenol aldehyde** was obtained by the Gattermann reaction on prehentenol in quantitative yield. Shining yellow needles from petroleum ether, m.p. 133–134°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 74.10; H, 7.90.

Oxime: m.p. 179°; phenylhydrazone: m.p. 180°; semicarbazone: m.p. above 330°; 2,4-dinitrophenylhydrazone: m.p. 283° (with dec.); benzoate: m.p. 117°; acetate: m.p. 106°.

(ii) **Sodium Amalgam Reduction of Prehentenolaldehyde to Prehentenolmethylol.**—Prehentenolaldehyde (2 g.) in alcohol–water (100 cc. of 1:1) was cooled to 5° in ice bath. Small pieces of 3% sodium-amalgam (200 g.) were added with stirring over a period of 10 hr., while maintaining the *p*H between 6 and 6.5 by the addition of acetic acid. The product recrystallized from petroleum ether m.p. 112°.

3,4,5,6,3′,4′,5′,6′ - Octamethyl 2,2′ - Dihydroxydiphenylmethane was prepared from prehentenol and formalin or prehentenol and prehentenolmethylol or by the self condensation of prehentenolmethylol all in the presence of hydrochloric acid. Number of hydroxyl groups per mole was found to be 1.86 (theoretical 2). Diacetate: m.p. 167–168°; dibenzoate, m.p. 185°.

Durenolmethylol could not be prepared by the method of Holmes.[18] It could be isolated from the reaction of durenol and formaldehyde. Durenol (1.5 g.) in dioxane–water (40 cc. of 50%) was warmed with formalin solution (2 cc. of 36%) and sodium hydroxide solution (3 cc. of 10%) at 50° for 5 hr. Dilute acetic acid was then added and the solution extracted with ether. A little unchanged durenol remaining in the product was separated by treatment with cold benzene, in which durenol is soluble in the cold. White shining crystals m.p. 168–169°.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.35; H, 8.88. Found: C, 72.60; H, 8.90.

Number of hydroxyl groups per mole found to be 1.93 (theoretical 2).

Diacetate: white shining needles, m.p. 126°.

(i) **Durenol aldehyde** was obtained in quantitative yield by the Gattermann reaction on durenol. Light yellow needles from petroleum ether, m. p. 131°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87; Found: C, 73.3; H, 7.80.

Oxime: m.p. 174°; semicarbazone: m.p. 238°; acetate: m.p. 150°.

(ii) **Lithium Aluminum Hydride Reduction of Durenolaldehyde to Durenolmethylol.**—Lithium aluminum hydride (0.6 g.) was suspended in dry ether (45 cc.) in a three-necked flask fitted with a mercury sealed stirrer, and reflux condenser. Durenolaldehyde (1 g.) dissolved in dry ether (30 cc.) was added drop by drop with stirring at room temperature. Excess lithium aluminum hydride was destroyed by adding water. The ether solution was decanted and the product was found by m.p. and mixed m.p. to be identical with a previous sample of durenolmethylol, m.p. 168°.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.35; H, 8.88. Found: C, 72.92; H, 8.86.

2,3,5,6,2′,3′,5′,6′ - Octamethyl 4,4′ - Dihydroxydiphenylmethane was prepared from durenolmethylol on treatment with alkali, as well as from durenol, formalin, and hydrochloric acid. Colorless needles from ethanol, m.p. 213–214° (lit.,[20] m.p. 214°). Acetate: m.p. 216°.

Hemimelletenol Monomethylol.—Hemimelletenol (1.36 g.), formalin (1 cc. 36%) and sodium hydroxide (0.4 g.) dissolved in water (100 cc.) were left at room temperature for 24 hr. after which time a crystalline high-melting solid insoluble in common organic solvents but soluble in dimethylformamide was formed. When hemimelletenol (2.72 g.) in alcohol (20 cc.) and a 10% sodium hydroxide solution (2 cc.) were heated with 36% formalin (2 cc.) on a water bath for 4 hr., cooled in an ice bath, acidified with dilute acetic acid and then diluted with water, a compound separated which recrystallized from alcohol–water as white prisms melting at 203–204° with effervescence.

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Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.30; H, 8.49. Found: C, 72.70; H, 8.20.

The compound gave characteristic green color with ferric chloride. The number of hydroxyl groups per mole was found to be 1.93 (theoretical 2). Acetate: m.p. 182°.

Sodium Amalgam Reduction of Hemimelletenol Aldehyde (IV) to Hemimelletenol Monomethylol.—The *o*-hydroxyaldehyde (IV) obtained by the Gattermann reaction on hemimelletenol could be smoothly reduced to hemimelletenolmonomethylol using sodium amalgam and alcohol-water (1:1) between 0 and 5°. The product was recrystallized from alcohol-water, m.p. 203°; a mixed melting point with previous sample was not depressed.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.30; H, 8.49. Found: C, 72.53; H, 8.70.

Hemimelletenoldimethylol.—A solution of hemimelletenol (1.36 g.), paraformaldehyde (0.9 g.) and sodium ethoxide (0.68 g.) in absolute ethanol (20 cc.) was left in an ice chest. The separation of crystalline sodium salt was complete within 3 days. This was dissolved in water and acidified with acetic acid. The product was recrystallized from ethyl acetate as white shining flakes, m.p. 150°, yield 85% (lit[14a] m.p. 148°).

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.33; H, 8.22. Found: C, 67.00; H, 8.70.

The number of hydroxyl groups per mole was found to be 2.87 (theoretical 3). Triacetate, m.p. 87°. The dimethylol gave an intense blue coloration with ferric chloride, observed to be characteristic of *O*-*O*-dimethylols from 3,5-xylenol, *p*-cresol.

2,3,4,2',3',4'-Hexamethyl 6,6'-dihydroxydiphenylmethane was obtained when a mixture of hemimelletenolmonomethylol (1.66 g.), hemimelletenol (2 g.) in dioxane-water (25 cc. of 50%) and hydrochloric acid (10 cc. of 1 *N*) was warmed on a water bath for 1 hr., as shining white flakes, m.p. 275°.

***o*-Monomethylol isopseudocumenol** could not be isolated by a direct reaction between isopseudocumenol and formaldehyde because of side reactions. However, application of Holmes'[18] method on isopseudocumenol resulted in the formation of *o*-methylol only (80% yield), no *p*-methylol or dimethylol being formed. The *o*-monomethylol was recrystallized from petroleum ether, m.p. 120°. It gave a green color with ferric chloride. The compound was considered to be *o*-monomethylol for the following reasons: (1) elemental analysis of the compound was in agreement with requirements for a monomethylol and not for a dimethylol.

Anal. Calcd. for monomethylol, $C_{10}H_{14}O_2$: C, 72.21; H, 8.49. Found: C, 73.10; H, 8.50.

(2) The number of hydroxyl groups per mole was found to be 1.94 (theoretical 2).

(3) The constitution of the *o*-monomethylol was further confirmed by preparation of 2-hydroxy-3,4,6-trimethylbenzaldehyde (IX, m.p. 78°) by a Gattermann reaction on isopseudocumenol and the subsequent reduction of the aldehyde by lithium aluminum hydride to the methylol, m.p. 120°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.21; H, 8.49. Found: C, 72.82; H, 8.61.

***p*-Monomethylolisopseudocumenol** could not be prepared by Holmes[18] method on isopseudocumenol. Its preparation was therefore carried out by the following method not involving formaldehyde addition. 4-Hydroxy-2,3,6-trimethylbenzaldehyde (VIII), m.p. 147°, was obtained by a Gattermann reaction on isopseudocumenol followed by steam distillation to remove the *o*-aldehyde. VIII was subjected to lithium aluminum hydride reduction in dry ether at room temperature. The product was recrystallized from ethyl acetate-petroleum ether, m.p. 169°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.21; H, 8.49. Found: C, 71.60; H, 8.90.

The number of hydroxyl groups per mole was found to be 1.96. Diacetate: m.p. 53°.

Acknowledgment.—We wish to thank C.S.I.R. New Delhi for the grant of a Junior Research Fellowship to one of us (H.D.) during the period of this investigation.

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o-Phenol Methylols–Ferric Iron Complex Formation. II.

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Received September 20, 1961

o-Phenol methylols from certain polymethyl phenols form green colored complexes with ferric chloride. The nature and composition of the complexes were investigated spectrophotometrically.

Lack of adequate analytical tools has been a big handicap for the systematic kinetic study of phenol-formaldehyde reaction. Formaldehyde, even in the presence of phenolic materials, is conveniently estimated[1-5] titrimetrically. A method by Gambier modified by Nordlander[6] involves titration with hydroxylamine hydrochloride. Determination of phenols, phenol methylols, and dihydroxydiphenylmethanes based on infrared absorption has been reported in a few cases.[7-9] Estimation of phenols or phenol methylols by the bromide method has several limitations.[10-12] Our experience has been that with methyl-substituted phenols and dihydroxydiphenylmethanes, overbromination occurs, probably because of substitution in the side chain or at the methylene bridge. Partition paper

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