CHAPTER II

MATERIALS AND EXPERIMENTAL PROCEDURE

Preparation of materials used in the experiments:

Phenol:
A.R. phenol (B.D.H.) was distilled and the fraction distilling at 180-180.5°C was used.

Saligenin:
Saligenin was prepared by the catalytic reduction of salicylaldehyde.¹

Salicylaldehyde (20 g.) was dissolved in 50 ml. of rectified spirits, Raney Nickel (about 2 g.) was added, and the mixture was reduced at room temperature in a Parr hydrogenation apparatus at an initial pressure of 55 p.s.i. After 2 hours the reduction was found to be almost complete. The reaction mixture was then centrifuged and the alcohol was evaporated off. The crude product was crystallised twice from benzene to give 17 gms. of white glistening flakes, melting at 86°C.

p-Methyl phenol:
The reduction of p-hydroxy benzaldehyde was carried out as in the previous case. The crude product was crystallised first
from water and then from a mixture of benzene and ethanol (1:1 v/v) to give colorless crystals melting at 118° C.

2,4-Dimethylol Phenol:

The reduction of 4-hydroxy isophthalaldehyde as described by Espen\(^2\) was utilised for the preparation of this compound.

Angyal et al\(^3\) have described the conversion of 5-chloromethyl salicylaldehyde into 4-hydroxy isophthalaldehyde by Fassmatt reaction.

The dialdehyde (1 g.) was dissolved in rectified spirits (25 ml.) and 0.2 g. of Adam's platinum oxide catalyst was added. The mixture was hydrogenated at an initial pressure of 60 p.s.i. till hydrogen absorption was complete (1 - 1.5 hours). The solution was filtered and the filtrate evaporated in vacuo, when a highly viscous colourless liquid was obtained. It was dried in a vacuum desiccator, when it slowly crystallised. It was re-crystallised from a mixture of dry chloroform and ethyl acetate. Fine white crystals, m.p. 95° C, yield 0.5 g.

* DMF hereafter denotes Dimethylol Phenol in this Thesis.
2,6-Dimethylol phenol:

This compound was prepared by a modification of the method of Hammerer and Grossman. The modification involves catalytic debromination of 4-bromo-2,6-dimethylolphenol with Raney Nickel. p-Bromo phenol (10 g.) was dissolved in 10 ml. of 25% Caustic Soda, formaldehyde (10 ml.) was added and the mixture was kept at room temperature for 75 hours. The sodium salt of 4-bromo-2,6-DMP from the reaction mixture separated and it was suspended in water and acidified with dilute sulphuric acid. The precipitated dimethylol compound was filtered and recrystallised from rectified spirits, yield 3 g., m.p. 155°C.

4-Bromo-2,6-dimethylol phenol (9.4 g.) was dissolved in a minimum amount of 10% NaOH solution. The solution was diluted with 50 ml. water, Raney Nickel (1 g.) was added, and the mixture hydrogenated at 55 p.s.i. for 2-5 hours. The resulting solution was filtered and was neutralised by passing CO₂. Some unreacted bromo compound precipitated at this state and was filtered off. The filtrate was saturated with NaCl and was repeatedly extracted with ether. The ether extract on evaporation gave white flakes of 2,6-DMP. It was recrystallised twice from benzene to give white flakes (4.3 g., m.p. 95°C).
**0.0'-DPM:**

This was prepared by zinc acetate catalysed phenol-formaldehyde reaction (Fraser et al\(^6\)).

*Phenol* and *formaldehyde* (in the molar ratio of 6:1) together with *zinc* acetate (1% by weight of phenol) were heated under reflux in an oil-bath at 120\(^\circ\)C for 4 hours. Water and part of the phenol were distilled off under atmospheric pressure until the temperature rose to 170\(^\circ\)C. The residue was steam distilled to remove the remaining phenol. Water was separated from the resin and the resin was fractionally distilled under reduced pressure (5 mm of Hg). The fraction collected at 160-190\(^\circ\)C was extracted with boiling water and the extract when cooled in ice yielded white crystals. The crystals obtained were repeatedly crystallised from boiling water until free from the 0,0'-isomer, as shown by paper chromatography. Obtained white needle-like crystals, m.p. 118\(^\circ\)C.

**o,p'-and p,p'-DPM:**

These compounds were isolated from an acid catalysed phenol-formaldehyde reaction mixture following the method of Finn and Masty\(^7\), with a few modifications.

A mixture of phenol (94g) and formaldehyde (12g of 37% solution) with sufficient concentrated sulphuric acid to give a pH of 1 was heated under reflux at 120-125\(^\circ\)C in an oil bath for 72 hours. The excess phenol was steam-distilled and the resin layer was separated from the solution. The solution on cooling to room temperature yielded white crystals which were found by paper chromatography to consist of p,p'-DPM with traces of the o,p'-isomer.
The fraction rich in p,p'-DFM was purified by repeated crystallizations from water in which it is only sparingly soluble in the cold. It was finally recrystallised from benzene, mp.159°C.

The mother liquor was concentrated on a water-bath till a turbidity appeared and then allowed to cool, yielding a further crop of crystals. This was found to be rich in o,p'-DFM by paper chromatography.

The product rich in o,p'-isomer also was recrystallised several times from water and finally from benzene to yield white needle-like crystals. mp.115°C.

O,O'-Di-hydroxy dibenzyl ether:

A sample of this compound was prepared according to the procedure described by Piegl and Belscher 1. Saligenin (10 g) was heated in a sealed tube at 120-140°C for 9 hours in an oil bath. The residue was recrystallised twice from benzene after removing the unreacted saligenin by repeated extraction with hot water to yield paper chromatographically pure o,o'-di-hydroxy dibenzyl ether. Yield 1 g; mp.119-120°C.

p,p'-Di-hydroxy dibenzyl ether:

The preparation of this compound was carried out using the method of Mose 8 by heating 2,6-dichloro-4-methylphenol at 140°C followed by dehalogenation. 3, 5-Dichloro-4-hydroxy benzaldehyde: Following the method of Anshler et. al 17, 3-chloro-4-hydroxy benzaldehyde was prepared by the controlled chlorination of p-hydroxy benzaldehyde. Through a solution of p-hydroxy benzaldehyde (3g in 100 ml of chloroform) dry
chlorine was passed for two hours at room temperature. On partial evaporation fine needle-like crystals separated out, m.p. 150°C.

3,5-Dichloro-4-hydroxy benzaldehyde (3.5 g.) was dissolved in 50 ml of ethyl acetate and hydrogenated in the presence of Raney Nickel at 40 p.s.i. White crystals of 2,6-dichloro-4-methylol phenol were obtained on partial evaporation of the solvent, m.p. 34°C. 2,6-Dichloro-4-methylol phenol (3 g.) was heated at 140°C for 3 hours in a boiling tube fitted with a water condenser. The product namely 3,5,3',5'-tetrachloro-4-4'dihydroxy dibenzyl ether, was re-crystallised twice from benzene-petroleum ether mixture, m.p. 120°C.

The dehalogenation of the ether obtained above was carried out by hydrogenation in the presence of Raney Ni/C6H6 CO3 for 3 hours at a pressure of 55 p.s.i. giving p,p'-dihydroxy-dibenzyl ether, m.p. 119°C.

The Trinuclear Novolacs:

Syntheses of all seven tri-nuclear novolacs were achieved by Finn, Jannes et al.11,12 They used 6 general types of reactions, each type being a special case of the interaction between a substituted halogeno methyl or hydroxy methyl compound and a substituted phenol. Halogens were removed in the final stage by reaction with Ni-Al alloy in alkaline solution.

1-Hydroxy-2,6-bis-2-hydroxy dibenzyl benzene:

This was originally prepared by Finn, Lewis and Negron12 by condensing 4-chloro-1-hydroxy-2,6-bis hydroxy
benzyl benzene with 4-chloro phenol, followed by dehalogenation.

a) 4-chloro-2,6-trihydroxy methyl phenol (m.p. 145°C) was prepared by hydroxy methylation of 4-chloro phenol by Namius.¹³

b) 1-Hydroxy-4-chloro-2,6-bis-(4-chloro-2-hydroxy benzyl) benzene:

The hydroxymethyl compound 3.9 g. was condensed with 10 times the weight of 4-chlorophenol (25 g.) on a water bath at 100°C, for 3 hours, a few drops of concentrated HCl being added occasionally. Excess of phenol was removed by steam distillation. The residue was recrystallised from ethanol-water mixture, m.p. 225°C.

c) The compound from (b) above was dehalogenated⁴ using H₂-Al₂.

2 g. were dissolved in 10 ml of NaOH and H₂-Al₂ alloy (2 g.) was added intermittently during 4 hours, so that a slight evolution of hydrogen was maintained. 1 to 2 ml of 10% NaOH solution was added 3 to 4 times during the above reaction. The mixture was filtered and acidified with 1:1 HCl, obtained powdery white crystals, m.p. 159°C (dil. ethanol.)

2) 1-Hydroxy-2,6-bis-(4-hydroxy-benzyl) benzene:

This compound was prepared using the method of Finn et al.¹¹ by condensing 2 moles of 2,6-dibromo-4-bromomethyl phenol with 4-chlorophenol (1 mole) in the presence of H₂SO₄.

a) 2,6-Dibromo-4-bromomethyl phenol:¹⁵ Bromine (109 g.) was added dropwise during the course of 3 hours to p-creosol (36 g.) which was maintained at 0-10°C and stirred well. After the bromine addition, the mixture was heated to 75°C and further quantity of bromine (54 g.) was added. The reaction mixture was set aside for overnight. The solid bromo compound was filtered
and reccrystallised twice from glacial acetic acid m.p. 148° C yield 29g.
b) 2,6-bis-(3,5-dibromo-4-hydroxy benzyl)-4-chloro-1-hydroxy bensene: 2,6-dibromo-4-bromomethyl phenol (79g.) was condensed with 4-chloro phenol (6g.) in presence of catalytic amount of con. H₂SO₄ at 140° C in a steam of nitrogen until the evolution of hydrogen halide ceased. The products were extracted with benzene and de-colorised with charcoal under reflux. Light petroleum ether was then added until the precipitation of the product was about to occur. The solution allowed to stand while benzene evaporated by blowing a steam of air across the surface of the liquid. An oil was generally precipitated first followed by solid. The solution and the solid were then immediately removed to another beaker and allowed to stand, when solid continued to be precipitated. It was crystallised twice from benzene, m.p. 223° C, yield 25g.

c) 1-Hydroxy-2, bis-4-hydroxy benzyl benzene: The halogeno trinuclear compound was dehalogenated as per 1 (a), m.p. 171° C yield 2g.

3) 1-Hydroxy-2-(2-hydroxy benzyl)-6-(4-hydroxy benzyl) benzene:
This was prepared by condensing 3',5'-Dibromo-5-chloro-2,4'-dihydroxy-3-hydroxy methyl DPM with excess of 4-chloro phenol and dehalogenation of the resulting product.

a) 3',5'-Dibromo-5-chloro-2,4'-DPM: - 2,6-dibromo-4-bromo methyl phenol (100g.) was condensed with 4-chloro phenol (160g.)
in the presence of conc. sulphuric acid at 100°C. A fairly rapid stream of nitrogen was passed through the solution to improve the yield by minimising oxidation. Excess of 4-chlorophenol was removed by steam distillation. The solid obtained was recrystallised twice from benzene to give colourless crystals; m.p. 127.5°C, yield 25g.

b) The dimuclear phenolic compound from above (24g.) was dissolved in NaOH solution (9g.) and allowed to stand for 7 days with 40% formalin solution (45g.). After reaction, the solution was poured into excess of dilute HCl (1:1) when the hydroxy methyl compound separated as a solid. It was washed with hot water and then recrystallised from ethanol-water mixture obtained colourless plates, m.p. 133°C, yield 32g.

c) 6-(3,5-dibromo-4-hydroxy benzyl)-4-chloro-2-(5-chloro-2-hydroxybenzyl)-1-hydroxy benzene: This compound was obtained by condensing the above dimuclear methylol compound (10g.) with excess of 4-chlorophenol as described under section 2(b)(p.22.) yield 12g, m.p. 167°C.

d) 1-hydroxy-2-(2-hydroxybenzyl)-6-(4-hydroxybenzyl) benzene: The halogenated trimuclear compound was dehalogenated using Ni-Al alloy as in section 1(c) (p.21.) m.p.134°C, yield 1 g.

4) 1-Hydroxy-2-(2-hydroxy benzyl)-4-(4-hydroxy benzyl) benzene:

a) 3,5-Dibromo -3' -chloro -4,4'-DFPM, 2,6-Dibromo -4-bromomethyl phenol (10g.) was condensed with 2-chlorophenol as described under section 3(a). Diamond shaped crystals
(Petroleum-benzene) m.p. 130.5°C yield (29 g.)

b) 2,4-Dibromo-6-bromomethyl phenol was prepared using the method of Auwers and Scholte as in 2(a) from 2-methyl phenol.

c) 4-(3,5-dibromo-4-hydroxybenzy1)-6-(3,5-dibromo-2-hydroxybenzy1)-2-chloro-1-hdroxy benzene: 3,5-Dibromo-5′-chloro-4,4′-(20 g) was condensed with (18 g.) of 2,4-dibromo-6-bromomethyl phenol as in 2(b) m.p. 175-76 (benzene) yield (21 g.).

d) Dehalogenation of the compound from (c) above was carried out. Considerable difficulty was experienced in getting the compound in crystalline form melted around 32°C. The compound was found to be hygroscopic as observed by Fimm et al.

5) 1-Hydroxy-2,4-bis-2-hydroxy benzyl benzene:

a) 4,6-Bis-(3,5-dibromo-2-hydroxybenzy1)-2-chloro-1-hydroxy benzene 2,4-Dibromo-6-bromomethyl phenol (79 g.) was condensed with 2-chlorophenol (6 g.) as in 2(b). Yield 29 g. m.p. 153°C (CHCl3)

b) The above compound was dehalogenated m.p. 118°C (ethanol-water) yield (2 g).

6) 1-Hydroxy-2,4-bis-4-hydroxybenzy1 benzene:

a) 4,6-Bis-(3,5-dibromo-4-hydroxybenzy1)-2-chloro-1-hydroxy benzene: 2,6-Dibromo-4-bromomethyl phenol (33g) was condensed with 2-chloro phenol (3g) as per 2(b) m.p. 172 (CHCl3) yield 25 g.

b) 1-Hydroxy-2,4-bis-4-hdroxy benzene: (a) was dehalogenated. The resulting resin was purified by dissolving it in benzene and passing it through a column of alumina using benzene as the eluting solvent. Different fractions were collected at different
intervals of time. The solvent on evaporation gave white solid m.p. 145.5°C yield 1g.

7) 1-Hydroxy-2-(4-hydroxybenzyl)-4-(2-hydroxybenzyl)benzene:
   a) 3,5-Dibromo-3'-chloro-2,4'-DPM: By condensing 2,4-dibromo-6-bromomethylphenol (50g) with 2-chlorophenol (150g) at 140°C under nitrogen, 3,5-dibromo-3'-chloro-2,4'-DPM was obtained as colourless prisms, m.p. 115°C, yield 19g.
   b) 4-(3,5-dibromo-2-hydroxybenzyl)-6-(3,5-dibromo-4-hydroxybenzyl)-2-chloro-1-hydroxy benzene: 3,5-dibromo-3'-chloro-2,4'-DPM was condensed with 2,6-dibromo-4-bromomethyl phenol in equimolar proportions to give the required compound, m.p. 155°C (benzene).
   a) The compound (b) was dehalogenated to give 1-hydroxy-2-(4-hydroxybenzyl)-4-(2-hydroxybenzyl) benzene, m.p. 133°C (ethanol-water).

The Mono-methylol DPMs

1) 3-Methylol 2-2',4'-DPM: Yeddannapalli and Francis 17 have prepared by hydrogenation of 3-formyl-5'-bromo-2',4'-DPM.
   a) 5-chloromethyl salicylaldehyde (7g) was heated with 9g of p-bromophenol to 90°C in an atmosphere of CO₂ until the evolution of HCl subsided (1 hour). The resulting resinous solid was repeatedly extracted with boiling water to get rid of the unreacted p-bromophenol and the residue was then dissolved in 40 ml of trichloro ethylene. On partial evaporation a white solid was deposited which was recrystallised from benzene to give pure 3-formyl-5'-bromo-2',4'-DPM, m.p. 150°C yield 6.2g.
b) 3-Formyl 5'-bromo 2',4'-DPM (2 g. in 30 ml. rectified spirit) was hydrogenated in presence of Raney Ni and a pinch of CaCO₃ to give almost quantitative yields of 3-methylol 2',4'-DPM. It was recrystallised from benzene. White needle like crystals m.p. 106°C.

2) 5-methylol -2,4'-DPM was prepared by using the method adopted by Francis by the reduction of 5-formyl 3'-5'-dibromo -2,4'-DPM.

3) 4-hydroxy -3-chloromethyl benzaldehyde: Hel gas was passed into a well stirred mixture of p-hydroxy benzaldehyde (25 g.), HClO (16 ml. of 40% solution) and concentrated HCl (130 ml.) for 3 hours. The temperature rose to 40°C and a red solution resulted followed by solid on standing. The solution was cooled and the solid was filtered m.p. 136°C (chloroform).

b) 5-Formyl -3',5'-dibromo -2,4'-DPM: 3-chloromethyl -4-hydroxy benzaldehyde (2 g.) was heated with 2,6- dibromophenol (3 g.) at 115°-120°C for 2 hours in an atmosphere of CO₂. After steam distilling the unreacted 2,6- dibromophenol, the residue was dissolved in ether and on partial evaporation, a white solid was deposited m.p. 224°C.

6) 5-Formyl -3',5'-dibromo -2,4'-DPM was reduced to 5-methylol 2,4'- DPM by hydrogenation in presence of Pd/Be Ca₃ to give 5-methylol -2,4'- DPM. m.p. 155°C.

3. 3-Methylol -2,4'-DPM: The procedure indicated by Finn et al 13 was adopted for preparing this compound.
a) 5,3',5'- Tribromo -5-Carbomethoxy -2,4'-DPM: 2,6-Dibromo -4-bromomethyl phenol (9 g.) and 4-bromo 2-methoxy carbonyl phenol (12.5 g.) were heated together with concentrated H₂SO₄ (1.5 g.) at 100°C for 3 hours and then at 120°C for 2 hours. Water was added and mixture steam distilled after the addition of CaCO₃ (4 g.). The residue was dried, dissolved in acetone and petroleum ether was added slowly. The resin which precipitated first was removed and the solution on standing deposited white powder m.p. 150°C yield 3 g.

b) 5,3',5'- Tribromo -5-Carbonyl -2,4'- DPM: 3 g. of (a) was boiled with 20 ml. of 10% NaOH for 1½ hours. The mixture was acidified with concentrated H₂SO₄ after cooling and extracted with ether. The ether layer was washed with H₂SO₄ solution. The Na₂CO₃ extract gave (b) on acidification, m.p. 240°C yield 3.9 g.

e) 3-Carbonyl -2,4'- DPM: (b) was made to dissolve in 10 ml. of NaOH and Ni/Al alloy (2 g.) was added periodically during 4½ hours along with some 10% NaOH solution. The mixture was filtered and acidified with 1:1 HCl. White crystals m.p. 190°C yield 1.2 g.

d) 3-Methylol -2,4'-DPM: Li Al H₄ (1.7 g.) was stirred in dry ether (55 ml.). A solution of (e) (1.5 g.) in dry ether (20 ml.) was added slowly during the course of 1 hour. The mixture was set aside overnight. Then it was cooled in ice and water was added to decompose the unreacted LiAlH₄. It was next shaken up with a saturated solution of sodium potassium tartrate and 0.5 ml. of
glacial acetic acid. The ether layer was separated and the aqueous layer extracted with ether. The combined ethereal extracts were washed with sodium bicarbonate and water and dried with anhydrous MgSO₄. Ether was then distilled off. m.p.112°C (benzene), yield 325 mg.

4) 3-Methylol - 4,4′-DFM:¹⁸
   a) 3′,5′-Dibromo-3-methoxy carbonyl-4,4′-DFM: 2,6-Dibromo-4-bromomethyl phenol (12.5g.) was heated at 140°C with methyl salicylate (38g.) for 6 hours in an atmosphere of CO₂. The excess of methyl salicylate was steam distilled off and the residue recrystallised from benzene. Yield 8 g, m.p.138°C.

   b) 3′,5′-Dibromo-3-carboxy-4,4′-DFM: Compound (a) (7g) was hydrolysed to (b) by the procedure described in 3 (b). White needles, m.p. 210°C, yield 7g.

   c) 3-Carboxy-4,4′-DFM: Compound (b) (6g.) was dehalogenated to (c) as in 3 (c). m.p. 174°C. (ethanol-water) yield 3.2g.

   d) 3-Methylol-4,4′-DFM: 1.5g. of (c) was reduced to (d) by LiAlH₄ as in 3(d). m.p.129°C (benzene) yield 370 mg.

5) 3-Methylol-2,2′-DFM:¹³
   a) 2,4-Dibromo-6-bromomethyl phenol: This was prepared by the bromination of e-cresol by following the procedure described earlier.

   b) 5,3′,5′-Tri-bromo-3-carboxymethoxy-2,2′-DFM(I): 2,4-bibromo-6-bromomethyl phenol (8.5g.) was condensed with 4-bromo-2-methoxy carbonyl phenol (12.5g.) (Cf. preparation 3(a)) in
the presence of 1.5 g of con. $\text{H}_2\text{SO}_4$ as in 3 (c). I is obtained as fine needles from benzene. Yield 5 g, m.p. 184°C.

e) 5,3',5'-Tribromo-3-carboxy-2,2'-DFM II: II (5g.) was hydrolysed by boiling with 10% NaOH as in 3 (d). The product was recrystallised from aqueous alcohol. White crystals, m.p. 230°C. Yield 5g.

d) 3-carboxy-2,2'-DFM III: II (5g.) was dehalogenated to III as in 3 (e). The product was recrystallised from ethanol-water. Yield 2.5g, m.p. 163°C.

e) 3-Methylol-2,2'-DFM (IV): 1.5g. of III was reduced to IV by LiAlH₄ as in 3(f). Recrystallisation was carried out using ethanol-water. Yield 500 mg. m.p. 121°C.

6) 5-Methylol-2,2'-DFM:¹⁸

a & b) 3',5'-Dibromo-5-carboxy-2,2'-DFM (I): 2,4-Dibromo-3-bromomethyl phenol (12.5g.) was condensed with ethyl p-hydroxy benzoate (12.5g) by heating at 140°C for 4 hours in an atm. of CO₂. The resulting oil was extracted with boiling water and the residue was dried in vacuo. It was dissolved in benzene and precipitated by the addition of petroleum ether. This oil was hydrolysed as in 3(d) to 3',5'-dibromo-5-carboxy-2,2'-DFM (I). Recrystallised from ethanol-water. Yield 5g, m.p. 230°C.

c) 5-carboxy 2,2'-DFM (II): 8g. of I was dehalogenated to II as in 3 (e). Yield 3g m.p. 125°C.

d) 5-Methylol-2,2'-DFM (III): Reduction of II as in 3(f) gave
a white solid m.p. 178°C. The reported m.p. of III is 135°C. On chromatographic analysis, it gave an Rf value different from 5-methylol -2,2'-DPN. The methyl ester of II was, therefore, prepared and reduced. 1.5g. of II was dissolved in methanol and dry HCl was passed in for 10 minutes. The mixture was then set aside for an hour. It was poured into water and the resulting oil was separated and dried well. This methyl ester of II on reduction with LiAlH₄ as 3(f) gave III, with traces of the other product as shown by chromatographic analysis. It was repeatedly crystallised from benzene. Yield 200 mg. m.p.135°C. Dioxane - water:¹⁹,²⁰ Dioxane used was of analytical grade ("B.D.") reagent. In view of the insolubility of the experimental phenols (DPN's) in water, it became necessary to use a mixed solvent. Dioxane-water (50% by weight) appeared to be ideal as a solvent. However this solvent was used only for the experiments in chapters IV and V. For other experimental chapters only water was used as solvent.

p-Nitrobenzene diazonium chloride solution:²¹

It was used as a spraying reagent in the paper chromatographic analysis. In ice cold 0.5% solution of p-nitro aniline in 3N HCl(5 ml) was mixed with 1 ml of a cold 2.5% solution of sodium nitrite. The mixture was cooled in ice and 15 ml of a cold 20% sodium acetate solution was added as buffer, before using it for spraying.

Experimental Procedure

The reactions were carried out in a 100 ml
three-necked flask fitted with a mercury sealed stirrer (A),
thermometer (B), reflux water condenser (C) and vacuum
sampling device (D)(Cf.Fig 1). The flask was heated in
a thermostat which was maintained at the required temperature
(60-80°C) with ± 0.1°C, using a toluene-mercury regulator
coupled with an electronic relay.

In the condensation reactions of phenol with
methylole phenols, calculated amounts of phenol, sulphuric
acid (or zinc acetate) and dioxane-water (or water) were
first introduced into the reaction vessel and then heated
to the required temperature. The solution of methylole
phenol, heated separately to the reaction temperature, was
then added to the phenol solution to start the reaction.
In the self condensation studies, the solution of methylole
phenol was first taken in the reaction vessel and the
catalyst (H₂SO₄ or \( \text{HNO}_₃ \)) was added to start the reaction.
In the case of reactions in the presence of H₂SO₄ aliquot
samples were withdrawn at regular intervals from the
reaction vessel into test tubes containing solid calcium
carbonate and cooled in ice to arrest the reaction. The
calcium carbonate was found to have no catalytic effect
on the condensation reactions at ordinary temperatures.
In the case of reaction with zinc acetate, calcium carbonate
was omitted. The methylole phenols, the NPM's, the methylole
NPMs and the trimolecular novolacs were estimated by quantitative
paper chromatographic technique, as described in Chapter III.
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