

Purified Chemicals and Resins from Phenol and Formaldehyde

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SUBSTITUTED phenols, because of their lower reactivity with formaldehyde, have been largely used (12, 19) to predict the course of the phenol-formaldehyde reaction. Some data on crystals found in the phenol-formaldehyde resin series have been lately published in patent form (3) and their contributions to commercial resin progress have been indicated. Phenol and formaldehyde condense to produce resins which are considered as chained phenolic products and from which a few definite crystalline compounds have been extracted (2). These crystalline and resinous chemicals increase in size by the addition of alternate increments consisting of one phenol residue and of one methylene group. Then later, at the massive or cross-linking stage, some variable excesses of methylene addition over the one to one ratio of phenolic to methylene groups are involved in the commercial production of the infusible resinous masses often called phenoplasts (6).

The crystals found in phenolic resins have varied in structure with conditions of condensation. These structural differences have proved to be of commercial importance and some are under patent protection (3). The crystals and the resins differ among themselves in the proportions of completed ortho and para reacted positions. The resins are conveniently described as averages of hydroxyl position content and of phenyl ring residues present per measured molecule.

Phenol reacts with formaldehyde to make many products. The molar ratio at which they react may vary from one formaldehyde with two phenols to that of one phenol with four formaldehydes (4). The heat-hardened phenolic resin field pioneered by Baekeland largely covered the final reacted ratios of one phenol with one to two moles formaldehyde. Ratios of formaldehyde over two slowed the reaction rate and thus at first were largely neglected. The two-step fusible resins (novolacs) are generally made by first using less than one mole of formaldehyde per mole of phenol. But in such cases the original deficiency of formaldehyde is changed later in the resinification cycle by adding either additional formaldehyde or using hexamethylenetetramine or other hardening agents to give heat-hardened resins of maximum strength.

Phenol is well known to form weak association products with itself or with other chemicals (16, 22). Formaldehyde forms a series of somewhat more firmly linked products now classed as polymers (26). Thus when phenol is cold-blended with formaldehyde it can be assumed that many of these weaker products are quickly formed. Under the influence of temperature changes and of catalysts these weakly associated forms may rapidly change into other definite chemicals or into resins (20). This paper is concerned primarily with the identification of such of these reaction products as are either well-defined chemicals or else are resins so purified as to melt like pure chemicals.

REACTION PRODUCTS

Many past attempts have been made to isolate these expected intermediate phenolic products. At present even a few more data of unsubstituted polyhydroxybenzylenes would greatly benefit the theories of phenolic resin structure.

The reaction of equal molar quantities of phenol with formalde-

hyde by simple addition gives the methylol phenols. These monomethylols in turn react with more phenol, with loss of water, to give the two-ring diphenylols. These, in turn, may add formaldehyde and react with more phenol to form the polyhydroxybenzylenes (Figure 1). In this series each two phenolic rings are separated by a methylene group. At each such reaction step the complications of an increasing number of reactive positions on the molecule reduce the expectation of reasonable yields of any single chemical, except where laws such as mass action or some special catalytic activity can be applied to favor one definite structure. Thus here the data are at first normally concerned with products extracted in small yields from resinous mixtures. However, once a new crystalline chemical has been isolated from such a resinous mass, then a proof of structure generally requires its synthesis. Some of these chemicals are indicated, as in Figures 7, 9, and 10.

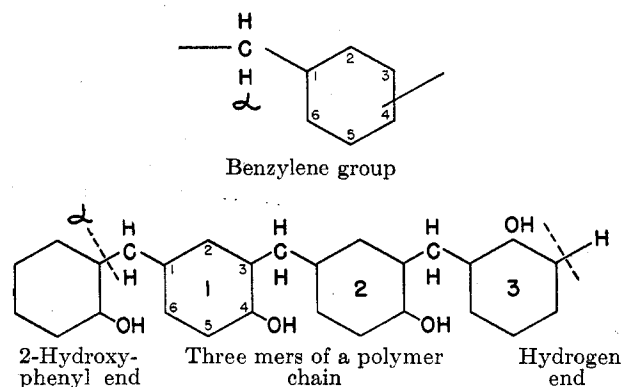


Figure 1. A Theoretical Resinous Chemical, α^1 -(2-Hydroxyphenyl)-3³-hydro-4¹, 4², 2³-trihydroxytribenzylene-1,3

A sharp melting product, when obtained from phenolic resins, may sometimes change either way from a crystalline form to a resinous (or glassy) form. A tentative theory that this behavior may result from rotational isomeric rearrangement is illustrated by Figure 2.

In general, the one phenyl- and the two phenyl-ring crystalline chemicals can each be produced in fair yields (3, 7) by some special direct production process from phenol and formaldehyde. The three-ring products are somewhat more difficult to produce as the main product, and methods to acquire over 50% yields often involve making first the purified one- and two-ring intermediates, then reacting these under conditions of controlled pH, selected catalysts, and temperature. Although seven isomers of three-ring form may be expected, three are still found only in the resinous form. It is expected that these three sharp melting resins will later be recorded in the crystalline forms as well as in the presently disclosed resinous mass forms.

Phenol has six reactive positions but the ordinary conditions used for reaction between phenol and formaldehyde give a reactivity to only three—that is, the two ortho and the

one para positions. The hydroxyl is reactive in many different tests yet here it is generally found unchanged at the end of a reaction sequence. If reaction does start with the hydroxyl to form ethers (2, 4) then the subsequent rearrangement of the connector to a position on the ring generally must be quite rapid. Such supposed rearrangement is often complete if an adjacent ortho position is open.

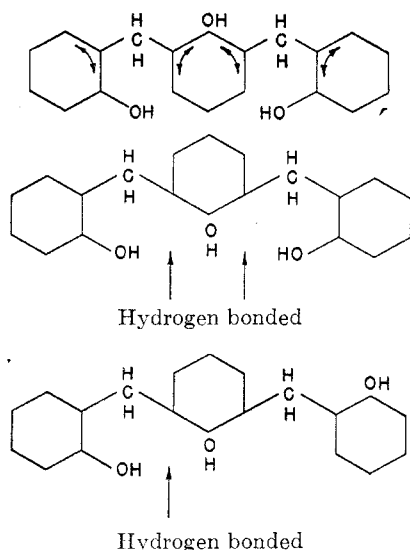


Figure 2. Rotational Isomeric Rearrangement

When carefully heated in the presence of alkaline catalysts, phenol reacts with formaldehyde to form crystalline one-ring addition products, the *o*- and *p*-monomethylol phenols, commonly called saligenin and *p*-hydroxybenzyl alcohol, respectively. A *m*-methylol phenol is known but since in the phenol-formaldehyde reaction series meta products do not easily form, this meta series is to be neglected here. With acid catalysts present such addition products are quickly changed by dehydration reaction to give resins.

Saligenin, the *o*-methylolphenol, is a crystalline, very reactive chemical, melting at 86° C. It will self-condense by dehydration (28). It is best handled slightly alkaline (6) but is not entirely stable either as a solid or as a melt. Traces of acids lower its stability to such a degree that at pH 4 the solid resinifies quite rapidly at room temperature. The solid crystals also change slowly to a resin when exposed to ordinary laboratory air. The *p*-hydroxybenzyl alcohol, melting at 126° C., is even more reactive and unstable than the ortho isomer. It often lowers 1° C. in melting point per each 10 seconds at 126° C.

Saligenin may be considered as a hydroxyphenyl-substituted methanol or as *o*-hydroxybenzyl alcohol. It is much more reactive than benzyl alcohol or methanol. The reactions of benzyl alcohol give at least some clue as to reactions which may be expected of the *o*- and *p*-hydroxybenzyl alcohols. A recent publication (23) lists a two phenyl-ring ether, a three phenyl-ring monoether, and a three phenyl-ring monomethylol product having two methylene connectors, as chain chemicals produced from benzyl alcohol. These are, of course, benzene- rather than phenol-based chains; yet when chilled they generally assume glasslike forms. Saligenin compared to benzyl alcohol is more self-reactive, making different classes of products under different conditions. The methylol group of saligenin reacts with itself to form ethers or reacts with the ring to form chained methylene products. It also reacts readily with other alcohols and with acids, aldehydes, and unsaturated compounds.

COVERAGE

This paper is concerned with the straight-chain reaction of such methylol groups with the ortho and para ring positions of phenol to form polyhydroxybenzylene chains (Figure 1), some of which can be purified and crystallized to definite single chemicals. Resinous chains so produced with excess phenols present are the novolacs of Baekeland's resinification process. The crystalline or the resinous chains, whether short or long, may react with excess formaldehyde to form the methylol (5, 10) (or reactive) products (14, 21). One of these multiple ring methylols has been described as a definite branched-chain chemical (25), but in general such products, when produced, have been the indefinite mixtures called A stage resinoids. Baekeland's B- and C-stage resinoids are resins still further reacted and more cross linked or branched.

Figure 3 indicates the structures of some self-condensation products resulting from the *o*- and *p*-hydroxybenzyl alcohols. The dibenzyl ether structures, the two-ring diphenylols, and some of the two-ring methylol products are now known (5). Figure 4 indicates some of the known polymethylol products (15).

Table I indicates the intermediates of special interest for production of the triphenylols listed in Table II.

TABLE I. INTERMEDIATES FOR TRIPHENYLOLS

	Melting Pt., ° C.	Notes
2-Hydroxybenzyl alcohol	86	Dehydrates to resin
4-Hydroxybenzyl alcohol	126	Dehydrates to resin
Di(2-hydroxybenzyl)oxide	124	Moderately stable
2,2'-Dihydroxydiphenylmethane	119	Stable to 250° C.
2,4'-Dihydroxydiphenylmethane	120	Stable to 250° C.
4,4'-Dihydroxydiphenylmethane	162	Stable to 250° C.
2,4-Dimethylol phenol	93	Dehydrates and resinifies
2,6-Dimethylol phenol	97	Dehydrates and resinifies
2,4,6-Trimethylol phenol	80	Dehydrates and resinifies
3,5,3',5'-Tetramethylol-4,4'-dihydroxydiphenylmethane	145	Very unstable, resinifies

TABLE II. TRIPHENYLOLS

2,4-Bis(2-hydroxybenzyl)phenol	Melts at 122° to 123° C.
2,4-Bis(4-hydroxybenzyl)phenol	Melts at 149° to 150° C.
2,6-Bis(2-hydroxybenzyl)phenol	Melts at 161° to 162° C.
2,6-Bis(4-hydroxybenzyl)phenol	Melts at 171° to 171.6° C.
2-(2-Hydroxybenzyl)-4-(4-hydroxybenzyl)phenol	Resinous
2-(4-Hydroxybenzyl)-4-(2-hydroxybenzyl)phenol	Resinous
2-(2-Hydroxybenzyl)-6-(4-hydroxybenzyl)phenol	Resinous

Of these chemicals, those that are stable and are obtained in yields high enough for volume production are saligenin, the 2,2'-dihydroxydiphenylmethane and its 2,4'- and 4,4'-isomers. The reactions of *o*- and *p*-hydroxybenzyl alcohols with phenol have given these two-ring chemicals in approximately 80% yield together with some resinous by-products. These three isomers shown in Figure 5 are crystalline products which act like novolac resins and are prone on rapid cooling from the melt to assume a glassy (18, 24) or resinous form of considerable stability. In the crystalline state these isomers occupy somewhat different volumes, as shown by their specific gravity, the one of lower gravity being more likely to assume the resinous physical form. The extreme effect of small traces of some impurities in preventing crystallization of these chemicals has apparently greatly delayed their discovery and publication. These two-ring crystalline chemicals add formaldehyde, then the resulting resins react with phenol to give still longer chains, at least some of which are crystalline.

The monomethylol (5) of any of these two-ring chemicals theoretically can be reacted with phenol to give a three-ring product. There are some complications—for instance, any monomethylol phenol, especially with open ortho and para positions, can react with itself to give a mixture of resins. However, from such resinous masses some three-ring crystalline products now have been

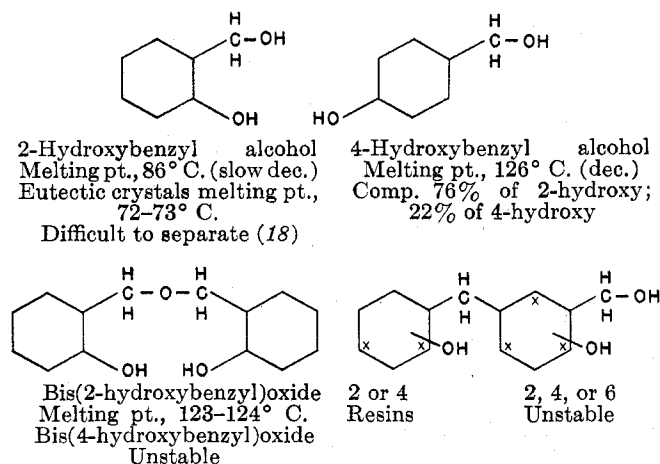


Figure 3. Structures of Self-Condensation Products Obtained from *o*- and *p*-Hydroxybenzyl Alcohols

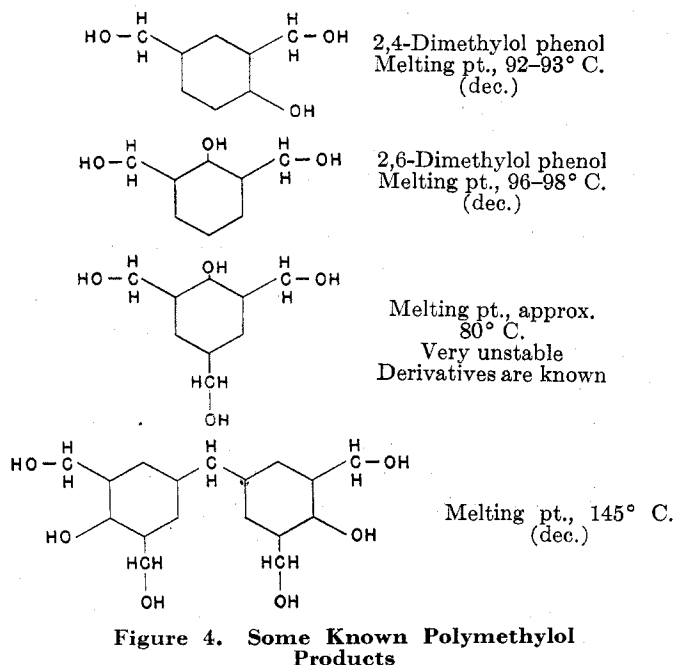


Figure 4. Some Known Polymethylol Products

isolated. In other cases, only resinous products have been obtained by extraction procedures from such reaction masses.

Figures 7, 9, and 10 show the structures for some new three-ring chemical products. The structure shown in Figure 7 is the only expected one with molecular weight 306 which might be formed from these starting materials.

Other data shows, as in Figure 8, that reactions which should give one single chemical do give resinous products. This resin, however, is a distillable product with molecular weight of 306 ± 5 under various conditions. It gives hydroxyl determinations $\pm 5\%$ of the expected value and has reasonable carbon and hydrogen values for the expected triphenylol product. Also, Figure 8 shows that two such resinous products which are produced are isomeric and test alike in general properties but differ in certain other properties, such as reactivity to bromine.

Four crystalline isomeric triphenylols were finally extracted from phenolic resins, synthesized in various ways, and cross checked by mixed melting point determinations as follows:

The structure of 2,6-bis(2-hydroxybenzyl)phenol and 2,4-bis(2-hydroxybenzyl)phenol are shown in Figure 9. The 2,4-

bis(4-hydroxybenzyl)phenol is shown as the only logical expectation in Figure 7. The synthesis of 2,4-bis(4-hydroxybenzyl)phenol, a three-ring crystalline product, is illustrated in Figure 7 by reaction of 4,4'-dihydroxydiphenylmethane with 4-hydroxybenzyl alcohol. Only one heat-stable and distillable product should be formed in the three-ring size region. In the same way in Figure 6 this 4,4'-dihydroxydiphenylmethane reacted with saligenin should give only one three-ring product. The reaction gave a resinous, fairly sharp-melting product with the molecular weight expected for a three-ring product. The arrows indicate where rotation would make an apparent difference in written structure. The properties of this resin fits into the reaction series with formaldehyde at the position expected for 2-(2-hydroxybenzyl)-4-(4-hydroxybenzyl)phenol.

The synthesis of 2,6-bis(4-hydroxybenzyl)phenol in a step-by-step process is shown in Figure 10.

The three structural two-ring diphenylol isomers of the phenol-formaldehyde reaction each have a usual reactivity to additional formaldehyde of four, or a gain of one over phenol itself. The seven structural isomers of the triphenylol series each have a usual reactivity to formaldehyde of five. Consideration of the phenolic hydroxyl activities, as used in making phenolic ethers, shows a progressive activity change from one for phenol, two for

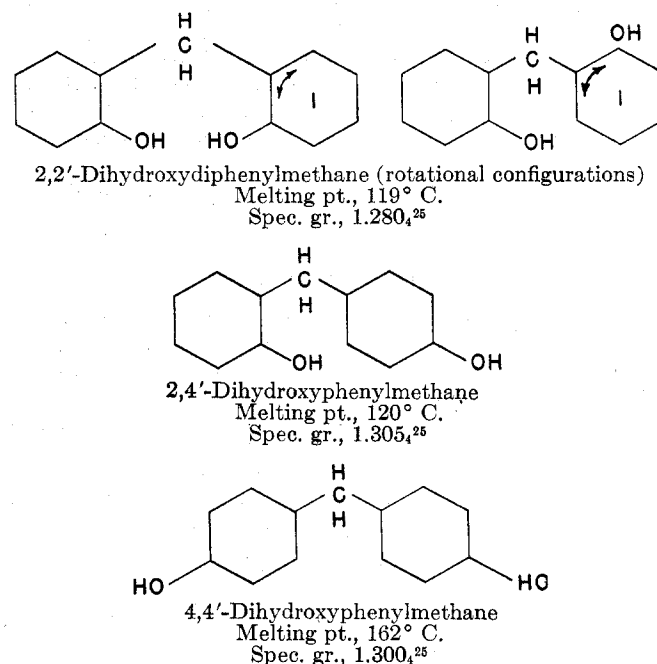


Figure 5. Crystalline Isomers Behaving Like Novolac Resins

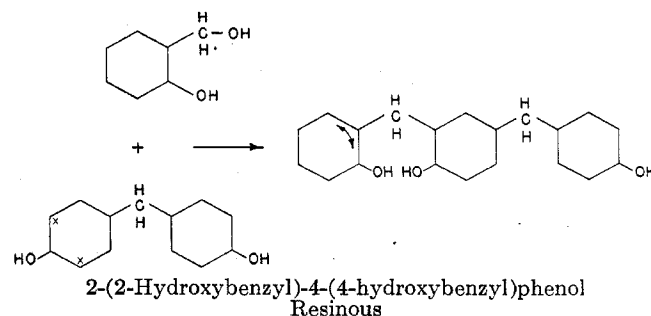


Figure 6. 4,4'-Dihydroxyphenylmethane Reacted with Saligenin

α = ortho, reactivities

diphenylols, and three for the triphenylols. Thus the triphenylols can be useful in making infusible and insoluble polyphenolic ethers with a doubly reactive agent like 1,2-dichlorethane, where the diphenylols produce fusible and soluble polyphenolic ethers (1).

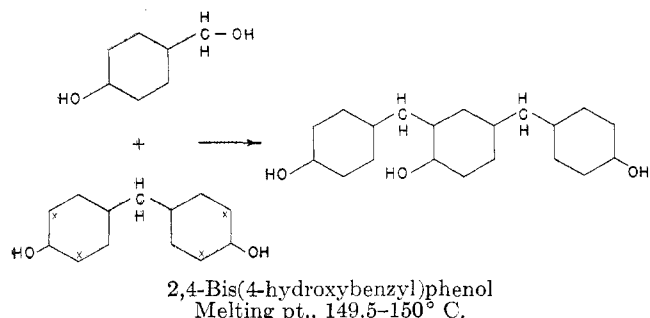


Figure 7. *p*-Methylolphenol Reacted with 4,4'-Dihydroxydiphenylmethane

x = all ortho reactivities

Some pertinent data have recently appeared (5, 8, 10). Finn, Lewis, and Megson (9) detail the production of a grade of 2,6-bis(2-hydroxybenzyl)phenol (melting point, 158° to 159° C.) from *p*-chlorophenyl dialcohol and *p*-chlorophenol dechlorinated by *n*-amyl alcohol and sodium to the triphenylol. In the present work, the melting point of the pure product was found to be 161° to 162° C.

Also Carpenter and Hunter (5, 12) have some mono-, di-, and trimethylol products having one and two phenyl rings.

NOMENCLATURE

Nomenclature as now used for the chained phenolic products is at present a handicap to publication in this field. In an attempt to improve this factor of nomenclature it is now proposed to give to this condensation polymer system a name based on the doubly reactive radical benzylene as shown in Figure 1. The phenol-formaldehyde resin intermediates generally are the more or less substituted 1,3-polybenzylenes but might also be found as the 1,2- or the 1,4-polybenzylenes. The phenolic intermediates have great activities induced by the ortho and para reactive effects of the hydroxyl on the phenyl rings; the total of active positions per molecule increases with molecular size until the reaction barriers of infusibility and insolubility are reached.

EXPERIMENTAL

2,6-BIS(2-HYDROXYBENZYL)PHENOL. From a phenol-formaldehyde reaction made in accordance with example 8 of U. S. Patent 2,464,207 (3) a few crystals were extracted with dilute acetic acid solvent. These melted at 160.8° to 161.8° C. They gave molecular weights in boiling acetone of 306 ± 5 and gave a crystalline triacetate melting point of 95.6° to 96.6° C. This was thought to be 2,6-bis(2-hydroxybenzyl)phenol.

One mole of 2-hydroxybenzyl alcohol, melting at 86° C. was reacted with 10 moles of 2,2'-dihydroxydiphenylmethane under reflux at 180° C. One mole of water was obtained. The excess diphenylol was largely removed by vacuum distillation and last traces were removed by crystallization from dilute acetic acid. The mother liquor was distilled free of water and acetic acid and then the residue was distilled under low pressure of less than 0.5 mm. The fraction distilling at 230° to 240° C. at 0.5 mm. when crystallized from toluene gave a 15% yield of crystals, which melted at 160.8° to 161.8° C. These were identical, by mixed melting point and acetate derivative methods, with the

crystals found in the high ortho structure resins. They reacted with 1 mole of phenol to give a 60% yield of 2 moles of pure 2,2'-dihydroxydiphenylmethane. Thus this crystal was the expected 2,6-bis(2-hydroxybenzyl)phenol.

2,6-BIS(4-HYDROXYBENZYL)PHENOL. A crystal melting at 171° C. was obtained from a phenol-formaldehyde resin using a magnesium oxide catalyst. This gave the properties expected for the 2,6-bis(4-hydroxybenzyl)phenol. The same product as determined by mixed melting point determinations was obtained as follows:

The 4-bromo-2,6-dimethylol phenol was prepared by reacting an aqueous solution of the sodium salt of *p*-bromophenol with an excess of formaldehyde. The dimethylol recovered by acidification of the reaction mixture had a melting point of 149° to 150° C. (with decomposition) as given in the literature (13, 27). This dimethylol was reacted with an excess of phenol with anhydrous hydrochloric acid. A product melting at 195° to 198° C. was obtained by crystallization. This bromine-containing product was reduced by Raney's alloy to give a triphenylol (melting point 170° to 171.6° C.). The molecular weight values in acetone were: low, 297; high, 308; and average, 300. The product on decomposition with phenol at elevated temperatures gave high yields of 4,4'-dihydroxydiphenylmethane, indicating that the end positions were para. The position of the hydroxyl on the central ring is defined by the starting material used (Figure 10).

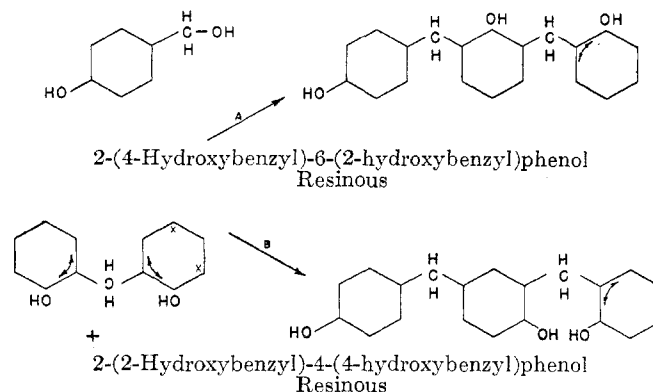


Figure 8. Resinous Triphenylols

x = ortho, para reactivities

2,4-BIS(2-HYDROXYBENZYL)PHENOL. A three-ring, trihydroxy crystalline product with a molecular weight of 306 ± 5 was found in a resin made from phenol and formaldehyde where oxalic acid was used for catalyst. This same product as shown by mixed melting point methods (melting point 121° to 123° C.) was made as follows:

The 2-chloro-4,6-dimethylol phenol melting at 124° to 124.8° C. was made by the method of Hanus (11) by reacting an aqueous solution of 1 mole of the sodium salt of *o*-chlorophenol with 4.1 moles of aqueous formaldehyde at 40° C. for 24 hours. The product recovered by acidification with dilute sulfuric acid was extracted with ether. The residue from the ether solution was recrystallized from methanol-benzene mixed solvent to yield 44% of the theoretical amount of the dimethylol (melting point 124.0° to 124.8° C.). These crystals gave a molecular weight of 192 and a formaldehyde equivalent of 31.9%, the theoretical values being 189 and 31.8%, respectively. One mole of the crystals was reacted with excess *p*-chlorophenol at 40° C. for 5 hours using a trace of hydrochloric acid. The excess phenol was removed by distillation and the crystalline residue was recrystallized from benzene to give a 70% yield of the triphenol 2-chloro-4,6-bis(5-chloro-2-hydroxybenzyl)phenol, melting at 185° to 187° C. The chlorine content found was 25.93%, theoretical 25.98%. A chlorine-free product was obtained from this when reduced by the method of Papa, Schwenk, and Whitman (17).

One tenth of a mole of 2-chloro-4,6-bis(5-chloro-2-hydroxybenzyl)phenol was dissolved in 125 ml. of 10% aqueous sodium hydroxide and was reduced by adding 124 grams of Raney's alloy

(30% nickel, 70% aluminum). The solution was acidified and filtered and the inorganic salts were extracted with acetone. The residue of the extract was crystallized from toluene to gain a 37% yield of chlorine-free product, melting at 121° to 123° C., having a molecular weight of 306, and having three hydroxyl groups per molecule. The method of production defines the final structure.

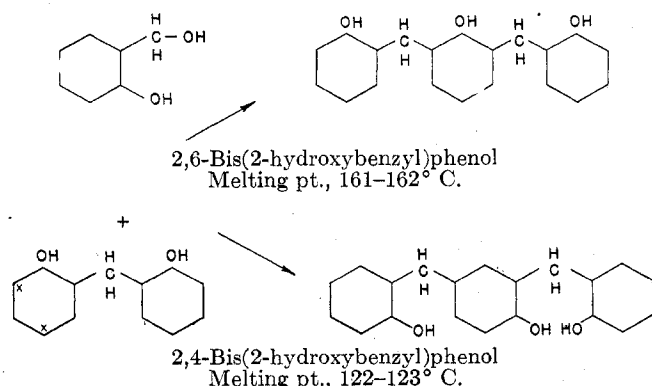


Figure 9. Crystalline Triphenylols

x = ortho, para reactivities

2,4-Bis(4-HYDROXYBENZYL)PHENOL. Crystals of a triphenylol which seemed to be this structure were first obtained from a resin made from phenol-formaldehyde and a hydrochloric acid catalyst.

The same crystalline material was obtained, as proved by mixed melting point tests, by reacting *p*-hydroxybenzyl alcohol with an excess of 4,4'-dihydroxydiphenylmethane in refluxing ethylene glycol. Removal of the solvent and excess 4,4'-dihydroxydiphenylmethane under vacuum gave a residue which crystallized. From it in toluene was obtained crystalline triphenylol melting at 149° to 150° C. The yield was 60% and the product analyzed: molecular weight found 300 ± 3, theoretical 306; and hydroxy content found 16.3%, theoretical 16.65%.

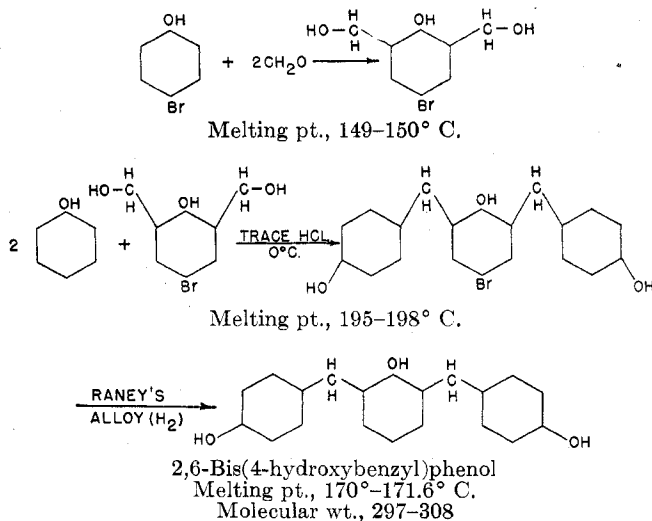


Figure 10. Stepwise Synthesis of 2,6-Bis(4-hydroxybenzyl)phenol

Since only one three-ring product can be expected from these starting materials the structure is assured by the high yield value.

The triacetate made by reacting the triphenylol with excess of acetic anhydride and pyridine has a melting point of 91.2° to 91.5° C.

RESINOUS ISOMERS. Three different resins with a molecular

weight of 306 ± 10 and a hydroxyl content of 16.2 to 16.8% were obtained. These were considered as 2-(2-hydroxybenzyl)-6-(4-hydroxybenzyl)phenol, 2-(2-hydroxybenzyl)-4-(4-hydroxybenzyl)phenol, and 2-(4-hydroxybenzyl)-4-(2-hydroxybenzyl)phenol. Data on these products will be delayed until they are located in the crystalline form. Methods for their production are indicated in Figures 6 and 8.

CONCLUSION

The ortho and para two-ring phenol-formaldehyde intermediates are reviewed. These, when phenol-ended, are often crystalline products. Three crystalline isomers are known which are considered here as crystallized novolacs, since they react chemically like the short-chain novolac resins.

Four new three-ring crystalline products are disclosed. Their reactions are similar to typical novolac resins and are here considered as crystallized novolacs. Attempted production of the other three-ring products still give resinous products some of which are sharp melting and apparently pure.

There are thus seven known products of molecular weight 306, blends of which are generally resinous and each of which differs in its reactivity to formaldehyde. By blending these structures the properties of commercial phenolic resins can be varied to cover a much wider range than has been previously known. Such changed properties would have to bear the cost of the purification and blending steps. Thus some new phenolic resins with new properties, produced at a higher price range, are now under market investigation.

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