[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MINNESOTA MINING AND MANUFACTURING CO.]

Self Catalysis by Certain Phenols in the Synthesis of Di- and Trinuclear Novolacs[1,2]

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Reaction between a halomethylphenol and another phenol has been investigated under various experimental conditions. In the absence of an added acid catalyst improved yields of the nuclearly alkylated phenol are obtained. Phenols which are deactivated by ring substituents—e.g. 2,6- and 2,4-dibromo—intramolecularly hydrogen bonded, or sterically hindered failed to react without the use of an external catalyst. A concerted nucleophilic displacement mechanism for *ortho* alkylation only is presented.

The use of halogen or alkyl blocked phenols as a research tool for studies concerning the formation and structure of phenolic resins is well established.[4-8] In a previous paper,[9] it was possible to show by means of such phenols that methylene bridge formation in the phenol-formaldehyde condensation occurs *via* a benzyl cation intermediate. Other workers in this field[10-12] have employed similar phenols to prepare linear and cyclic novolacs varying in chain length from a dimer to a decamer.

Customary experimental conditions for effecting reaction between a halogen substituted phenol and a similarly protected halomethyl or methylol phenol involve the use of a strong acid as a catalyst and heat. Low yields of condensation product are obtained generally because of oxidation of phenolic hydroxyl or isomerization of alkylated product.[13] Finn and co-workers[10] in their extensive use of this reaction reported intractable oils before crystallization of product occurred, and this required prolonged boiling with activated charcoal.

In the course of employing this reaction to synthesize some di- and trinuclear phenolic intermediates, it was found that 3,5-dibromo-2-hydroxylbenzyl bromide (I) reacted with 2,4-xylenol in the absence of an acid catalyst to yield 3,5-dibromo - 3′,5′ - dimethyl - 2,2′ - dihydroxydiphenylmethane. In light of previous work this was unexpected and was investigated further by extension to other blocked phenols, namely, 2,6-dibromophenol. In this case as well as with the 2,4-isomer under similar experimental conditions, condensation with I failed to occur. Additional experimental evidence for self-catalysis by specific phenols was obtained when reaction proceeded smoothly between *p*-chlorophenol and 2,6-bis(chloromethyl)-4-chlorophenol (III) at 100° in a nitrogen atmosphere. Yield of crude, 2,6-bis(2′-hydroxy-5′-chlorobenzyl)-4-chlorophenol was quantitative. In comparison when prepared from 2,6-bis(hydroxymethyl)-4-chlorophenol and *p*-chlorophenol with *p*-toluenesulfonic acid as catalyst a yield of only 15% was realized. Likewise, 2,6-dibromophenol with compound I and the same acid catalyst gave 3,3′,5,5′ - tetrabromo - 2,4′ - dihydroxydiphenylmethane only in low yield.

A similar study with 3,5-dibromo-4-hydroxybenzyl bromide (II) in its reaction with *p*-chlorophenol showed a behavior similar to that of the 2-hydroxy isomer (I). With no catalyst, 3,5-dibromo-4′-chloro-2′,4-dihydroxydiphenylmethane was obtained in 70% yield. An inseparable mixture of compounds was produced when the same reaction was performed in the presence of *p*-toluenesulfonic acid. This is in contrast to the work of Finn and Lewis,[14] who found II unreactive toward *p*-bromophenol with hydrochloric acid as a catalyst in a number of different solvents.

In contrast to those synthetic procedures which employ strong acids for alkylation of the phenolic nucleus with concomitant poor yields, it has been found that certain phenols (phenol, *p*-chlorophenol, and 2,4-dimethylphenol) can be alkylated without an added catalyst and in excellent yields. Evidence for this significant difference was found in the preparation of 2,6-bis(2′-hydroxy-5′-chlorobenzyl)-4-chlorophenol in 99.3% yield as compared to a yield of approximately 15% with *p*-toluenesulfonic acid as a catalyst.

The exclusive formation of a monosubstituted

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[4] A. Zinke, *J. Appl. Chem.*, **1**, 257 (1951).

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[6] E. Ziegler, *Monatsh. Chem.*, **78**, 334 (1947); **79**, 142 (1948).

[7] H. V. Euler, E. Adler, J. O. Cedwall, and O. Törngren, *Arkiv Kemi, Mineral. Geol.*, **15A**, No. 11, 1 (1941).

[8] K. Hultzch, *Kunstoffe*, **32**, 69 (1942); **37**, 205 (1947).

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[10] S. R. Finn, J. W. James, and C. J. S. Standen, *J. Appl. Chem.*, **4**, 497 (1954).

[11] R. F. Hunter and C. Turner, *J. Appl. Chem.*, **7**, 528 (1957).

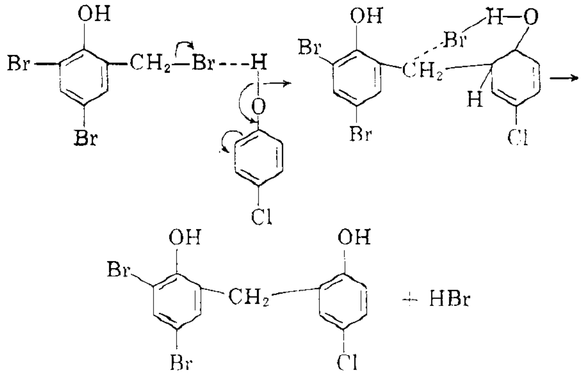
[12] B. T. Hayes and R. F. Hunter, *Chem. & Ind.* (*London*), 193 (1956).

[13] H. E. Hoyt, H. W. Keuchel, and R. B. Dean, *Paint Varnish Production*, **48**, No. 13, 33 (1958).

[14] S. R. Finn and G. J. Lewis, *J. Appl. Chem.*, **1**, 560 (1951).

product in the uncatalyzed alkylation of *p*-chlorophenol by hydroxyl substituted benzyl halides as compared to formation of both mono- and disubstitution products when an acid (*p*-toluenesulfonic) or silver perchlorate is employed necessitates a mechanism other than the accepted ionic mechanism of the Friedel-Crafts reaction. Aromatic alkylation catalyzed by acids is generally accepted as proceeding *via* a carbonium ion intermediate which tends toward di-, tri-, and polysubstitution.[9,15]

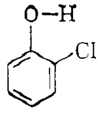
A possible mechanism for explaining why only monosubstitution of *p*-chlorophenol occurs is one in which the phenol and substituted benzyl halide react *via* a cyclic path in which the hydrogen atom of the phenolic hydroxyl group through hydrogen bond formation initiates reaction which then proceeds *via* a concerted process.



Obviously such a cyclic mechanism is possible only when alkylation *ortho* to the phenolic hydroxyl can occur. It furnishes additional evidence for a nucleophilic displacement mechanism in acidic aromatic alkylations.

This demonstration of enhanced reactivity of substituted benzyl halides by certain phenols has been observed with other halides. Swain[16] obtained a seven-fold acceleration in the reaction rate in the solvolysis of triphenylmethyl chloride in methanol with the addition of phenol. Also, in the synthesis of aminosubstituted acridines[17] and quinolines[18] from their corresponding chloro compounds, the increase in yields observed has been attributed to the catalytic effect of added phenol. Similarly, Hart, *et al.*[19-21] have interpreted the alkylation of phenol and *o*-cresol by triphenylmethyl chloride and by *tert*-butyl chloride as an autocatalytic reaction which is inhibited by such ethers as dioxane and tetrahydrofuran which preferentially bind the hydroxyl group.

Failure of 2,6-dibromo- and 2,4-dibromphenol to undergo reaction without an added catalyst may be explained on the basis that the hydroxyl group of these phenols is intramolecularly hydrogen bonded and rendered incapable for intermolecular association with halogen. Such an explanation receives support from the infrared spectra of chlorophenols,[22] in which *o*-chlorophenol exists in two spectroscopically distinguished forms 1 and 2.



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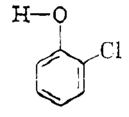

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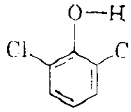
Because of the possibility of forming a hydrogen bond in the *cis* form 1 results in its predominance (estimated as 10 to 1) over the *trans* form 2. Examination reveals that in its *trans* form there is no hindrance to association with external halogen as compared to the *cis* form which requires rupture of the intramolecular hydrogen bond in order to form an intermolecular one. In 2,6-dichlorophenol the two configurations, 3 and 4, are equivalent, hence only the *cis* form exists.



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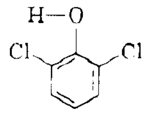

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Concerning this point it would be appropriate to mention the work of Bartlett and Dauben,[23] who, with a series of phenols, observed that the increase in acid strength of hydrogen chloride in an ethereal solution paralleled the acid strength of phenols investigated. Exceptions were those with *ortho* substituents capable of intramolecular hydrogen bonding—*e.g.* *o*-chlorophenol and *s*-trichlorophenol—which were less efficient than would be expected from their acid strength.

A further factor in the reluctance of 2,6- and 2,4-dihalophenols to undergo alkylation is the ring deactivating effect of halogen atoms toward electrophilic attack. In a previous paper[9] it was shown that a hydroxybenzyl cation reacted with toluene in preference to 2,6-dibromophenol.

EXPERIMENTAL

The phenols used were high grade commercial products and where necessary were redistilled or recrystallized.

3,5-Dibromo-2-hydroxybenzyl bromide (I) was prepared and purified as described previously,[9] m.p. 118.5–119°.

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(15) H. C. Haas, D. I. Livingston, and M. Saunders, *J. Polymer Sci.*, **15**, 503 (1955).

(16) C. G. Swain, *J. Am. Chem. Soc.*, **70**, 1119 (1948).

(17) O. J. Magidson and A. M. Grigorowski, *Ber.*, **66**, 866 (1933); **69**, 346 (1936).

(18) A. R. Surrey and R. A. Cutler, *J. Am. Chem. Soc.*, **73**, 2623 (1951).

(19) H. Hart and J. H. Simons, *J. Am. Chem. Soc.*, **71**, 345 (1954).

(20) H. Hart and F. A. Cassis, *J. Am. Chem. Soc.*, **76**, 1634 (1954).

(21) H. Hart, F. A. Cassis, and J. J. Bordeaux, *J. Am. Chem. Soc.*, **76**, 1639 (1954).

(22) L. Pauling, *J. Am. Chem. Soc.*, **58**, 94 (1936).

(23) P. D. Bartlett and Hyp. J. Dauben, Jr., *J. Am. Chem. Soc.*, **62**, 1339 (1940).

3,5-Dibromo-4-hydroxybenzyl bromide (II) was prepared according to a procedure described by Finn and Lewis.[14] Recrystallization from benzene gave a white crystalline product, m.p. 148–149°.

2,6-Bis(chloromethyl)-4-chlorophenol (III) was obtained by reaction of 2,6-bis(hydroxymethyl)-4-chlorophenol and concentrated hydrochloric acid at room temperature. A product melting at 91.0–91.6° was obtained from *n*-hexane.

2,6-Bis(hydroxymethyl)-4-chlorophenol (IV) was prepared by reaction of *p*-chlorophenol, formalin, and sodium hydroxide for 2 days at room temperature. Recrystallization from hot water gave a product melting at 164° dec.[24]

Reactions of 3,5-dibromo-2-hydroxybenzyl bromide (I). *2,6-Dibromophenol.* A mixture of 48 g. (0.14 mole) of I and 35.9 g. (0.14 mole) of 2,6-dibromophenol was heated at 140° for 12 hr. in an atmosphere of nitrogen. Recrystallization of the crude product from benzene with activated charcoal gave a crystalline substance, m.p. 116.5–117.5°. An admixture of this material with I showed no depression of melting point. Additional unchanged starting material was obtained from the mother liquor.

2,6-Dibromophenol with p-toluenesulfonic acid. The same procedure as described above was used except for the addition of 0.5 g. of *p*-toluenesulfonic acid. Recrystallization of crude product from benzene with activated charcoal followed by a second recrystallization from glacial acetic acid gave 21.8 g. (21%) of a product melting at 168–185°. The 3,3′,5,5′-tetrabromo-2,4′-dihydroxydiphenylmethane, m.p. 194–195°, was obtained after a third recrystallization from glacial acetic acid. Concentration of acetic acid mother liquor yielded 7.4 g. of the unchanged benzyl bromide. Evaporation of benzene mother liquor and extraction of residue with petroleum ether (b.p. 40–60°) yielded 25 g. of original 2,6-dibromophenol. An additional 5.2 g. of the starting benzyl bromide was isolated from the residue of the petroleum ether extract after further extraction with hot ligroin (b.p. 60–80°).

2,4-Xylenol. A yield of 7.6 g., (40%) of 3,5-dibromo-3′,5′-dimethyl-2,2′-dihydroxydiphenylmethane was obtained by reaction of 17.3 g. (0.05 mole) of I and 6.7 g. (0.055 mole) of 2,4-xylenol at 140° for 5 hr. in an atmosphere of nitrogen. A white crystalline material, m.p. 178.6–179.6°, was obtained from dilute alcohol.

Anal. Calcd. for $C_{15}H_{14}O_2Br_2$: Br, 41.40. Found: Br, 41.23.

2,6-Xylenol. Reaction of 13.7 g. (0.04 mole) of I and 48.5 g. (0.4 mole) of 2,6-xylenol at 100° for 4 hr. under nitrogen gave the crude 3,5-dibromo-3′,5′-dimethyl-2,4′-dihydroxydiphenylmethane after removal of excess xylenol by distillation under reduced pressure. Recrystallization from benzene yielded 11.3 g., 73.4%, of a slightly colored crystalline solid, m.p. 164.0–164.8°.

Anal. Calcd. for $C_{15}H_{14}O_2Br_2$: Br, 41.40. Found: Br, 41.27.

Phenol. A yield of 20.7 g. (98%) of a mixture of 3,5-dibromo-2,2′-dihydroxydiphenylmethane and the corresponding 2,4′-dihydroxy isomer was realized when I and phenol reacted as described for 2,6-xylenol. This mixture was dehalogenated with nickel-aluminum alloy[10] and analyzed by infrared spectroscopy[25] using a Perkin Elmer Model 21 spectrophotometer with a lithium fluoride prism. For analysis, a cell of 1.00 cm. thickness and 0.001 molar solutions of the pure isomers in dry carbon tetrachloride were used. By utilizing high resolution spectra of the fundamental hydroxyl stretching vibration bands a quantitative estimation of the percentage of the two isomers was made. The amount of 2,2′-isomer was estimated from relative band intensities of the hydrogen-bonded band at 3460 cm.^{1} After computation it was found that approximately 39–43% of the mixture was 2,2′-isomer. Using a similar calculation with the 3606 cm.$^{-1}$ band showed that 65% of the mixture was 2,4′-isomer. A synthetic mixture of 40% of 2,2′ and 60% of 2,4′-isomers was prepared and its solution (10.0 mg./50 cc. carbon tetrachloride) compared. It was found to be identical with that of the reaction mixture, (see Fig. 1).

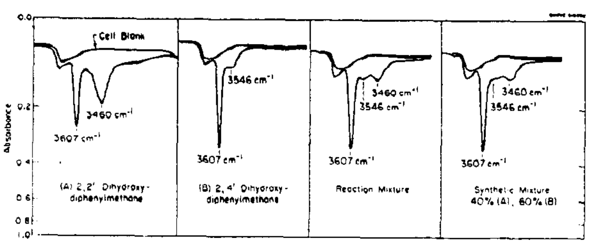

Fig. 1. Infrared spectra of the hydroxyl absorption band

p-Chlorophenol. Reaction of 0.058 mole of I and 0.58 mole of *p*-chlorophenol as described above produced a slightly colored crystalline residue after removal of excess *p*-chlorophenol by vacuum distillation. Yield of 3,5-dibromo-5′-chloro-2,2′-dihydroxydiphenylmethane, m.p. 192–193°, was 90%.

2,4-Dibromophenol. After heating 0.074 mole of I and 0.37 mole of 2,4-dibromophenol for 12 hr. at 130° in an atmosphere of nitrogen, only starting materials were isolated.

Reactions of 3,5-dibromo-4-hydroxybenzyl bromide (II). *p-Chlorophenol.* Reaction of 0.058 mole of II and 0.58 mole *p*-chlorophenol employing the same conditions as above gave 15.8 g. (68.7%) of 5-chloro-3′-5′-dibromo-2,4′-dihydroxydiphenylmethane, m.p. 127.2–128.0°, after recrystallization from benzene. Finn *et al.*[10] give a melting point of 127.5°.

p-Bromophenol with p-toluenesulfonic acid. Compound II (0.05 mole), 0.25 mole of *p*-bromophenol, and 0.3 g. of *p*-toluenesulfonic acid were heated at 110° for 2 hr. A continuous evolution of hydrogen bromide took place during this period. After excess *p*-bromophenol was distilled under reduced pressure, the reddish brown colored residue was dissolved in hot benzene and incremental additions of petroleum ether (b.p. 40–60°) were made to the solution until a gummy material was no longer precipitated. Further additions to the benzene filtrate yielded a white crystalline solid, m.p. 112–129°. Attempts to purify this material further resulted in a substance melting at 122–126°, yield 5.4 g. Recrystallization from carbon tetrachloride elevated the melting point to 146–149°. A mixed melting point with starting benzyl bromide produced a depression.

Employing 3,5-dibromo-4-hydroxybenzyl alcohol instead of the bromide gave similar results.

2,6-Bis(2′-hydroxy-5′-chlorobenzyl)-4-chlorophenol. A. *From 2,6-bis(chloromethyl)-4-chlorophenol* (III). A mixture of 23.2 g. (0.11 mole) of III and 257.2 g. (2.0 mole) of *p*-chlorophenol was heated in an oil bath at 100° for 6 hr. while dry nitrogen was passed into the flask. A copious evolution of hydrogen chloride set in quickly and after 1 hr. a solid began to precipitate from the reaction mixture. After standing overnight excess *p*-chlorophenol was steam distilled and the crystalline residue, light pink in color, was filtered by suction and air dried. A yield of 41.9 g. (99.3%) of a tan colored solid was obtained, m.p. 230.5–232.5.° Recrystallization from glacial acetic acid gave a white crystalline solid, m.p. 230–231°.

B. *From 2,6-bis(hydroxymethyl)-4-chlorophenol* (IV) *with p-toluenesulfonic acid.* A residue dark in color was isolated after reaction at 130° for 7 hr. Recrystallizations from benzene and an alcohol-water mixture produced a small amount of 2,6-bis(2′-hydroxy-5′-chlorobenzyl)-4-chlorophenol, m.p. 230-231°. An admixture of this compound with crystalline solid obtained from reaction of 2,6-bis(chloromethyl)-4-

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(24) R. W. Martin, *Chemistry of Phenolic Resins*, Wiley, New York, 1956, p. 35.

(25) For this phase of the work the author is indebted to Dr. Harold Lady, formerly of the Technology Department, Westinghouse Research Laboratories, Pittsburgh 35, Pa.

chlorophenol and *p*-chlorophenol showed no depression in melting point. Efforts to isolate additional trinuclear material from the benzene mother liquor by additions of petroleum ether (b.p. 40–60°) yielded gummy, uncrystallizabl. materials.

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The Autoxidation of Liquid Allylic Chlorides

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The autoxidation of allyl chloride, methallyl chloride, 1,4-dichlorobutene-2, and 3,4-dichlorobutene-1 forms chloro hydrins by attack at the double bonds. Analysis of the initial products from methallyl chloride indicates an epoxide precursor is involved. Oxidation rates for the dichlorobutenes were studied and show an unusual dependency on added anions.

Little is known about the autoxidation of liquid allylic halides.[1] This paper reports the oxidation of methallyl chloride, allyl chloride, 1,4-dichlorobutene-2 and 3,4-dichlorobutene-1 and describes the major products formed.

While a complex mixture of compounds was produced in each case, a single α-chlorocarbonyl compound and a chlorohydrin constituted a major portion of the products as shown in Table I. It was apparent from the nature of the compounds found that products arise not only from the decomposition of hydroperoxides, the primary intermediates usually postulated, but also from the addition of hydrogen chloride and carboxylic acids to a reactive epoxide. This epoxide could be identified and isolated in the oxidation of methallyl chloride and in fact constituted a major component in the very early stages of the reaction.

TABLE I

OXIDATION PRODUCTS OF ALLYLIC CHLORIDES

Compound, % Reacted	Product	% of Products[a]
Methallyl chloride	Chloroacetone	28
27% reacted	1,3-dichloro-2-methyl-propanol-2	19
Allyl chloride	Chloroacetaldehyde	22
25% reacted	1,3-dichloropropanol-2	19
1,4-Dichlorobutene-2	1,3,4-trichlorobutanol-2	
3,4-Dichlorobutene-1		

[a] Analysis by gas chromatography.

The initial reaction of methallyl chloride with oxygen produces unexpectedly few products as shown by gas chromatographic analysis. Figure 1 shows that chloroacetaldehyde and 1,2-epoxy-3-chloro-2-methylpropane constituted nearly all the products when less than 1% of the allylic chloride had reacted. Only one other product, which must be considered minor, could be detected while products more volatile than methallyl chloride may have been obscured by impurities originally present. As the oxidation progressed, 1,3-dichloro-2-methylpropanol-2 appeared and formed in significant amount until it was present in the second largest concentration. The production of epoxide, however, became slower with time. Measurement of the oxygen consumed showed that for every mole of oxygen 1.5 moles of allylic chloride reacted.

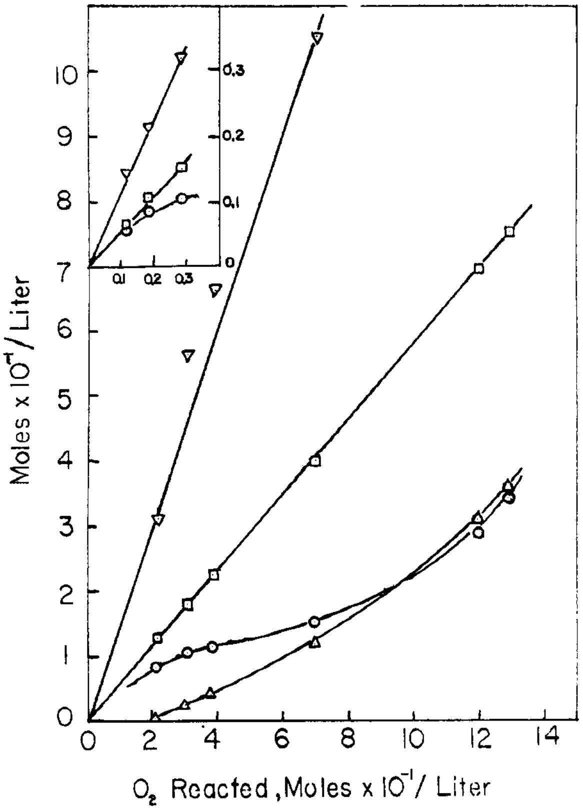

Fig. 1. The oxidation of methallyl chloride with insert showing products at less than 1% reacted

△ 1,3-dichloro-2-methylpropanol-2
○ 1,2-epoxy-2-methylpropane
□ chloroacetone
△ methallyl chloride reacted

As this was true even at the very advanced stages of the oxidation, where as many as seventeen prod-

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[1] D. J. Loder and A. McAlevey, U. S. Pat. 2,316,604 (1943) describing the production of glycerol from allyl chloride appears to be the only reference to this reaction.