pound has been prepared previously by the ammonolysis of 2,2-diethylmalonyl chloride[9] or diethyl 2,2-diethylmalonate.[10]

2-Isoamylmalonamide was prepared in 89% yield by Method I using isoamyl iodide as the alkylating agent; m.p. 219.5–220.5°, after recrystallization from dilute alcohol.

Anal. Calcd. for $C_8H_{16}N_2O_2$: C, 55.81; H, 9.30; N, 16.28. Found: C, 55.76; H, 9.23; N, 16.35.

Hoffman[11] reported a melting point of 210° for this compound which he prepared by the ammonolysis of the corresponding diethyl ester in a closed tube.

2-Allylmalonamide (Method II). A 65% yield was obtained from malonamide and allyl bromide using sodium hydroxide as the condensing agent. After recrystallization from alcohol the product melted at 167°.

Anal. Calcd. for $C_6H_{10}N_2O_2$: N, 19.72. Found: N, 20.15.

2,2-Diallylmalonamide. This compound was synthesized in 66% yield from allylmalonamide and allyl bromide (Method I). The crude product melted at 194–199°. Using Method II, with potassium amide as the condensing agent, the yield was increased to 90% and the melting point raised to 201–202°.

The introduction of both allyl groups in a single step was achieved in 81% yield (Method II) by starting with malonamide and using two molar equivalent each of allyl bromide and sodium hydroxide; m.p. 198–200.5° (crude product). Meyer[12] prepared this compound by the ammonolysis of the corresponding dimethyl ester.

2-Ethyl-2-isoamylmalonamide (*Method I*) was prepared in 55% yield from ethylmalonamide and isoamyl iodide using sodium hydroxide as the condensing agent. The yield increased to 75% when potassium amide (prepared in the reaction vessel indicated in Fig. 2)[13] was used. The product, after recrystallization from dilute alcohol, melted at 191–192.5°.

Anal. Calcd. for $C_{10}H_{20}N_2O_2$: C, 60.00; H, 10.00; N, 14.00. Found: C, 59.82; H, 10.09; N, 13.77.

Synthesis of barbituric acid derivatives. In general the best results were obtained when the reactants were used in the approximate ratio of one mole of the appropriate malonamide to 1.3 moles of ethyl carbonate and 2 moles of an alkali hydroxide[14] or alkali amide. The following two examples represent typical procedures.

Barbituric acid. In a glass pressure vessel were placed 1.28 g. (0.0125 mole) of malonamide, 2. g. (0.017 mole) of ethyl carbonate, 1.1 g. (0.025 mole) of sodium hydroxide and 10–25 ml. of liquid ammonia. The mixture was then shaken at room temperature. In a moment most of the sodium hydroxide had disappeared and a brown precipitate (sodium barbiturate) began to separate. After 3 hr. the ammonia was evaporated off and the product, along with the easily soluble unreacted malonamide, was extracted with water. Neutralization of the extract with 50% sulfuric acid gave fine crystals of barbituric acid; yield 0.9 g. (56%), m.p. 243–244° (crude product).

5,5-Diallylbarbituric acid. A mixture of 1.82 g. (0.01 mole) of 2,2-diallylmalonamide, 1.5 g. (0.0127 mole) of ethyl carbonate, 0.9 g. (0.02 mole) of sodium hydroxide and 25 cc. of liquid ammonia was placed in a glass pressure vessel. After shaking for about 0.5 hr. at room temperature the reaction was substantially complete. The reaction was allowed to shake for a total of 3 hr. and then the ammonia removed. The sodium salt of the reaction product was extracted with water. Since the unreacted 2,2-diallylmalonamide was practically water insoluble it could be quantitatively recovered. Neutralization of the aqueous extract with concentrated hydrochloric acid precipitated the fine crystals of 5,5-diallylbarbituric acid; yield, 1.7 g. (82% based on starting amide). After recrystallization from water it melted at 171°.

YOKOSUKA, JAPAN

---

[9] K. Böttcher, *Ber.*, **39**, 1596 (1906).

[10] B. Russell, *J. Am. Chem. Soc.*, **72**, 1853 (1950).

[11] P. Hoffman, *Ber.*, **23**, 1498 (1890).

[12] H. Meyer, *Monatsh.*, **27**, 1091 (1906).

[13] Potassium amide was readily prepared in the reaction vessel pictured in Fig. 2 and filtered directly into the reaction mixture through the fitted glass filter. However, sodium amide, being insoluble in ammonia, could not be prepared in the same fashion so was used directly as a suspension.

[14] The particle size of the commercial granulated product was reduced in a mortar before use.

[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES]

Methylene Bridge Formation *via* Carbonium Ions in the Phenol-Formaldehyde Reaction

JACOB S. RODIA AND JAMES H. FREEMAN

Received August 20, 1958

Polyphenylmethylene structures are accepted as the principal component of polymers derived from the reaction of phenol and formaldehyde. The reaction between methylolphenol or halomethylphenol compounds and phenols to yield dihydroxydiphenylmethanes is interpreted in terms of a common, hydroxy substituted, benzyl cation intermediate. Experimental evidence in support of this intermediate is presented for the first time. In terms of this mechanism dibenzyl ether formation is viewed as a competing reaction which may predominate under special conditions. A case of preferential reaction between a hydroxybenzyl cation and an aromatic hydrocarbon is presented in which a phenol, although present, failed to react.

Reaction between phenol and formaldehyde to give resins is now well recognized to proceed stepwise.[1–5] There is first an addition of formaldehyde to phenol to give methylolphenols and second, a condensation of methylolphenol compounds with other phenols to form polymers joined predomi-

---

[1] R. W. Martin, *Chemistry of Phenolic Resins*, J. Wiley and Sons, New York (1956).

[2] K. Hultzsch, *Chemie der Phenolharze*, Springer Verlag, Berlin (1950).

[3] J. F. Walker, *Formaldehyde*, 2nd ed., Chap. 12, Reinhold Corp., New York (1953).

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

[5] M. Imoto, *J. Inst. Polytechn., Osaka*, **2**, (2) Series C (1952).

nately by methylene bridges and termed hydroxyphenylmethanes.

The reaction of suitable ring substituted methylolphenol derivatives with other substituted phenols is an important tool for the synthesis of representative intermediate compounds of unequivocal structure.[6-10] Such blocked phenols also were employed by many prior investigators[4, 11-15] for the purpose of permitting isolation of intermediate substances by reducing the number of possible isomers. Although at times criticized[16,17] as not necessarily representative of what happens when such trireactive compounds as phenol itself or *m*-cresol are used, experiments of this type did provide knowledge of what reactions might occur under given conditions. What actually happens with the commercially important phenols will be, of course, the result of the relative attractiveness (as determined by concentration and reaction rates) of the several alternate paths available under the environmental conditions at any given stage of polymerization.

Since the reaction is much used and of considerable importance from both a theoretical and practical standpoint, possible mechanisms by which it may proceed have been suggested by several workers. For example, Hultzsch[18] postulated formation of a quinone methide intermediate (formed by internal loss of water from a methylolphenol) which then, in an ionic form, attacked another phenol nucleus at positions of highest electron density to establish the methylene bridge.

Ziegler,[11-13] envisioned conversion of methylolphenols to halomethylphenols when halogen acids were used as catalysts. He and his coworkers advanced the successful reaction between a halomethylphenol and a phenol giving a diphenylmethane as experimental support for this theory. However, the fact that he was able to convert a methylolphenol to a chloromethylphenol in the presence of excess strong hydrochloric acid, and that chloromethylphenols can react with phenols to form diphenylolmethanes are not, *per se*, conclusive proof that the halomethylphenol is an actual intermediate in the conversion of methylolphenol to diphenylmethane. It is more difficult to envision the mixed ester as intermediate in cases where other acids such as sulfuric, *p*-toluenesulfonic, perchloric, etc. are used as catalysts, particularly in dilute form, yet these are known to promote the reaction in question.

It would also follow that a presynthesized halomethylphenol should therefore condense with a phenol in absence of a catalyst. Our attempts to employ this principle in the preparation of 3,3′,5,5′-tetrabromo-2,4′-dihydroxydiphenylmethane by reaction between 3,5-dibromo-2-hydroxybenzyl bromide and 2,6-dibromophenol resulted in a complete failure to react in the absence of catalyst. Similar difficulties in carrying out the reaction when a halogen substituted (therefore less reactive) addend is used had also been reported by Finn and Lewis.[9] On the other hand Yamazaki[19] has reported successful formation of the diphenylmethane from a melt of 2,6-dichloro-4-hydroxymethylphenol and *p*-bromophenol using a trace of perchloric acid as catalyst. In our experiment the reaction also proceeded smoothly to methylene bridged compound when only a trace of catalyst (H^+ion) was added.

Pepper[20] and Lilley[16] independently have proposed a mechanism for diphenylmethane formation from phenol alcohols which involves a benzyl cation as the active intermediate. Lilley further expanded this view to explain benzyl ether formation but neither of these authors was able to furnish substantial experimental data to support it. Imoto[5] also regards the reaction intermediate to be the benzyl cation on the basis of his consideration of relative kinetic rates and activation energies for the methylol addition and condensation steps respectively. Likewise Dewar[21] in his textbook *The Electronic Theory of Organic Chemistry* depicts an interesting mechanistic analogy between the phenol-formaldehyde condensation and a Friedel-Crafts reaction. Unfortunately references and experimental data are again lacking.

The authors reasoned that if methylene bridges in phenolic resins occur *via* a benzyl cation then reagents and conditions known to produce such ions[22] (*i.e.*, reaction of silver salts with alkyl halides) should be capable of catalyzing a reaction between a halomethylphenol and another phenol. This was found to be the case as evidenced by successful reaction between 3,5-dibromo-2-hydroxybenzyl bromide and 2,6-dichlorophenol, employing a molecular equivalent of silver perchlorate as promoter and nitromethane as solvent. When less than one

---

(6) A. C. Davis, B. T. Hayes, and R. F. Hunter, *J. Appl. Chem.*, **7**, 521 (1957).

(7) S. R. Finn, J. W. James, and C. J. S. Standen, *J. Appl. Chem.*, **4**, 296 (1954).

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

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

(10) W. J. Burke, W. E. Craven, A. Rosenthal, S. H. Ruetman, C. W. Stephens, and C. Weatherbee, *J. Polymer Sci.*, **20**, 75 (1956).

(11) E. Ziegler, *Ost. Chem. Ztg.*, **49**, 92 (1948).

(12) E. Ziegler, *Monatsh.*, **78**, 334 (1947).

(13) E. Ziegler, *Monatsh.*, **79**, 142 (1948).

(14) H. v. Euler, E. Adler, J. O. Cedwall, and O. Törngren, *Arkiv. Kemi. Min. Geol.*, **15A** (11) (1941).

(15) K. Hultzsch, *Kunst.*, **32**, 69 (1942); **37**, 205 (1947).

(16) H. S. Lilley, *J. Soc. Chem. Ind.*, **67**, 196 (1948).

(17) E. G. K. Pritchett, *Chem. and Ind.* (*London*), 295 (1949).

(18) K. Hultzsch, *Angew. Chem.*, **61**, 93 (1949).

(19) T. Yamazaki, *J. Ind. Chem., Japan*, **58**, (12) 972 (1955).

(20) D. C. Pepper, *Chem. and Ind.* (*London*), 866 (1941).

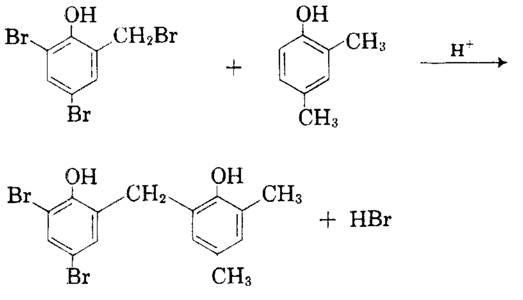
(21) M. J. S. Dewar, *Electronic Theory of Organic Chemistry*, Oxford University Press, London, 180 (1949).

(22) E. R. Alexander, *Ionic Organic Reactions*, Chap. 3 J. Wiley & Sons, New York (1950).

equivalent of silver perchlorate was used, the reaction stopped short of completion. The silver halide formed precipitated from the solution and further generation of the carbonium ion was prevented. We also repeated the experiment of Finn and Lewis[9] and confirmed the inability of 3,5-dibromo-4-hydroxybenzyl bromide to condense with *p*-bromophenol even with use of an acid catalyst. However, we were able to bring about a successful reaction between these reagents in nitromethane solution using silver perchlorate (one equivalent) as catalyst.

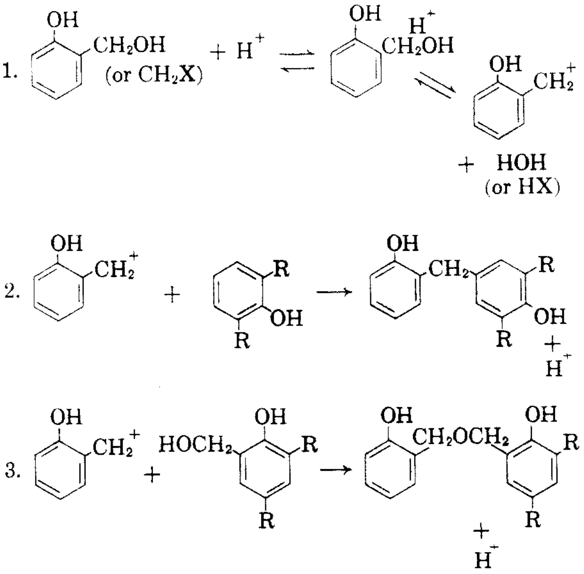
Additional support for the carbonium ion theory was obtained by an experiment in which toluene was substituted for nitromethane as solvent. In this case the main product of the reaction was found to be a methyl, monohydroxydiphenylmethane produced by reaction between the benzyl halide and toluene. The phenyl nucleus in toluene is sufficiently activated by the presence of the methyl group to permit it to act as the addend for the benzyl cation and its relatively high concentration completely swamped the reaction potential of the normally reactive ring position in the phenol. The latter in this case is handicapped further by the ring deactivating inductive effect of the 2 6-halogen atoms.

In cases where the addend is of enhanced reactivity *i.e.* contains ring positions of relatively increased electron density, due to the presence of substituent groups as the methyl group, instead of deactivated as by halogen, the relative yield of diphenylolmethane is increased and the reaction conditions are correspondingly less severe. Thus, 3,5-dibromo-2-hydroxybenzyl bromide combines readily with 2,4-dimethylphenol, though only indifferently with 2,6-dihalophenols.



It would also be expected that the relative ease of formation of the benzyl cation would have a bearing on the success of the reaction. In this respect it appears qualitatively easier to form such a carbonium ion from the hydroxymethyl group by protonation and release of HOH than it is to eliminate the corresponding HX moity from the halomethyl compound. This result is consistent with the relative hydrogen bond forming power of halogen and hydroxy groups.[23]

The benzyl cation which we postulate as common intermediate in the reaction of methylolphenols or halomethylphenols can be considered to arise readily from the reversible solvation of a proton by the benzylic hydroxyl group. The phenolic hydroxyl group as well as the solvent (water in most cases) will, of course, compete reversibly for protons, but the benzyl alcohol group is capable of a further reaction—loss of a stable small molecule (H_2O or HX) and formation of the benzyl cation. (Equation 1.) The reaction may then be propagated in several fashions by reacting with any substance HA which will regenerate the proton.



The presence of carbonium ion in neutral or acidic medium is thus capable of accounting for the conversion of methylolphenol to dibenzyl ether (Equation 3.) as well as to diphenylmethane (Equation 2.). The available protons will be distributed randomly through the system among water molecules, methylol and phenolic hydroxyl groups. Not all the methylol groups will be protonated—hence able to form carbonium ion, simultaneously. Methylol groups which are not in the carbonium ion state will act as electron centers and compete with unsubstituted ring positions as loci for the attachment of the carbonium ion. Elimination of a proton allows the reaction to continue and leaves as product the dibenzyl ether (Equation 3.).

It is to be expected that the free methylol groups will compete best when their number is great in proportion to the number which have been sacrificed to produce benzyl carbonium ions. Thus, ethers should form most readily in nearly neutral solutions and, in fact, this is where most evidence for ether formation has been adduced. In particular cases, competition of free ring positions is eliminated by special circumstances. If active positions are blocked by non-reactive substituents, or if complete methylolation has occurred, as in trimethylol-

---

[23] L. Pauling, *Nature of the Chemical Bond,* 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 287.

phenol,[24] the methylol is the only available target for the carbonium ion and ethers can be expected under very mild conditions. This is aptly demonstrated by our isolation of a 44% yield of dibenzyl ether by trituration of a blocked methylol phenol with dilute hydrochloric acid at room temperature. The ready reaction between highly methylolated phenols and alcohols or glycols[25,26] to give alkylbenzyl ethers is also in accord with this mechanism. Similar cases of ether formation when the electron density at ring positions is reduced, relative to the methylol hydroxyl groups, by presence of chloro or nitro groups have been reported.[27] When it is considered that none of his compounds contained any free *ortho-* or *para*-ring positions capable of reacting with a methylol group to form a methylene bridged compound, the extensive work of Ziegler[11–13,28] is explainable as well on the basis of the carbonium ion theory as it is on the premise of the halomethyl intermediate. His findings can likewise be used to support our conclusions. With high concentrations of both chloride and carbonium ion, isolation of the halomethyl phenol is to be expected. In our view it is regarded as a by-product rather than an intermediate of the reaction.

Since the phenolic hydroxyl group is also capable of solvating protons, it will be present to an extent as $ArOH_2^+$. The benzyl carbonium ion likewise carries a positive charge and the mutual repulsion of these charges may provide an indication of why the *para-* position of a phenol seems to be a favored point of condensation although two *ortho-* positions are available. The preferred orientation toward the *para-* position would be a maximum at very low *p*H values and be less effective as *p*H rises. It has already been reported that the percent of *ortho-* linked diphenylmethane isomer increases with increasing *p*H.[29]

We may also extend our consideration to the relative reactivity of *para- versus ortho*-methylol groups. Lack of ability of the *p*-methylol moiety to be internally stabilized by formation of intramolecular hydrogen bonds (as found between the *ortho-* methylol and phenolic hydroxyl groups) would render the *para* group more accessible to protons, thus more readily generate carbonium ions, and contribute to the observed greater reactivity of these compounds versus their *ortho*-isomers.[30]

Conclusion. On the basis of the experimental evidence presented it is concluded that under acid conditions methylene bridges in phenolic resins occur *via* a benzyl cation. This ion forms by addition of a proton to the hydroxymethyl or halomethyl group of the intermediate phenolformaldehyde addition product, followed by loss of a stable small molecule such as water. The reaction is propagated by coupling of the ion with a position of high electron density in another molecule and regeneration of a proton. In normal resinification reactions the preferred coupling point is the *ortho-* or *para-* position of another phenolic ring. Benzyl ethers are formed when the circumstances are such that the concentration of available ring positions is low and the concentration of unprotonated methylol groups is high. Other ion engendering agents (as silver salts acting on halomethylphenols) may be used instead of hydrogen ion to generate benzyl carbonium ion in non aqueous media. In a case where carbonium ion was generated in the presence of excess toluene, the product of reaction with the toluene rather than phenol was isolated in good yield.

EXPERIMENTAL

All of the phenols used were high grade commercial products, redistilled or recrystallized as appropriate, except 2,6-dichlorophenol which was prepared from ethyl *p*-hydroxybenzoate by a standard method,[31] m.p. 62°.

3,5-Dibromo 2-hydroxybenzyl bromide (I) was prepared in high yield (85%) by the bromination of saligenin (m.p. 85°) in an ether–chloroform mixture at 5–10°. The product was recrystallized from glacial acetic acid, then from benzene–hexane mixture. M.p. 118.5–119°; m.p. (lit.) 116–118.[32]

3,5,3′,5′-Tetrabromo-2,4′-dihydroxydiphenylmethane. Initially we attempted to prepare this compound by reaction between I and 2,6-dibromophenol. Equimolar amounts of the reagents were heated at 140°C. for 12 hr. in a nitrogen atmosphere. Only a negligible amount of hydrogen bromide was evolved and more than 75% of the original benzyl bromide (I) was recovered by recrystallization from benzene. The experiment was repeated with identical results.

Next the experiment was repeated but with the addition of 0.5 g. of *p*-toluenesulfonic acid to a 0.2 mole batch. HBr was evolved. The crude product was recrystallized, first from benzene (with charcoal) and then from glacial acetic acid. A 21% yield of the desired dimer was obtained melting at 195°. Evaporation of the solvents gave a residue which could be separated by extraction with hot petroleum ether into two fractions representing 15% of the original benzyl bromide (I, m.p. 116°) and 50% of the original 2,6-dibromophenol (m.p. 51°).

Greater success was achieved by reaction between 3,5-dibromo-2-hydroxybenzyl alcohol[32] (m.p. 88°) and about 10 mole per cent excess of 2,6-dibromophenol using *p*-toluenesulfonic acid as catalyst. At 140°, under nitrogen, a 56% yield of tetrabromo dihydroxydiphenylmethane was obtained after only 1.5 hr. heating. After two recrystallizations from benzene, the melting point was 196–197°, m.p. (lit.) 199°.[33]

3,5-Dibromo 3′,5′-dichloro 2,4′-dihydroxydiphenylmethane (II). Obtained by a similar experiment using 3,5-dibromo 2-hydroxybenzyl alcohol and two equivalents of 2,6-di-

---

(24) H. Kammerer and M. Grossman, *Angew. Chem.*, **65**, 263 (1953).

(25) W. Krumbhaar, U. S. Patent **2,268,946** (1942).

(26) A. Greth, *Angew. Chem.*, **51**, 719 (1938).

(27) W. Borsche and A. D. Berkhout, *Liebig's Ann.*, **330**, 82 (1904).

(28) G. Zigeuner and E. Ziegler, *Monatsh.*, **79**, 100 (1948).

(29) S. R. Finn and J. W. G. Musty, *J. Soc. Chem. Ind.*, Suppl. Issue No. 2, S.49 (1950).

(30) J. Reese, *Kunst* **45**, 137 (1955).

(31) *Org. Syntheses*, **29**, 35 (1949).

(32) K. von Auwers and G. Büttner, *Liebig's Ann.*, **302**, 131 (1898).

(33) N. J. L. Megson and A. A. Drummond, *J. Soc. Chem. Ind.*, 251T (1930).

chlorophenol with *p*-toluenesulfonic acid as catalyst. After 5 hr. at 140° the excess dichlorophenol was removed by vacuum distillation and the residue recrystallized from benzene containing a little ligroin, then from glacial acetic acid. Yield of purified product was 23% of theory, m.p. 167–168.5°.

Anal.[34] Calcd. for $C_{13}H_8O_2Br_2Cl_2$: Br, 37.44; Cl, 16.38. Found: Br, 36.65; Cl, 15.90. Molec. Wt. (Rast in D-camphor): Calcd. 426.9; found: 427.6.

Reactions of 3,5-dibromo 2-hydroxybenzyl bromide (I) *in presence of silver perchlorate. A. Nitromethane as solvent.* Silver perchlorate (0.025 mole) and 2,6-dichlorophenol (0.075 mole) were dissolved in 30 ml. of nitromethane and a solution of 0.025 mole of I in 170 ml. of nitromethane was added dropwise. The solution became warm, turned yellow in color, and an immediate precipitate of AgBr appeared. Stirring was continued for 1 hr. after addition of benzyl bromide was complete. The precipitate was removed by filtration, washed with nitromethane, and the combined filtrates shaken with calcium carbonate (0.025 mole) to neutralize acid. Filtration followed by distillation of solvent under reduced pressure left a tan residue. This was purified by dissolving in hot benzene, decolorizing with charcoal and adding petroleum ether to the first appearance of cloudiness. Chilling overnight gave 6.6 g. (62%) of light yellow crystals, m.p. 165.5–167°. There was no depression of melting point on admixture with compound II, above.

A similar experiment in which only 0.5 g. of silver perchlorate was used as catalyst instead of an equivalent amount, as above, gave essentially no reaction. On evaporating the solvent and recrystallizing, only the starting materials were recovered.

B. Toluene as solvent. 3,5-dibromo 2-hydroxy 4'-(or 2'?)-methyldiphenylmethane. The preceding experiment was repeated but substituting a total of 180 ml. of toleune for the nitromethane as solvent. The filtration yielded 93% of the calculated amount of AgBr. The toluene solution was treated with solid calcium carbonate to remove acid and dried with anhydrous calcium sulfate. Toluene was removed under vacuum and the residue recrystallized from glacial acetic acid, then from aqueous alcohol. The melting point was 117–118°, and a mixture with the starting benzyl bromide (m.p. 118°) caused a depression of melting point. Yield of the purified material corresponded to 39% of theory based on equimolar reaction between the benzyl bromide (I) and toluene. Analyses confirmed the conclusion that the product was a diphenylmethane compound, free of chlorine, and containing two bromine atoms and one hydroxyl group per molecule. Location of the methyl group was not positively established, but the infrared absorption pattern in the 5.1–6.0 micron region, together with a strong band at 12.5 microns support the structure in which the methyl group is in the 4 position with respect to the methylene bridge.[35]

Anal.[34] Calcd. for $C_{14}H_{12}OBr_2$: C, 47.22; H, 3.40; Br, 44.77. Found: C, 47.74; H, 3.25; Br, 45.11. Hydroxyl content (acetic anhydride in pyridine): Calcd. 4.77; found 4.62% OH. Molecular weight (Rast in D-camphor): Calcd. 356.1; found 362.4.

3,5-Dibromo-3',5'-dimethyl 2,2'-dihydroxydiphenylmethane. Compound I (0.05 mole) and 2,4-dimethylphenol (0.05 mole) were heated 5 hr. at 140° in an atmosphere of nitrogen. Hydrogen bromide was evolved continuously. After cooling, the residue was recrystallized from benzene (charcoal), then from aqueous alcohol. Yield, 40% (7.6 g.) of crystals, m.p. 178.6–179.6°.

Anal.[34] Calcd. for $C_{15}H_{14}O_2Br_2$: Br, 41.40. Found: Br, 41.23.

It is here evident that the increased ability of the reaction to propagate (dependent on the relative reactivity of the addend) is important, as well as the initiation step (carbonium ion formation).

3',5',5-Tribromo 2,4'-dihydroxydiphenylmethane. In agreement with Finn and Lewis,[9] we were unable to obtain this compound from the starting materials alone or in combination with acids. However, a solution of 0.05 mole of 3,5-dibromo-4-hydroxybenzyl bromide (prepared by bromination of *p*-cresol[9]) in 300 ml. of nitromethane, added dropwise to a solution of 0.05 mole of *p*-bromophenol and 0.05 mole of silver perchlorate in 50 ml. of nitromethane gave a precipitate of silver bromide. The organic product, after removal of the nitromethane, yielded two distinct crystalline substances following separation of oily and resinous material by fractional precipitation from benzene with petroleum ether. The first crop of crystals (1.4 g.) had m.p. 195–197° which increased to 211° on further recrystallization from benzene. On the basis of its infrared spectrum indicating 1,2,3,5 aromatic substitution,[35] it appears to be 2,6-bis(3',5'-dibromo-4'-hydroxybenzyl)-4-bromophenol, a product of condensation of 4-bromophenol with two molecules of the *p*-hydroxybenzyl compound. The spectrum was also very similar to that of the corresponding trinuclear compound in which all halogens are replaced by methyl groups.

The second fraction after recrystallization from benzene-petroleum ether gave 1.6 g. of light yellow solid, m.p. 131.5–132.5°.

Anal.[34] Calcd. for $C_{13}H_9O_2Br_3$: Br, 54.9. Found: Br, 54.8.

Infrared absorption bands in the 11–12.5 micron region indicate presence of 1,2,3,5 and 1,2,4 substituion.[35]

2,2'-Dihydroxy-3,3'-dimethyl-5,5'-di-tert-butyldibenzyl ether. This compound was obtained from an experiment intended to produce the monomethylol of *p-tert*-butyl-*o*-cresol as reported by Hultzsch.[36] The procedure had been used previously by Dr. G. R. Sprengling in our laboratory to prepare the methylol compound successfully, the only change being his use of dilute acetic acid where we have used hydrochloric acid.

In our experiment, 1.5 moles (246.2 g.) of *p*-tert-butyl-*o*-cresol was dissolved in a solution of 1.5 moles (60 g.) of sodium hydroxide in 550 ml. of water by warming at 60°. After cooling to 35°, 1.7 moles (138 g.) of 37% formaldehyde solution was added. On shaking, a slight exothermic reaction raised the temperature briefly to 43°. After 24 hr. at room temperature, the solution was acidified to *p*H 5 by dilute HCl while cooling in ice. A heavy oil separated and, on standing over the week end, it solidified. After separation by filtering, the substance was ground in a mortar with 150 ml. of 1.0*N* HCl. It was again filtered and the mass dissolved in 250 ml. of ethyl ether, dried over anhydrous calcium sulfate and the ether evaporated on a water bath. The temperature did not rise above 70°. On standing in a vacuum desiccator, the residual oil again solidified.

The product was recrystallized from 150 ml. of hot hexane by chilling. After separation of the initial crop of 86 g. of crystals, the filtrate was evaporated to give a resinous oil which on long standing produced an additional crop of 36 g. of crystals plus some oil. The combined crystalline fractions represented a yield of 44% of theoretical for the dibenzyl ether. Subsequent recrystallization from hexane containing a little benzene gave white needles, m.p. 130° and producing no depression of melting point when mixed with an authentic sample of the dibenzyl ether prepared according to

---

(34) Analyses reported for C, H, were performed by Galbraith Laboratory, Knoxville, Tenn. Halogen determinations are by Miss M. Mistrick of this laboratory.

(35) Infrared data were provided by Dr. J. H. Lady, of this laboratory, using a Perkin-Elmer, Model 21 Spectrophotometer. Assignment of absorption bands was in accordance with L. J. Bellamy, "Infrared Spectra of Complex Molecules," J. Wiley and Sons, New York, 1956, p. 57.

(36) K. Hultzsch, *J. prakt. Chem.*, **158**, 275 (1941).

Hultzsch[37] by heating the intermediate methylol compound (m.p. 64°).

Zigeuner and Ziegler[28] have likewise reported formation of the dibenzyl ether of the analogous 2,4-dimethylphenol without use of high temperatures, simply by treating the corresponding methylol compound with dilute HCl in boiling acetone–benzene mixture.

PITTSBURGH, PA.

---

(37) K. Hultzsch, *J. prakt. Chem.*, **159**, 169 (1942).

[CONTRIBUTION FROM BATTELLE MEMORIAL INSTITUTE]

Synthesis of Pyromellitonitrile and Related Compounds[1]

EMIL A. LAWTON[2] AND DONNA D. McRITCHIE

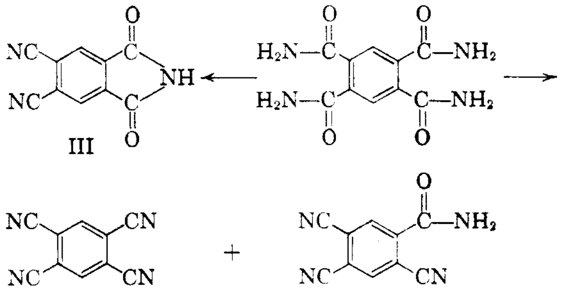
Received June 23, 1958

Pyromellitonitrile was prepared by the dehydration of pyromellitamide with thionyl chloride in dimethylformamide. The tetramide could not be dehydrated to the tetranitrile with acetic anhydride, phosphorus oxychloride, phosphorus pentachloride, or benzenesulfonyl chloride. By-products of the thionyl chloride dehydration were 4,5-dicyanophthalimide, and 2,4,5-tricyanobenzamide. 2,5-Dibromoterephthalic acid reacted quantitatively with cuprous cyanide to form pyromellitimide, but dimethyl 2,5-dibromoterephthalate reacted under the same conditions to form dimethyl 2,5-dicyanoterephthalate. Tetrakis(*N*-ethyl)pyromellitamide reacted with phosphorus pentachloride to form *N,N'*-diethylpyromellitimide.

During a study of the preparation of various phthalocyanines, it was necessary to prepare pyromellitonitrile (1,2,4,5-tetracyanobenzene, I) as an intermediate. The compound proved unexpectedly difficult to prepare and until a successful synthesis was achieved several new compounds were prepared, the syntheses of which we are reporting. The only reference to I in the literature was a patent[3] which stated that it was prepared "from pyromellitic acid tetramide by conventional methods"; no other description was given. Accordingly, pyromellitamide was prepared from pyromellitic acid by the method of Meyer and Steiner[4] in 88 per cent yield. However, the next step of dehydration of the tetramide to I proved unexpectedly difficult. Although good yields of *o*-phthalonitrile can be obtained by dehydration of *o*-phthalamide, using various methods, the analogous dehydrations of the tetramide to I were generally unsuccessful. For example, acetic anhydride in the presence of chlorobenzene was reported[5] to give a quantitative yield of *o*-phthalonitrile from *o*-phthalamide. An attempt to dehydrate the tetramide by a similar procedure gave only starting material. Similarly, dehydrations with phosphorus pentachloride, phosphorus oxychloride,[6] benzenesulfonyl chloride,[7] phosphorus pentoxide, and carbonyl chloride, yielded starting material, pyromellitimide, or chars.

This dehydration was finally accomplished with thionyl chloride in dimethylformamide at 60°. Stoichiometric proportions yielded a mixture of 2,4,5-tricyanobenzamide (II), pyromellitimide, and some I. Further reacting this mixture with additional thionyl chloride and recrystallizing from ethanol gave I.

When pyromellitamide reacted with an excess of thionyl chloride at a slightly higher tmeperature, the new compound 4,5-dicyanophthalimide (III) was the major product. All these *o*-dicyanobenzenes pass through a characteristic sequence of color changes from white at room temperature, slowly changing to green on heating above 200°, and abruptly turning deep blue between 255° and 260°. *o*-Phthalonitrile does likewise in a sealed capillary. This apparently is a characteristic of the *o*-dinitrile grouping.



Pyromellitamide is high melting and very insoluble in common solvents, due to strong hydrogen bonding in this planar molecule. With the objective of reducing the hydrogen bonding, leaving the molecule more susceptible to attack by dehydrating agents, both tetrakis(*N,N*-diethyl)pyromellitamide (IV) and tetrakis(*N*-ethyl)pyromel-

---

(1) This project was supported by the Unites States Air Force under Contract No. AF33(616)-3477, monitored by the Aeronautical Research Laboratory, Wright Air Development Center.

(2) Present address: Rocketdyne, 6633 Canoga Avenue, Canoga Park, Calif.

(3) Farbenfabriken Bayer, Brit. Patent **698,049** (1953).

(4) H. Meyer and K. Steiner, *Monatsch.*, **35**, 39 (1914).

(5) E. Koike, M. Okawa, and K. Uchiyama, *J. Chem. Soc., Japan, Ind. Chem. Sect.* **57**, 925 (1954); *Chem. Abstr.*, **50**, 884*g* (1956).

(6) M. H. Fleysher, U. S. Patent **2,387,435** (1945).

(7) C. R. Stephens, F. J. Bianco, and F. J. Pilgrim, *J. Am. Chem. Soc.*, **77**, 1701 (1955).