[SCIENTIFIC PAPER NO. 1449 FROM WESTINGHOUSE RESEARCH LABORATORIES, EAST PITTSBURGH, PENNSYLVANIA]

The Reaction of Phenol with Formaldehyde

BY G. R. SPRENGLING AND J. H. FREEMAN

It is generally agreed that the first isolable products of the alkali catalyzed reaction between phenols and formaldehyde in aqueous solution are hydroxybenzyl alcohols, commonly called methylol phenols. It seems very probable that all of the bonds tying the phenol residues together in phenolic resins have been formed by subsequent reactions of the methylol groups thus initially introduced. The position of the methylol groups and the ratio in which the various methylol derivatives are formed will thus largely determine the rate of resinification as well as the structure of the higher molecular weight products thus formed. Study of the reaction of phenols with formaldehyde leading to methylol phenols has so far been restricted almost entirely to substituted phenols, which are easier to work with because they are slower in both the initial and subsequent reactions and because only a small number of methylol derivatives is possible. By their very nature such substituted phenols are least suited to producing phenolic resins. The purpose of this paper is to study which methylol derivatives are formed in the case of phenol itself.

Theoretically, phenol can react with formaldehyde in only the ortho and para positions, with a possible yield of two isomeric monomethylol, two isomeric dimethylol, and a trimethylol derivative. So far as is known there is no reaction in the meta-position. Of these five methylol phenols only the ortho- (saligenin) and the para-methylol derivatives have ever been isolated,[1] though fractions supposed to contain the polymethylol derivatives have been obtained.[2] The only attempt to determine what methylol phenols actually are formed known to the authors is that of K. Meyer,[3] reported only as a part of the discussion on another article. Meyer treated phenol with formaldehyde, using an alkaline catalyst, then methylated the phenolic hydroxyls in the product thus obtained, and oxidized the methylol groups to carboxyl groups with permanganate. From the resulting mixture of methoxybenzenecarboxylic acids, he claimed to have isolated the ortho and para monoacids, and the 2,4- and 2,6-di-acids, but was unable to find methoxytrimesic acid. No further particulars were given.

Since even approximately quantitative chemical isolation of the individual methylol phenols from their mixture with each other, with free phenol, and with possible products of further reaction between these primary products did not seem feasible, Meyer's method was adopted. The methoxybenzenecarboxylic acids obtained by this method from the products of reaction between phenol and formaldehyde in aqueous, alkaline solution are relatively stable, and all of them are known and can be synthesized by other means for comparison.

In order to give all the possible methylol phenols opportunity to form, a mole ratio of phenol to formaldehyde of 1:1.4 was used, which Stager and Biert[1b] found best suited for isolation of *p*-hydroxybenzyl alcohol, and which also falls within the range of commercial applications. The reaction was catalyzed with sodium hydroxide, a little more than equivalent to the phenol used, and run at room temperature. Our experience has been that under these conditions the highest possible yields of methylol phenols are obtained. The total reaction product was then methylated.

The products of methylation extracted from the aqueous layer were oxidized at max. 40–50° with potassium permanganate in alkaline suspension. Filtering off the manganese dioxide formed left a slightly alkaline solution and an alkali and water insoluble oil identified as anisole. The alkaline solution was acidified and evaporated to obtain a mixture of methoxybenzenecarboxylic acids, which were separated from inorganic matter by solution in absolute alcohol or acetone.

It is possible to isolate the individual acids present in this mixture by fractional recrystallization from water, whereafter they can be purified by recrystallization. However, in order to achieve a more complete separation, the solubilities of samples of the pure, individual acids found or suspected were determined experimentally. The results are shown in Table I.

These solubility relationships were used as the basis for a roughly quantitative separation of the acids. All of the acids shown in Table I were found in the mixture except 2-methoxyisophthalic acid.

Admittedly, the separations achieved by this method are by no means quantitative. Neither is the original methylation reaction, nor the oxidation reaction quantitative. We have nevertheless estimated the amounts of each of the methylol phenols present in the original reaction mixture from the relative amounts of the corresponding methoxy acids found. In doing so we make the somewhat hazardous assumption that the per cent. loss in methylation, oxidation, and separation is the same for each acid. Moreover, we assume that the product of the initial reaction between phenol and formaldehyde consisted entirely of the methylol derivatives and unreacted phenol. This is probably also not quite true, for we may assume that some secondary reactions, for instance to diphenylmethanes, took place. With

---

[1] (a) O. Manasse, *Ber.*, **27**, 2409 (1894); L. Lederer, *J. prakt. Chem.*, **50**, 223 (1894); (b) H. Staeger and J. Biert, *Helv. Chim. Acta*, **21**, 641 (1938).

[2] F. S. Granger, *Ind. Eng. Chem.*, **24**, 442 (1932).

[3] K. H. Meyer, *Trans. Faraday Soc.*, **32**, 345 (1936).

TABLE I

	Solubility in g./100 ml. in:					
	H_2O at:		$CHCl_3$ at:		AcOH glac., at:	
Substance	20°	95°	20°	60°	20°	118°
o-Methoxybenzoic acid	0.4	2	20	V. sol.	V. sol.	V. sol.
p-Methoxybenzoic acid	.02–0.03	0.3–0.4	0.7	2.2	3	20
4-Methoxyisophthalic acid	.01–0.02	.1–0.25	Insol.	0.008	0.4	3
2-Methoxyisophthalic acid	.1	3.5	.01	.1	1–1.5	10–15
Methoxytrimesic acid	.7	10	Insol.	Insol.	0.5	6

All acids are quite soluble in ethanol at 20°.

these reservations, the figures in Table II may serve as an estimate, which, of course, holds good only for the particular phenol–formaldehyde ratio and conditions used here.

TABLE II

Components of reaction product	Mole % present
Phenol	5–10
o-Methylolphenol	10–15
p-Methylolphenol	35–40
2,4-Dimethylolphenol	30–35
2,6-Dimethylolphenol	None
2,4,6-Trimethylolphenol	4–8

Calculation shows almost exactly 1.4 methylol groups average for each phenol nucleus, which is the ratio of formaldehyde to phenol originally employed, thus corroborating our assumptions.

It has thus been shown that the products of the alkaline reaction of phenol with formaldehyde include not only the known ortho-methylol and para-methylolphenol but also very appreciable amounts of the so far unknown 2,4-dimethylol and the 2,4,6-trimethylolphenol.

No evidence of the presence of 2,6-dimethylolphenol was found. In view of the estimate as to the relative quantities of the other methylol phenols present this is not surprising. The 2,6-dimethylolphenol could be formed only from ortho-methylolphenol, which is present in smaller amount than the para-methylol derivative, and is only about one-third as reactive toward formaldehyde as phenol itself.[3a] Assuming that the para-position would be favored about as much in the second substitution as in the first, by far the largest amount of ortho-methylolphenol reacting with a second molecule of formaldehyde would give 2,4-dimethylolphenol instead of the 2,6-dimethylol derivative. And finally, any 2,6-dimethylphenol formed might be expected to react further rather easily to 2,4,6-trimethylolphenol.

No evidence was found for reaction of formaldehyde with phenol in the meta-position.

Experimental

Preparation and Methylation of Methylol Phenols.—A typical charge consisted of 94 g. (1.0 mole) of phenol, 42 g. (1.4 moles) of formaldehyde (as 37% aq. soln.), and 48 g. (1.2 moles) of sodium hydroxide dissolved in 550 ml. of water. The odor of formaldehyde disappears entirely in 3–4 days at 20–25°. After four days the charge was methylated by shaking with 1.5 moles of dimethyl sulfate plus 1.5 moles of sodium hydroxide, so that the charge was still alkaline after standing at room temperature for twenty-four hours to hydrolyze excess methyl sulfate. The layer of alkali insoluble oil was then separated from the water layer, and the latter extracted repeatedly with ether followed by ethyl acetate. The extracts were evaporated and their residue combined with the oil and dried. Total yield thus obtained amounted to 75–85% of theoretical calculated from the sum of phenol and formaldehyde used. Approximately the same percentage yield of methylated product was also obtained in the case, for example, of pure saligenin. We may assume, therefore, that at least a major portion of the 15–25% of the product not accounted for may also have consisted of methylol phenols, the rest perhaps of secondary reaction products. Oxidation of the alkaline, aqueous solution remaining after the above extraction yielded only small amounts of 4-methoxyisophthalic acid and methoxytrimesic acid and a larger amount of oxalic acid. The latter was assumed to have resulted from oxidation of phenol or methylol phenols not methylated on the phenolic hydroxyl. As is to be expected, 2,4-bis-(hydroxymethyl)-anisole—and presumably also the other polymethylols of anisole—is quite soluble in water and only moderately soluble in ether or even in ethyl acetate, though in mixture with monohydroxymethyl anisoles its solubility in ether is greatly increased.

Oxidation of Methylol Groups.—An average oxidation charge was as follows: methylation product, 65 g. (0.434 mole, assuming mol. wt. 150, based on 1.4 methylol groups per phenol residue); sodium hydroxide, 40 g. (1.0 mole) in 200 ml. of water; potassium permanganate, 137 g. (0.867 mole) in 600 ml. of water. The oxidation was carried out with vigorous stirring in the course of one and one-half to two hours at max. 50°, after which the charge was quickly heated to boiling and the small excess of permanganate immediately destroyed with alcohol. The manganese dioxide formed was then filtered off and washed well with hot dil. sodium hydroxide solution. An alkali insoluble oil extracted from the filtrate and manganese dioxide at this point was identified as anisole (containing some dissolved solid matter, probably a dihydroxydiphenylmethane). The filtrate and washings were neutralized and concentrated on the hot plate, acidified strongly with hydrochloric acid, and evaporated to dryness in a vacuum desiccator. Extraction of the residue with alcohol or acetone separated the organic acids from the inorganic salts. After evaporation of the solvent, the total yield of carboxylic acids obtained corresponded to approximately 80 mole % of the methylation products charged (or 65% of original phenol plus formaldehyde). Under the conditions employed no acid was produced from methyl groups or diphenylmethane bonds while methylol groups were quickly and essentially completely oxidized to carboxyl groups.

Separation of the Individual Acids.—*o*-Methoxybenzoic acid was separated from the mixture by triturating with cold chloroform. The residue was then refluxed with chloroform and filtered hot to separate the anisic acid. The approximate amounts of solvent needed in each case were calculated from the amounts of the various acids found in a trial run and the solubilities in Table I. The 4-methoxyisophthalic acid was separated from the remaining mixture as an insoluble residue on triturating with hot water. The aqueous solution was evaporated, leaving a residue possibly containing methoxytrimesic acid and 2-methoxyisophthalic acid, in addition to some residual 4-methoxyisophthalic acid.

(3a) M. Sprung, THIS JOURNAL, **63**, 334 (1941).

This mixture of acids was demethylated by refluxing for fifteen minutes with a mixture of hydriodic acid (d. 1.7) and concd. hydrochloric acid. Under these conditions, without a solvent for the acids, 2-methoxyisophthalic acid and methoxytrimesic acid are demethylated completely, 4-methoxyisophthalic acid hardly at all. However, the barium salt of either 4-methoxyisophthalic acid or 4-hydroxyisophthalic acid does not precipitate from a neutral aqueous solution of the ammonium salt; the barium salts of 2-hydroxyisophthalic and hydroxytrimesic acids are insoluble under these conditions. The products of demethylation were therefore directly diluted with water and neutralized with ammonium hydroxide, then precipitated with barium chloride solution in excess. Under these conditions 2-hydroxyisophthalic acid and hydroxytrimesic acid are precipitated virtually quantitatively, though the former often takes some time to precipitate. The barium precipitate was treated with sulfuric acid to liberate the acids, which were then brought into solution with ethanol, the barium sulfate filtered off, and the ethanol removed by boiling. Any 4-methoxyisophthalic acid remaining in the filtrate of the barium precipitation was recovered by concentrating the filtrate and acidifying with hydrochloric acid.

It was found that 2-hydroxyisophthalic acid can be separated from hydroxytrimesic acid almost quantitatively by the method of Seebach.[4] The precipitate in the acid, aqueous solution obtained from the barium-precipitation was therefore dissolved by making alkaline with potassium hydroxide. When this solution was brought down to *p*H 4.6–4.9 with hydrochloric acid, a precipitate consisting of the monopotassium salt of hydroxytrimesic acid formed. Further acidification of the filtrate from this precipitate should precipitate 2-hydroxyisophthalic acid. In no case, however, was an identifiable amount of this acid obtained.

These methods of separation yielded an average of 80–85% of the original acids mixture as reasonably pure individuals.

***o*-Methoxybenzoic Acid.**—The material isolated from the oxidation mixture was recrystd. from water, m. p. 100–101° (cor.). A sample prepared for comparison by complete methylation of salicylic acid (Eimer & Amend, No. A-277) with dimethyl sulfate and alkaline hydrolysis of the ester was recrystd. from water plus ethanol, m. p. 100.5–101.5° (cor.); mixture of these two samples m. p. 100–101° (cor.). The acid often comes out of solution as a supercooled liquid before crystallizing.

***p*-Methoxybenzoic Acid.**—The material isolated from the oxidation mixture was recrystd. from dilute ethanol, long, white needles, m. p. 183.5–184.5° (cor.). Comparison sample (Eimer & Amend, No. A-50) m. p. 183.5–184.5° (cor.); mixture of these samples m. p. 183.5–184.0° (cor.).

4-Methoxyisophthalic Acid.—The material isolated was recrystd. from glacial AcOH, white, micro-crystalline product, m. p. 274.5–275.5° (cor.). A comparison sample was prepared by methylating 2,4-xylenol (Eastman Kodak, No. 1150), then oxidizing hot with alkaline permanganate. The product was recrystd. from glacial AcOH, m. p. 275.0–275.5° (cor.); mixed m. p. of these two products 275.0–275.5° (cor.). All melting points were accompanied by decomposition of the melt, with evolution of carbon dioxide; titrated equivalent weight 98.04 (theor. 98.08).

This acid is insoluble in hydriodic acid (d. 1.7), and is not demethylated even by refluxing for one-half hour with an excess of the latter. To demethylate, the acid was dissolved in about an equal quantity of phenol and acetic anhydride and then refluxed for one hour with an excess of hydriodic acid. The resulting **4-hydroxyisophthalic acid** crystallized from dilute ethanol in fine, white needles, m. p. 314–315° (cor.) (dec.). A mixture of equal quantities of 4-hydroxyisophthalic acid prepared from the comparison sample and from the isolated sample of the methoxy acid had m. p. 314–315° (cor.). A mixture of approximately equal parts of 4-hydroxyisophthalic acid and hydroxytrimesic acid m. p. 300°.

The dimethyl ester of 4-hydroxyisophthalic acid was prepared by reaction of a methanol solution of the acid with diazomethane at $-10°$ until the yellow color of a slight excess of diazomethane persisted for a minute or more at this temperature. The alkali soluble di-ester was recrystd. from dilute methanol, giving long, fine, white needles, m. p. 95.2–95.7° (cor.); calcd. C, 57.14; H, 4.80. Found: C, 57.30; H, 4.89.

The dimethyl ester of 4-methoxyisophthalic acid was prepared by methylation of the methoxy acid in methanol with diazomethane in excess. The product crystd. from hexane in feathery, white needles, m. p. 96.1–96.7° (cor.); calcd.: C, 58.92; H, 5.39. Found: C, 58.89; H, 5.49. The mixed melting point of these two esters was below 90° while the mixed melting point of either of them with the trimethyl ester of methoxytrimesic acid was below 75°.

2-Methoxyisophthalic Acid.—A sample of this acid was prepared by methylating 2-hydroxy-3-methylbenzaldehyde prepared from *o*-cresol by the Reimer–Tiemann reaction,[5] and oxidizing the product to the desired acid with hot, alkaline permanganate. The product was recrystd. from glacial acetic acid, m. p. 222.7–223.5° (cor.)—no apparent decomposition; titrated acid equivalent weight 97.86 (calcd. 98.08).

This acid is very easily demethylated by hot hydriodic acid, heating to the boil for ten to fifteen minutes being sufficient. The **2-hydroxyisophthalic acid** obtained crystallized from water in long, hair-fine, white needles, m. p. 245–246° (cor.) (dec. with evolution of carbon dioxide—immersed at 237° and heated at 2–3°/min.). Dilute aqueous solutions show a strong, blue fluorescence. Long, bunched needles of barium salt form slowly when a dilute aqueous soln. of the acid neutralized with ammonia is treated with barium chloride.

Methoxytrimesic Acid.—A sample of this acid was prepared from 2,6-bis-(hydroxymethyl)-4-methylphenol by the method of Ullmann and Brittner.[6] The product was recrystd. from water—from which it crystallizes very slowly—and then from glacial acetic acid. Taken in the ordinary manner, the substance partly melts at about 240–244°, then resolidifies slowly, and finally melts completely at 270–275°. Dip melting points with a preheated bath show a sharp melting point at 249–250° (cor.). However, the melted substance immediately begins to decompose with evolution of carbon dioxide and begins to solidify again after fifteen to twenty seconds, thereafter showing a second m. p. at 270–275°. Apparently a rapid decomposition, probably to the 2,4-diacid takes place even below the melting point; neutralization equivalent weight found 80.13 (calcd. 80.05).

We were unable to obtain the trimethyl ester of this acid by treatment with dimethyl sulfate in sodium carbonate solution, by the method of Ullmann and Brittner.[6] However, this ester is formed quickly and quantitatively by treatment of a methanol solution of either the hydroxy- or methoxytrimesic acid with diazomethane in slight excess. The ester was recrystd. from hexane—fine, white, wadded needles, m. p. 85.7–86.1° (cor.); calcd.: C, 55.32; H, 5.00. Found: C, 55.22; H, 5.04. A mixture of equal quantities of the ester prepared from comparison samples of methoxytrimesic acid and ester prepared from hydroxytrimesic acid from the unknown m. p. 85.7–86.1 (cor.).

This acid is demethylated to hydroxytrimesic acid with extreme ease, either by treatment with hot hydriodic acid, or even by boiling with concd. hydrochloric acid or 10% sodium hydroxide for twenty to thirty minutes. In fact, care is necessary to prevent demethylation by the alkali used in oxidation. The product is very soluble in glacial acetic acid and quite soluble even in cold water. It was recrystd. from water or dilute acetic acid; m. p. 316–317° (cor.), the substance being placed in the bath at about 305° and the temperature raised at 3–4°/min., as otherwise erroneously low readings are obtained due to decomposition. The substance decomposes quickly with evolution of carbon dioxide immediately after melting. The

---

(4) F. Seebach, *Ber.*, **73**, 1345 (1940).

(5) F. Tiemann and C. Schotten, *ibid.*, **11**, 767 (1878).

(6) F. Ullmann and K. Brittner, *ibid.*, **42**, 2542 (1909).

acid forms an insoluble mono-K-salt stable at pH 4.6–4.8, and an insoluble mono-Na-salt stable at about the same pH. The acid is quickly and completely precipitated by barium chloride from aqueous solution neutralized with ammonia.

Summary

The reaction between formaldehyde and phenol in alkaline medium has been investigated with the object of determining which of the several possible mono- and polymethylols of phenol are formed as initial products of the reaction, and to what relative extent. Evidence in the form of the corresponding methoxybenzenecarboxylic acids has been obtained for the formation of 10–15 mole % *o*-methylol phenol, 35–45% *p*-methylol, 30–35% 2,4-dimethylol and 4–8% trimethylol phenol, plus 5–10% of unreacted phenol as the primary products of reaction of 1 mole of phenol with 1.4 moles of formaldehyde. No 2,6-dimethylol phenol was detected nor was any evidence found for the presence of methylol groups in the meta-position to the phenolic hydroxyl.

The respective methoxybenzenecarboxylic acids have also been synthesized by other means. A method is described for the separation of anisic acid, *o*-methoxybenzoic acid, 4-methoxyisophthalic acid, 2-methoxyisophthalic acid, and methoxytrimesic acid when present as a mixture.

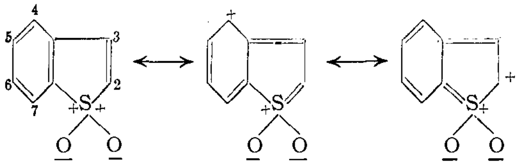
EAST PITTSBURGH, PA. RECEIVED JULY 8, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Benzothiophene[1] Chemistry. IV.[2] Some Addition Reactions of Benzothiophene-1-dioxide[3]

BY F. G. BORDWELL AND W. H. MCKELLIN

Benzothiophene-1-dioxide (I) may be looked on as containing a heteroaromatic system if resonance forms such as Ia and Ib, which give the sulfur atom ten electrons, are recognized as important. Chemically, carbon–carbon bonds in aromatic systems differ from olefinic bonds in showing less susceptibility to attack by addition-type reagents. Therefore, it seemed of interest to see whether or not the 2–3 bond in I would undergo, under comparable conditions, the reactions typical of the similarly situated bond in other α,β-unsaturated sulfones.



I Ia Ib

Kohler and Potter[4] reported that β-phenylvinyl *p*-tolyl sulfone ($C_6H_5CH{=}CHSO_2C_7H_7$), which is somewhat analogous to I in structure, underwent addition reactions with hydrogen (incomplete in the presence of platinum catalyst), bromine (irradiation was necessary), phenylmagnesium bromide, thiocresol (basic catalyst used) and sodiomalonic ester. It was found that I underwent reaction with all of these reagents under conditions similar to those used by Kohler and Potter.[4] The addition of one mole of hydrogen to I was complete in a short time in the presence of palladium on charcoal catalyst. Addition of bromine was brought about either by irradiation in carbon tetrachloride solution or by heating in acetic acid solution.[2] Thiophenol was added in benzene solution according to the directions of Kohler and Potter,[4] or in alcohol solution. The latter method was more convenient but the product was less pure, probably due to contamination by the alcohol-addition product. The product from the reaction with phenylmagnesium bromide resisted attempts at purification, and no identifiable substance was obtained.

Vinyl sulfone has been reported[5] to undergo addition reactions with: (1) hydrobromic and hydroiodic acids; (2) water, methanol, ethanol, 3-methylbutanol and phenol (all with basic catalysis); (3) hydrogen sulfide and thiophenol; (4) glycine and phenylhydrazine. As representative of these and other reagents mentioned in the literature,[6] hydrobromic acid, water, ethanol, 2-propanol, 2-methyl-2-propanol, diethylamine, morpholine, piperidine, phenol and malonic ester were chosen. The addition reactions were successful with all of these except phenol.[7] In general the reactions proceeded rapidly and gave excellent yields of addition products.

By analogy with a large number of examples

---

[1] The name *thianaphthene* was adopted in the first three papers of this series, following the current usage in *Chemical Abstracts*. Prior to 1937 the name *thionaphthene* was preferred by *Chemical Abstracts*. Since both *thia* and *naphthene* have meanings which are not borne out in the structure, the name *thianaphthene* appears to be an unfortunate choice. Henceforth it will be abandoned in favor of *benzothiophene*, as suggested by Ball and Haines, *Chem. Eng. News*, **24**, 2765 (1946), and by the committee on nomenclature of the Petroleum Division of the American Chemical Society.

[2] For Paper III see Bordwell, Lampert and McKellin, THIS JOURNAL, **71**, 1702 (1949).

[3] This work was supported by a grant from The Texas Company, New York, N. Y.

[4] Kohler and Potter, THIS JOURNAL, **57**, 1316 (1935).

[5] Alexander and McCombie, *J. Chem. Soc.*, 1913 (1931).

[6] See Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., p. 727–728, for further references.

[7] After this work had been completed Challenger and Clapham, *J. Chem. Soc.*, 1615 (1948), reported the addition of hydrogen iodide, methanol, ethanol and hydrogen to I.