

drous sodium sulfate, and then concentrated. The yield was 12.7 g. The product was identified as *m*-bromophenol by the preparation of its phenoxyacetic acid derivative.⁷ It melted at 110°; mol. wt. (titration), calcd. 231; found 235.

***m*-Iodophenyldiazonium Borofluoride.**—This compound was prepared in the usual manner from *m*-iodophenyldiazonium chloride and 40% hydrofluoroboric acid. The yield was 80.5%. It melted at 134°.

***m*-Iodophenyl Acetate.**—This compound was prepared from *m*-iodophenyldiazonium borofluoride and acetic acid according to the procedure described for the corresponding bromo compound. It boiled at 132–133° (7 mm.); yield 65.0%.

(7) Koelsch, *THIS JOURNAL*, **53**, 304 (1931).

Anal. Calcd. for C₆H₇IO₂: C, 36.64; H, 2.67. Found: C, 35.91; H, 2.68.

***m*-Iodophenol.**—Eleven grams of the acetate, on hydrolysis with 30 cc. of 10% aqueous potassium hydroxide, gave 8.7 g. of the free phenol, which was identified as its phenoxyacetic acid derivative. The melting point was 118°; mol. wt. (titration), calcd. 278; found 273.

Summary

m-Bromophenol and *m*-iodophenol have been prepared by hydrolysis of the acetate obtained by the action of acetic acid on the corresponding diazonium borofluorides.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

Certain Derivatives of the Ethers of Hydroxyhydroquinone¹

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A systematic investigation of the literature for information concerning the derivatives of the ethers of hydroxyhydroquinone revealed that very few had been prepared. Because monosubstitution by halogenation, nitration and sulfonation of the 1,2,4-trimethyl ether yielded only the 5-derivative, the number of mono- and disubstituted compounds possible was limited. But since a means was devised whereby a 3- or 6-monosubstituted hydroxyhydroquinone could be obtained, entirely new series of derivatives were prepared.

Such a synthesis was available from the fact that a hydroxybenzaldehyde in an alkaline medium can be oxidized to a polyphenol by hydrogen peroxide.² We were in this way able to transform certain vanillin and isovanillin derivatives into otherwise unattainable hydroxyhydroquinone compounds.

Theoretical

Bromo Derivatives.—Of the three monobromohydroxyhydroquinone trimethyl ethers possible, the 5-compound has been prepared by direct bromination.³

The 6-bromotrimethyl ether has not been prepared but Dakin² synthesized the 6-bromohydroxyhydroquinone 2-methyl ether by the action of hydrogen peroxide on the potassium salt of 5-

bromovanillin. We prepared this compound and then treated it with dimethyl sulfate in the usual manner to obtain the corresponding trimethyl ether.

An attempt was made to prepare the third isomer starting with 2-bromoisovanillin.⁴ This was treated with hydrogen peroxide and the product methylated. A small yield of highly colored crystals was obtained which did not give analytical results of sufficient accuracy to indicate the presence of only 3-bromohydroxyhydroquinone trimethyl ether.

Concerning the dibromo bodies, only one of uncertain structure³ has been prepared. Assuming this to be the 3,5-(rather than 5,6-)dibromohydroxyhydroquinone trimethyl ether, we prepared the 6-bromotrimethyl ether and treated this with bromine in benzene solution. The product was the 3,6-dibromo compound, the 5,6-possibility being eliminated as follows: Dimroth⁵ prepared a 2,3(or 5,6)-dibromoquinone but on reduction the compound rearranged to the more stable 3,6-dibromo derivative of hydroquinone. Also, Kohn and Guttmann⁶ have shown that when 3,6-dibromo structures are treated with nitric acid, the radicals attached to the phenolic oxygen on the 1,4-carbon atoms are eliminated and a quinone results. We obtained such a quinone from the new dibromotrimethyl ether.

By brominating the 5-bromotrimethyl ether

(1) This paper was constructed from a portion of a dissertation presented by H. W. Dorn to the Department of Chemistry of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1938.

(2) H. D. Dakin, *Am. Chem. J.*, **42**, 492 (1909).

(3) R. Fabinyi and T. Széki, *Ber.*, **43**, 2681 (1910).

(4) H. Pauly, *ibid.*, **48**, 2018 (1915).

(5) Dimroth, Eber and Weber, *Ann.*, **446**, 132 (1925).

(6) M. Kohn and L. W. Guttmann, *Monatsh.*, **45**, 573 (1924).

in glacial acetic acid at 100°, we were able to prepare the tribromotrimethyl ether.

Nitro Derivatives.—Fabinyi and Széki⁷ prepared the 5-nitrohydroxyhydroquinone trimethyl ether and Thiele and Jaeger⁸ obtained a nitro derivative of the triacetate but did not determine the structure. We prepared this α -nitrotriacetate and upon methylation found it to be the same as the 5-nitrohydroxyhydroquinone trimethyl ether.

Occurring with the " α "-nitrotriacetate was a compound containing no nitrogen. An analysis indicated a diacetate, the identity of which was ascertained from the fact that two such hydroxydiacetoxybenzenes are known in the form of their monomethyl ethers. Both were prepared by Moore.⁹ The side-product was shown to be the 1,4-diacetoxy-2-hydroxybenzene.

In view of the proof of the α -nitro position, the α,α -dibromo- α -nitro derivative prepared by Thiele and Jaeger⁸ can only be 3,6-dibromo-5-nitrohydroxyhydroquinone. From this compound, we prepared 3,6-dibromohydroxyhydroquinone trimethyl ether through trimethylation followed by reduction of the nitro group and elimination of the nitrogen by diazotization. This product was identical with that previously prepared from vanillin.

Sulfono Derivatives.—No sulfonic acids of hydroxyhydroquinone or its ethers have been prepared. We synthesized the 5-acid by direct sulfonation of the trimethyl ether. Its structure was proved by treating the sodium salt of this sulfonic acid with nitric acid. A compound melting at 129° and containing no sulfur resulted, the product being identical with the 5-nitro body previously described by Fabinyi and Széki.⁷ The sulfonyl chloride, sulfonamide and sulfanilide were prepared to characterize the 5-sulfonic acid more fully.

A means of synthesizing the 6-sulfonic acid was devised using the vanillin-5-sulfonic acid of Finger and Schott.¹⁰ We treated this material with hydrogen peroxide and *N* potassium hydroxide solution and by subsequent dimethylation prepared the 6-sulfonic acid of hydroxyhydroquinone trimethyl ether. This compound was analyzed as the sulfonyl chloride.

As with the nitro derivatives, no disulfonic acids were obtained by direct action on the trimethyl ether or 5-monosubstituted derivative.

Experimental

Trimethyl Ether of Hydroxyhydroquinone.—From quinone¹¹ triacetylhydroxyhydroquinone¹² was prepared and the latter product was converted directly to the trimethyl ether.¹³

Trimethyl Ether of 6-Bromohydroxyhydroquinone.—To a cooled solution of 15 g. of vanillin in 30 ml. of glacial acetic acid, 5.5 ml. of bromine in 20 ml. of glacial acetic acid was added rapidly with stirring. On addition of water, the 5-bromovanillin crystallized out and, after recrystallization from alcohol in a yield of 23 g., the substance melted at 163–164°. On treatment of this material in 105 ml. of *N* potassium hydroxide with 225 ml. of 3% hydrogen peroxide, the dark purple solution was heated for some time, then cooled, acidified and extracted with ether. On evaporation of the ether, the residue was crystallized from water. This slightly colored product melting sharply at 141° was methylated with dimethyl sulfate, giving in 62% yield the trimethyl ether, m. p. 37–38°. With the exception of water, it is readily soluble in the common solvents.

Anal. Calcd. for $C_9H_{11}O_3Br$: Br, 32.39. Found: Br, 32.25.

Preparation of the 3,6-Dibromotrimethyl Ether.—To 10 g. of the 6-bromohydroxyhydroquinone trimethyl ether dissolved in 30 ml. of benzene was added 2.5 ml. of bromine. The resulting solution was freed of excess bromine with aqueous sodium carbonate and the benzene layer dried with potassium carbonate. After filtering off the carbonate, the benzene was evaporated, leaving a good yield of the dibromotrimethyl ether. It was recrystallized from benzene as long white needles melting at 97° and insoluble in water but soluble in acetone, chloroform and ethyl acetate. The final yield was 90% of the theoretical.

Anal. Calcd. for $C_9H_9O_3Br_2$: Br, 49.08. Found: Br, 48.94.

The Quinone from the 3,6-Dibromotrimethyl Ether.—To 2 g. of dry 3,6-dibromohydroxyhydroquinone trimethyl ether was added 5 ml. of concd. nitric acid (sp. gr. 1.41). The mixture was warmed for a short time and on cooling precipitated out small orange-red platelets. The acid medium was diluted and the crystals filtered off, then recrystallized from benzene, m. p. 172°, being slightly soluble in hot alcohol but more so in benzene and glacial acetic acid; yield 84%.

Anal. Calcd. for $C_7H_4O_3Br_2$: Br, 54.42. Found: Br, 54.35.

Reduction of the above Quinone.—A stream of sulfur dioxide was bubbled through an aqueous alcoholic suspension of the red 3,6-dibromo-2-methoxyquinone which soon became a colorless solution. This was evaporated, leaving clusters of white needles which on recrystallization from dilute alcohol melted at 155° (dec.). It is slightly soluble in water but soluble in alcohol and acetone.

Anal. Calcd. for $C_7H_6O_3Br_2$: Br, 54.05. Found: Br, 53.91.

(7) R. Fabinyi and T. Széki, *Ber.*, **39**, 3679 (1906).

(8) J. Thiele and K. Jaeger, *ibid.*, **34**, 2837 (1901).

(9) C. W. Moore, *J. Chem. Soc.*, **99**, 1046 (1911).

(10) H. Finger and W. Schott, *J. prakt. Chem.*, **115**, 287 (1927).

(11) H. N. McCoy, *J. Chem. Ed.*, **14**, 494 (1937).

(12) E. B. Vliet, *Org. Syntheses*, **4**, 35 (1925).

(13) G. Bargellini and E. Martegiani, *Gazz. chim. ital.*, **41**, 448 (1911).

Tribromohydroxyhydroquinone Trimethyl Ether.—To a solution of 5 g. of 5-bromohydroxyhydroquinone trimethyl ether in 30 ml. of glacial acetic acid there was added 2.5 ml. of bromine at 100°. On cooling, the mixture was poured into 100 ml. of ether, then agitated with water and aqueous sulfurous acid. The ether layer, freed of excess bromine, was evaporated to dryness. The residue was melted with potassium hydroxide, treated with water, filtered and crystallized from alcohol as small white needles which reddened on exposure to air. This compound, melting at 85–86°, does not split off bromine when treated with alcoholic potassium hydroxide. It is soluble in hot alcohol, ether and glacial acetic acid; yield 67%.

Anal. Calcd. for $C_9H_5O_3Br_3$: Br, 59.25. Found: Br, 59.11.

Preparation of 1,4-Diacetoxy-2-hydroxybenzene.—In the preparation of the *x*-nitrotriacetate, the product was filtered off and the filtrate was evaporated to 50 ml. and allowed to stand overnight. There resulted a well-crystallized white compound which on recrystallization from water gave needles over 3 cm. in length. This material melts at 104°, occurs in 50% yield and is soluble in the common solvents.

Anal. Calcd. for $C_{10}H_{10}O_6$: C, 57.14; H, 4.76. Found: C, 56.97; H, 4.65.

***x*(5)-Nitrohydroxyhydroquinone Trimethyl Ether.**—The *x*-nitrohydroxyhydroquinone triacetate was methylated directly with dimethyl sulfate in the usual way. The product was poured into ice water, filtered off and crystallized from warm alcohol as fine yellow needles melting at 130°, being identical in every respect with the 5-nitrohydroxyhydroquinone trimethyl ether of Fabinyi and Széki.⁷

Anal. Calcd. for $C_9H_{11}O_5N$: N, 6.63. Found: N (Dumas), 6.71.

5-Nitro-3,6-dibromohydroxyhydroquinone Trimethyl Ether.—Ten grams of 5-nitro-3,6-dibromohydroxyhydroquinone⁸ in methyl alcohol was methylated with dimethyl sulfate. The product was crystallized from benzene in the form of yellow needles which melted at 127° and occurred in 63% yield. It is insoluble in water, soluble in hot alcohol, petroleum ether, carbon disulfide and benzene.

Anal. Calcd. for $C_9H_5O_5Br_2N$: Br, 43.12. Found: Br, 43.07.

5-Amino-3,6-dibromohydroxyhydroquinone Trimethyl Ether.—Four grams of 5-nitro-3,6-dibromohydroxyhydroquinone trimethyl ether was reduced with 25 ml. of concd. hydrochloric acid and 10 g. of tin. The mass was warmed until it became colorless, then diluted with water to 200 ml. and the tin removed by treatment with hydrogen sulfide. After filtration, the filtrate was evaporated to 75 ml. *in vacuo*, then made alkaline, after which the free amine separated out. The product, purified by dissolving it in benzene then adding petroleum ether, results as white needles, in 48% yield, turning violet on exposure to air and melting at 115°. It is soluble in boiling benzene, cold ether and alcohol.

Anal. Calcd. for $C_9H_{11}O_3Br_2N$: Br, 46.92. Found: Br, 46.78.

Replacement of the Amino Group by Hydrogen.—Diazotization of 2.5 g. of 5-amino-3,6-dibromohydroxyhydro-

droquinone trimethyl ether was carried out with sodium nitrite and concd. hydrochloric acid. While the diazonium solution was kept cool, an alkaline stannite reagent was prepared as follows: 6 g. of sodium hydroxide in 7.5 ml. of water was shaken with a turbid solution of 5 g. of stannous chloride in 25 ml. of water. The reagent was added in small amounts to the diazonium salt solution, then the product was extracted with ether and when the ether was removed white needles melting at 96–97° remained. This compound was identical with the 3,6-dibromotrimethyl ether previously obtained by brominating the 6-bromo compound in benzene. The yield was poor, being only 28%.

The 5-Sulfonic Acid of Hydroxyhydroquinone Trimethyl Ether.—A solution of 22.5 ml. of hydroxyhydroquinone trimethyl ether and 11 ml. of concd. sulfuric acid (sp. gr. 1.8) was warmed gently until it began to solidify. On cooling, water was added cautiously with stirring and the entire mass became a white paste of fine needles. This free sulfonic acid was converted into the sodium salt from which the sulfonyl chloride was prepared readily. It melts at 130° after crystallization from chloroform and is only slightly soluble in ether but is soluble in acetone and glacial acetic acid; yield 60%.

Anal. Calcd. for $C_9H_{11}O_6ClS$: S, 12.00. Found: S, 11.93.

The sulfonamide crystallized from alcohol melts at 76°. It is soluble in hot alcohol and acids, only slightly soluble in water, benzene, acetone and ethyl acetate, but insoluble in chloroform and ether.

Anal. Calcd. for $C_9H_{13}O_6NS$: S, 12.95. Found: S, 12.86.

The sulfanilide crystallized from alcohol melts at 170°. It is soluble in hot alcohol, acetone, chloroform and acids but is insoluble in water and benzene.

Anal. Calcd. for $C_{15}H_{17}O_6NS$: S, 9.91. Found: S, 9.85.

Proof of the Position of the Sulfonic Acid Group.—To 10 g. of the 5-sulfonic acid sodium salt there was added 15 ml. of nitric acid (10 *N*). The salt passed into solution, turning a deep orange color, then suddenly began to solidify finally forming a solid yellow mass. This was diluted, filtered and crystallized from hot alcohol as silky yellow needles melting at 129°. Analysis showed that no sulfur was present and that this was a mononitro compound identical in all properties with 5-nitrohydroxyhydroquinone trimethyl ether.

Anal. Calcd. for $C_9H_{11}O_5N$: N, 6.63. Found: N (Dumas), 6.74.

6-Sulfonic Acid of Hydroxyhydroquinone 2-Methyl Ether.—To 30 g. of vanillin was added 90 g. of fuming sulfuric acid, containing 20% trioxide, at ice-bath temperature with vigorous stirring. After the reaction mass had attained a temperature of 70°, it was cooled and placed in a vacuum desiccator overnight to harden, then filtered through glass wool with strong suction and crystallized from glacial acetic acid giving a 54% yield of white needles, m. p. 124°.

To a solution of 3 g. of vanillin-5-sulfonic acid and 50 ml. of *N* sodium hydroxide there was added 20 ml. of 3%

hydrogen peroxide. With constant stirring, the reaction was carried out on the water-bath, cooled and left overnight. The unchanged material, being soluble in water, was removed while the white product was crystallized from boiling water. It gave no aldehyde test with semicarbazide or Schiff's reagent, but gave a dark purple coloration when treated with aqueous ferric chloride. This derivative decomposes at 290° and has the form of long, white, rhombic crystals soluble in glacial acetic acid but insoluble in ether. The yield was only 20%.

Anal. Calcd. for $C_7H_8O_6S$: S, 14.54. Found: S, 14.31.

6-Sulfonic Acid of Hydroxyhydroquinone Trimethyl Ether.—The 2-methyl ether was methylated with dimethyl sulfate, giving the sodium salt of the 6-sulfonic acid of hydroxyhydroquinone trimethyl ether. The compound was analyzed as the sulfonyl chloride which melts at 98° and is soluble in acetone, chloroform and glacial acetic acid.

Anal. Calcd. for $C_9H_{11}O_6ClS$: S, 12.00. Found: S, 11.95.

Summary

A number of new derivatives of hydroxyhydroquinone have been prepared, and the structures of the following have been established. (1) Fabinyi and Széki's dibromohydroxyhydroquinone trimethyl ether is the 3,5-dibromo compound. (2) Bromination of the 6-bromotrimethyl ether gives the 3,6-dibromo compound as proved by quinone formation. (3) The α -nitrotriacetate is the 5-nitro compound. (4) The α -nitro- α,α -dibromohydroxyhydroquinone is the 5-nitro-3,6-dibromo body. (5) The side-product occurring with the α -nitrotriacetate is the 1,4-diacetoxy-2-hydroxybenzene. (6) Direct sulfonation of hydroxyhydroquinone trimethyl ether gives the 5-sulfonic acid since, on treatment with nitric acid, the sulfur derivative is converted into the 5-nitro compound.

WORCESTER, MASS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Hittorf Transference Numbers of Sodium and Ammonium Acetates in Anhydrous Acetic Acid¹

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Since the determination of transference numbers in non-aqueous solutions presents a number of difficulties not encountered in aqueous solutions, the data on this subject to be found in the literature² are comparatively scarce, and, with a few exceptions, not very accurate. Among studies of solutions in anhydrous acetic acid which have been made in this Laboratory, a few measurements of transference numbers have been included. Longworth³ made use of the moving boundary method on solutions of sodium and potassium acetates in this solvent. The transference numbers so found were between 0.4 and 0.5, and increased with increasing dilution. In later work by Davidson and Holm,⁴ the results of some preliminary determinations by the Hittorf method were reported. The results appeared to indicate highly abnormal behavior, as the apparent cation transference numbers decreased with increasing dilution, and were practically zero in the most dilute solutions stud-

ied. It would be difficult to account for such extreme abnormality in the dilute solutions; furthermore, it has been shown⁵ that in aqueous solutions closely concordant results can be obtained by moving boundary and Hittorf methods. In view of these facts it seemed of interest to redetermine the transference numbers by the Hittorf method under conditions which promised greater accuracy.

The chief difficulty encountered in such determinations lies in the fact that solutions of electrolytes in acetic acid are very much poorer conductors of electricity than similar aqueous solutions. In order to make possible the passage of a satisfactory quantity of electricity, either the distance between electrodes must be comparatively short or the cross section of the cell must be large. These conditions are exactly opposite to those which would be favorable to sharp separation of the several compartments of a cell and to the attaining of accuracy in the measurement of transference numbers. Further, electrode reactions which are suitable with regard to density changes, absence of gas evolution and accurate

(1) Presented before the Division of Physical and Inorganic Chemistry at the Dallas meeting of the American Chemical Society, April, 1938.

(2) Walden, "Elektrochemie nichtwässriger Lösungen," Johann Ambrosius Barth, Leipzig, 1924, p. 176.

(3) Longworth, Thesis, University of Kansas, 1928.

(4) Davidson and Holm, *University of Kansas Science Bulletin*, **21**, 9 (1933).

(5) MacInnes and Dole, *THIS JOURNAL*, **53**, 1357 (1931); MacInnes and Longworth, *Chem. Rev.*, **11**, 213 (1932).