[CONTRIBUTION FROM THE ORGANIC LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

ORIENTATION IN THE BENZENE RING. THE CHLORINATION OF PYROGALLOL-2,6-DIMETHYL ETHER

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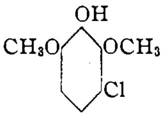
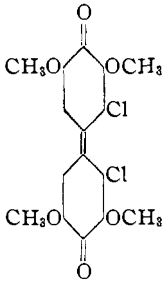
In a previous article[1] it has been shown that pyrogallol-2,6-dimethyl ether, on bromination in an anhydrous medium, gives the 3- (or 5-) bromo derivative, that is, the substituent bromine atom enters the *meta* position to the hydroxyl group. The chlorination of this phenol has since been studied, and it has been found that in this reaction as well, the substituent chlorine atom enters the *meta* position to the hydroxyl group.



I



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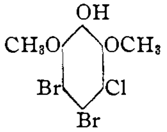

III

The position taken by the chlorine atom was established by methods analogous to those used in determining the position of the bromine in the 3- (or 5-) bromo derivative. Thus the monochloro derivative (I) was oxidized with chromium trioxide, giving a 60% yield of 3,3′-dichloro-2,6,-2′,6′-tetramethoxy-diphenoquinone (dichlorocedriret II), and a small quantity of another substance, presumably 3-chloro-2,6-dimethoxy-*p*-benzoquinone. The latter was not obtained in sufficient quantity for analysis. The dinuclear quinone on reduction with sulfur dioxide gave the corresponding hydroquinone. This was found to be identical with the dichlorohydrocedriret obtained by Hayduck.[2]

The 3-chloro-2,6-dimethyl ether was brominated with an excess of bromine, forming the 3-chloro-4,5-dibromo-2,6-dimethyl ether of pyrogallol (III). This in turn gave, on oxidation with chromium trioxide in glacial acetic acid, 3-chloro-5-bromo-2,6-dimethoxy-*p*-benzoquinone, identical with the substance obtained on chlorination of 3-bromo-2,6-dimethoxy-*p*-benzoquinone previously described.[1]

Experimental Part

3-Chloropyrogallol-2,6-dimethyl Ether.—Ten g. of pyrogallol-2,6-dimethyl ether was dissolved in 100 cc. of carbon disulfide. Chlorine was passed into this solution until

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[1] Levine, THIS JOURNAL, **48**, 797 (1926).

[2] Hayduck, *Ber.*, **9**, 929 (1876).

it had increased sufficiently to replace one hydrogen of the molecule. The carbon disulfide was distilled and the residue fractionated in a vacuum, giving an 80% yield of 3-chloro-pyrogallol-2,6-dimethyl ether distilling at 154–156° (12 mm.) and about 2 g. of a substance distilling between 156–170° (12 mm.), consisting presumably of the monochloro derivative contaminated with some of the higher chlorinated products.

Anal. Subs., 0.1859, 0.2243: AgCl, 0.1440, 0.1707. Calcd. for $C_8H_9O_3Cl$: Cl, 18.82. Found: 19.16, 18.82.

3-Chloropyrogallol-2,6-dimethyl ether is a colorless liquid which it has not been possible to obtain in solid form. It is soluble in the usual organic solvents but insoluble in water and ligroin.

THE BENZOATE, prepared by the Schotten-Baumann process, crystallizes from 95% alcohol in scales; m. p., 89–90°.

Anal. Subs., 0.1557: AgCl, 0.0761. Calcd. for $C_{15}H_{13}O_4Cl$: Cl, 12.12. Found: 12.09.

3-Chloro-4,5-dibromopyrogallol-2,6-dimethyl Ether.—Five g. of the monochloro derivative was dissolved in 100 cc. of carbon disulfide, and an excess of bromine was added. The solvent was distilled and the residue crystallized first from 80% acetic acid and then from dil. alcohol. It crystallizes in long needles melting at 124–125°. This substance is soluble in most organic solvents but insoluble in water.

Anal. Subs., 0.1842, 0.2145: mixed halides, 0.2745, 0.3200. Calcd. for $C_8H_7O_3Br_2Cl$: Cl, 10.23; Br, 46.14. Found: Cl, 10.18, 10.19; Br, 45.90, 45.94.

THE ACETATE, prepared by acetylation of the compound described above with acetyl chloride, crystallizes from dilute alcohol in small plates; it melts at 107–108°.

Anal. Subs., 0.1967: mixed halides: 0.2634. Calcd. for $C_{10}H_9O_4Br_2Cl$: Cl, 9.14; Br, 41.18. Found: Cl, 9.15; Br, 41.24.

THE BENZOATE was prepared by the Schotten-Baumann process. It was crystallized from glacial acetic acid and from 95% alcohol, forming plates melting at 119–120°.

Anal. Subs., 0.2025: mixed halides, 0.2310. Calcd. for $C_{15}H_{11}O_4Br_2Cl$: Cl, 7.87; Br, 35.48. Found: Cl, 7.79; Br, 35.11.

Oxidation of 3-Chloropyrogallol-2,6-dimethyl Ether.—Three g. of the phenol described above was dissolved in 50 cc. of 20% acetic acid. To this solution was added 2.5 g. of chromium trioxide. 3,3'-Dichloro-2,6,2',6'-tetramethoxy-biphenoquinone precipitated on standing; yield, 60%. The filtrate, on extraction with ether, gave a small quantity of presumably 3-chloro-2,6-dimethoxy-*p*-benzoquinone, since on bromination 3-chloro-2,6-dimethoxy-*p*-benzoquinone was formed.

3,3'-Dichloro-2,6,2',6'-tetramethoxy-biphenoquinone.—This substance, obtained as described above, was crystallized from glacial acetic acid, forming scale-like crystals, with a grayish-purple luster. It is difficultly soluble in alcohol, ether, benzene and cold glacial acetic acid, but readily soluble in hot glacial acetic acid and nitrobenzene. It does not give a blue color with concd. sulfuric acid, differing in this respect from cedriret itself.

Anal. Subs., 0.1885: AgCl, 0.1428. Calcd. for $C_{16}H_{14}O_6Cl_2$: Cl, 18.95. Found: 18.74.

Oxidation of 3-Chloro-4,5-dibromopyrogallol-2,6-dimethyl Ether.—Two g. of this phenol was dissolved in 100 cc. of carbon disulfide, and to this solution 2 g. of chromium trioxide was added. After one-half hour the reaction mixture was poured into 400 cc. of water. A reddish-yellow precipitate formed; yield, 50%. This was crystallized from glacial acetic acid and was found to be identical in every respect with 3-chloro-5-bromo-2,6-dimethoxy-*p*-benzoquinone previously described.[1]

3-Chloro-5-bromo-2,6-dimethoxy-hydroquinone.—One g. of the quinone described above was dissolved in 100 cc. of acetone containing a little water. Sulfur dioxide was passed into this solution until it was decolorized. The solution was concentrated to about one-half its original volume from which long, needle-like crystals formed on cooling. These were recrystallized from dil. alcohol, giving a pure product of 3-chloro-5-bromo-2,6-dimethoxy-hydroquinone; m. p., 146°; yield, almost quantitative. It was not analyzed.

THE DIACETATE.—The hydroquinone described above was treated with an excess of acetyl chloride and the resulting product crystallized from dilute alcohol; m. p., 85–86°.

Anal. Subs., 0.1765: mixed halides, 0.1676. Calcd. for $C_{12}H_{12}O_6BrCl$: Cl, 9.64; Br, 21.74. Found: Cl, 9.56; Br, 21.55.

Summary

It has been shown that the first substituent chlorine atom enters the *meta* position to the hydroxyl group.

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[CONTRIBUTION FROM THE PHYTOCHEMICAL LABORATORY OF THE BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

NON-VOLATILE CONSTITUENTS OF THE COTTON PLANT

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In a previous communication by the present authors[1] an account was given of the odorous constituents of the cotton plant. As those substances were all of a volatile nature, the respective investigation was restricted to such products from the plant as could be obtained by distillation with steam. It seemed to us, however, of importance and interest to extend the investigation by examining also the non-volatile constituents of the plant, as so little had been known regarding them and the work on the subject would thus be rendered more complete. With this purpose in view a quantity of material was collected during the same season and from the same field at Tallulah, Louisiana, as the plants which were previously employed for distillation.

The material used, which was collected during the month of July, 1923, consisted of the branches of the plant which had been stripped from the coarse, woody stems. It therefore comprised chiefly the foliage, "squares" and flowers, all the bolls which had then been developed having been carefully removed. The total weight of fresh material was 169.2 kg., and when thoroughly air-dried and ground it amounted to 34 kg. The loss of weight on drying was thus nearly 80%.

Experimental Part

Test for Alkaloid.—A small portion (25 g.) of the ground, dried material was digested for three days with Prollius' fluid, the liquid then filtered,

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[1] Power and Chesnut, THIS JOURNAL, **47**, 1751 (1925).