just below 19° for then the alpha crystals can be seen to melt and the liquid to recrystallize into the beta form.

Discussion.—We are dealing here without doubt with a case of dimorphism. The very marked difference in melting point of the two forms, a difference which cannot be accounted for on the basis of chemical composition, would be sufficient evidence. In addition, however, we have shown the difference in the crystalline structure, the stable form belonging, as usual, to a less symmetric system than the unstable. Again, the difference in densities is quite marked, being higher by nearly 6% in the case of the stable beta form.

Furthermore, the fact brought out in a previous paper that the passage from the alpha to the beta form takes place with evolution of heat settles the question as to which is the stable and which the unstable form under atmospheric conditions.

Summary

1. The two forms of furfuryl furoate have been shown to crystallize in different systems. The unstable form crystallizes in the monoclinic system, prismatic class and the stable beta form in the triclinic system, pinacoidal class.
2. The alpha form shows d_4 1.330 and the beta form d_4 1.395.
3. Attention is called to the pseudomorphism of the beta form.

NEW YORK, N. Y.

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

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

BY ARTHUR A. LEVINE

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In an investigation on the oxidation of certain halogenated derivatives of pyrogalloldimethyl ether, it was desired to make the *p*-bromo derivative. On account of the strong orienting influence of the methoxyl groups, it did not seem certain that the bromine would enter the *para* position to the hydroxyl. For instance, Brand and Collischonn[1] showed that the action of acetic anhydride introduces an acetyl group *meta* to the hydroxyl. On the other hand Hofmann,[2] and Graebe and Martz[3] showed that by the Reimer-Tiemann's reaction, syringic aldehyde is formed.

It has been found that the first bromine atom substitutes in the *meta* position, giving the 3-bromo derivative as the sole product that can be

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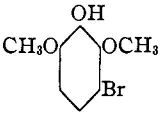
[1] Brand and Collischonn, *J. prakt. Chem.*, **103**, 329 (1922).

[2] Hofmann, *Ber.*, **11**, 1455 (1878).

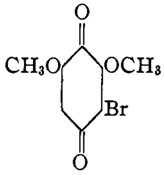
[3] Graebe and Martz, *Ber.*, **36**, 1031 (1903).

identified as present. If any of the isomeric 4-bromo derivative was formed it could not be detected, nor has it been possible to find experimental conditions which will lead to its formation.

The position taken by the bromine atom has been determined by three different methods.



I



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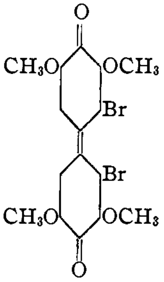

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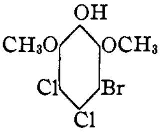

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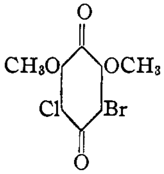
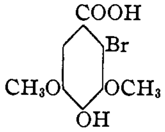


V



VI

1.—The monobromodimethyl ether was oxidized with chromium trioxide, which produced a 5% yield of 3-bromo-2,6-dimethoxy-*p*-benzoquinone II, and 90% of 3,3′-dibromo-2,6,2′,6′-tetramethoxy-biphenoquinone [3,3′-dibromo-cedriret] III. The formation of these brominated *para*-quinones is possible only when the bromine atom is in the *meta* position to the hydroxyl in the original phenol.

2.—The monobromodimethyl ether was chlorinated to 3-bromo-4,5-dichloropyrogallol-2,6-dimethyl ether IV, which in turn gave on oxidation with chromium trioxide in glacial acetic acid, 3-bromo-5-chloro-2,6-dimethoxy-*p*-benzoquinone V.

3.—In order to prove the position of the bromine atom in II, syringic acid was brominated, giving the monobromo derivative VI, which in turn was oxidized to 3-bromo-2,6-dimethoxy-*p*-benzoquinone II. This on chlorination gave 3-bromo-5-chloro-2,6-dimethoxy-*p*-benzoquinone.

Experimental Part

3-Bromopyrogallol-2,6-dimethyl Ether.—To 10 g. of pyrogallol-2,6-dimethyl ether in 100 cc. of carbon disulfide was added 26.4 cc. of a solution of bromine in carbon disulfide containing 0.384 g. of bromine per cc. The solvent was distilled and the residue fractionated in a vacuum, giving a product boiling at 185–190° (40 mm.); yield, 80%.

Anal. Subs., 0.1746, 0.1524: AgBr, 0.1391, 0.1225. Calcd. for $C_8H_9O_3Br$: Br, 34.30. Found: 33.93, 34.21.

3-Bromo-4,5-dichloropyrogallol-2,6-dimethyl Ether.—This was prepared by brominating 10 g. of the dimethyl ether as described above and subsequently passing into the carbon disulfide solution an excess of chlorine. The carbon disulfide was evaporated, and the residue was crystallized from dil. alcohol, forming long needle-like crystals; m. p., 127–128°; yield, 85%. It is soluble in the usual organic solvents save ligroin, and insoluble in water.

Anal. Subs., 0.1710: mixed halides, 0.2665. Calcd. for $C_8H_7O_3BrCl_2$: Br, 26.47; Cl, 23.59. Found: Br, 26.30; Cl, 23.30.

THE BENZOATE.—This was prepared by treating the sodium salt of the compound, prepared as described above, with benzoyl chloride and crystallizing the resulting product from dil. alcohol, from which it crystallizes in scales; m. p., 114–115°.

Anal. Subs., 0.1231: mixed halides, 0.1444. Calcd. for $C_{15}H_{11}O_4BrCl_2$: Br, 19.69; Cl, 17.47. Found: Br, 19.72; Cl, 17.53.

THE ACETATE was prepared by acetylation of 3-bromo-4,5-dichloropyrogallol-2,6-dimethyl ether with acetyl chloride. It crystallizes from dilute alcohol in scales; m. p., 97–98°.

Anal. Subs., 0.0738: mixed halides, 0.1017. Calcd. for $C_{10}H_9O_4BrCl_2$: Br, 23.24; Cl, 20.62. Found: Br, 23.21; Cl, 20.59.

2-Bromosyringic Acid.—Ten g. of syringic acid in 150 cc. of chloroform and 8.4 g. of bromine were refluxed together for two hours. The chloroform was evaporated and the product was crystallized from very dilute acetic acid, forming long needles; m. p., 155°. This substance is readily soluble in chloroform, acetic acid and alcohol, but moderately soluble in other solvents; yield, 95%.

Anal. Subs., 0.1285: AgBr, 0.0873. Calcd. for $C_9H_9O_5Br$: Br, 28.85. Found: 28.91.

OXIDATION.—To 5 g. of 2-bromosyringic acid, dissolved in 200 cc. of water acidified with 10 cc. of dil. sulfuric acid, was added 2.4 g. of chromium trioxide in small portions at a time, during vigorous stirring. The reddish-yellow precipitate that formed on standing was filtered off and was found to be 3-bromo-2,6-dimethoxy-*p*-benzoquinone, as is shown in the next section.

3-Bromo-2,6-dimethoxy-*p*-benzoquinone.—This was obtained on oxidation of bromosyringic acid as described above, in a yield of 62%, and was crystallized from glacial acetic acid, forming short, reddish-yellow needles; m. p., 148°. It is soluble in benzene, alcohol, chloroform and glacial acetic acid, but insoluble in water and ligroin.

Anal. Subs., 0.2439, 0.1722: AgBr, 0.1863, 0.1315. Calcd. for $C_8H_7O_4Br$: Br, 32.37. Found: 32.50, 32.43.

OXIDATION OF 3-BROMOPYROGALLOL-2,6-DIMETHYL ETHER.—Five g. of the compound described above was dissolved in 200 cc. of 50% acetic acid, and to this solution 2.5 g. of chromium trioxide was added. The precipitate, 3,3′-dibromo-2,6,2′,6′-tetramethoxy-biphenoquinonine, was filtered off; yield, 90% of impure product. The filtrate was extracted with ether, giving a 5% yield of 3-bromo-2,6-dimethoxy-*p*-benzoquinone.

3,3′-Dibromo-2,6,2′,6′-tetramethoxy-biphenoquinone, (Dibromo-cedriret).—The oxidation product obtained as described above was crystallized from nitrobenzene, forming gray scales; m. p., 254°. It is moderately soluble in ordinary organic solvents, and readily soluble in nitrobenzene.

Anal. Subs., 0.2408, 0.2627: AgBr, 0.1935, 0.2105. Calcd. for $C_{16}H_{14}O_6Br_2$: Br, 34.60. Found: 34.20, 34.10.

3,3′-Dibromo-hexahydroxybiphenyl-2,6,2′,6′-tetramethyl Ether, (Dibromohydrocedriret).—This was prepared by reducing dibromo-cedriret with sulfur dioxide in moist acetone. Upon addition of water a precipitate formed. This was crystallized from glacial acetic acid, forming scales melting at 262° and is identical with the dibromohexahydroxy-biphenyltetramethyl ether, obtained by Hayduck[4] on bromination of the diacetate of hydrocedriret and subsequent hydrolysis of that product.

Anal. Subs., 0.1149: AgBr, 0.0924. Calcd. for $C_{16}H_{18}O_6Br_2$: Br, 34.45. Found: 34.22.

Oxidation of 3-Bromo-4,5-dichloropyrogallol-2,6-dimethyl Ether.—This was effected by dissolving 5 g. of the phenol in 200 cc. of glacial acetic acid and adding 2.5 g. of chromium trioxide. After one-half hour, the solution was poured into about 400 cc. of water, from which 3-bromo-5-chloro-2,6-dimethoxy-*p*-benzoquinone separated; yield, 45%.

3-Bromo-5-chloro-2,6-dimethoxy-*p*-benzoquinone.—This was recrystallized from glacial acetic acid, forming red, scale-like crystals. It melts at 164–165° and is soluble in most organic solvents, save ligroin. It is insoluble in water. It is identical with the substance obtained on chlorination of 3-bromo-2,6-dimethoxy-*p*-benzoquinone, dissolved in chloroform.

Anal. Subs., 0.1743, 0.0942: mixed halides, 0.2050, 0.1102. Calcd. for $C_8H_6O_4BrCl$: Br, 28.46; Cl, 12.45. Found: Br, 28.39, 28.40; Cl, 12.74, 12.60.

Summary

It has been shown that the first substituent bromine atom enters the *meta* position to the hydroxyl in pyrogallol-2,6-dimethyl ether. That is, the combined orienting effect of the two methoxy groups is greater than that of the hydroxyl.

Pullman, Washington

[Contribution from the Chemical Laboratory of the University of Louisville]

CONDENSATION OF 9-METHYLACRIDINE WITH FORMALDEHYDE AND THE PREPARATION OF ACRIDINE-9-CARBOXYLIC ACID

By A. W. Homberger and H. Jensen

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Introduction

It is known that the methyl group of 9-methylacridine forms condensation products with aldehydes.[1]

The first possible reaction will give a condensation product of the aldol type; the second reaction takes place with elimination of water.

The present investigation was undertaken with a view to prepare condensation products of methylacridine with formaldehyde in order to use these products as starting material in the preparation of acridine-9-carboxylic acid.

Koenig tried to condense methylacridine with formaldehyde but was unable to secure a crystalline product.[1b] The authors chose conditions

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

[1] (a) Bernthsen, *Ber.*, **20**, 1541 (1887). (b) Koenig, *Ber.*, **32**, 3599 (1899). (c) Friedländer, *Ber.*, **38**, 2840 (1905). (d) Porai-Koschitz, *Chem. Centr.*, **1907**, [II] 1528. (e) Kaufmann, *Ber.*, **45**, 1737 (1912).