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THE REDUCTION OF BROMO DERIVATIVES OF CATECHOL, RESORCINOL, AND PYROGALLOL

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In the course of investigations of the reduction of brominated phenols (1) by zinc dust in acetic acid, among the dihydroxybenzenes a series of hydroquinone derivatives was studied. It developed, however, that brominated catechols also are attacked in the same reaction with extraordinary ease and rapidity. Thus, from tetrabromocatechol, even by quite brief action of zinc dust and acetic acid, a tribromocatechol (m.p. 106°) was obtained, which was characterized by preparation of its dimethyl ether (m.p. 69°) and its diacetate (m.p. 141°). The existence of two isomeric tribromocatechols can be predicted, 1,2-dihydroxy-3,4,5-tribromobenzene (I) and 1,2-dihydroxy-3,4,6-tribromobenzene (II).



I is the 3,4,5-tribromocatechol of m.p. 139°, dimethyl ether m.p. 86°, which is obtained by direct bromination of catechol (2). There can therefore be no doubt that the above described tribromocatechol is the 3,4,6-tribromocatechol (II). Observations in the Vienna laboratory have shown that in debromination of brominated phenols with zinc and acetic acid, bromine atoms ortho to the hydroxyl are replaced by hydrogen with special ease. It was therefore from the outset to be expected that in this case also an ortho bromine would be replaced, which would give I, a presumption that did not hold.²

Tetrabromoguaiacol (III) is also debrominated with extreme ease, with formation of a dibromoguaiacol. On the basis of previous experiences, it was to be expected that two bromine atoms para to each other would be removed, as was actually the case. The dibromoguaiacol obtained melted at 94°, and is therefore identical with 4,5-dibromoguaiacol (IV) (3). This was confirmed by methylation, which yielded 4,5-dibromoveratrole (V) (4) of m.p. 92°.

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² In the reductive acetylation of tetrabromocatechol with zinc dust and acetic anhydride, Kohn and Pfeifer (1 a) obtained a dibromocatechol diacetate of m.p. 173°. Purely by analogy, the substance was regarded as 3,5-dibromocatechol diacetate. The results of the present investigation, showing that a bromine para to a hydroxyl can be removed, casts doubt on the structure of the 173° acetate.



In the reductive acetylation of 2,4,6-tribromoresorcinol, Kohn and Pfeifer (1 a) obtained a dibromoresorcinol diacetate of m.p. 94°. This was regarded as 4,6-dibromoresorcinol diacetate (VI), formed by replacement of the bromine between the two hydroxyls by hydrogen. Proof of the validity of this assumption can now be offered; boiling 2,4,6-tribromoresorcinol with zinc dust and acetic acid gave 4,6-dibromoresorcinol, which was further identified through its dimethyl ether (5) of m.p. 141°. Acetylation of 4,6-dibromoresorcinol gave the same diacetate as that from the reductive acetylation of tribromoresorcinol.

With other reducing agents, as sulfites or stannous chloride, tribromoresorcinol behaves quite differently. Davis and Harrington (6) established that under these conditions the bromine between the hydroxyls did not exchange.

4,5,6-Tribromopyrogallol 1,3-dimethyl ether (VII) (7) exchanges two bromine atoms for hydrogen with zinc dust and acetic acid, with formation of a new monobromopyrogallol dimethyl ether. Here also was to be expected that the bromine para to the hydroxyl would not be removed, and that 5-bromopyrogallol 1,3-dimethyl ether (VIII) would result. That this is actually so was shown by methylation, which gave a compound which must be 5-bromopyrogallol trimethyl ether (IX), since it is a solid (m.p. 78°), whereas the isomeric 4-bromopyrogallol trimethyl ether (X) (7, 8) is a liquid.



That the 5-bromo compound would melt higher than the 4-bromo would be expected from the symmetrical structure of the molecule. This fact is also in agreement with the observation of Gräbe and Suter (9) with the two isomeric chloropyrogallol trimethyl ethers. The 5-chloro ether is solid, whereas the 4chloro ether is liquid.

EXPERIMENTAL

3,4,6-Tribromocatechol (II). Ten grams of tetrabromocatechol (10) in 30 cc. of glacial acetic acid, with 10 cc. of water and 8 g. of zinc dust, was refluxed for 4 minutes with continuous shaking. The filtered liquid, on dilution with water, precipitated a solid, which was recrystallized from boiling water; thin needles of m.p. 106°.

Anal. Calc'd for C₆H₈Br₃O₂: C, 20.7; H, 0.86.

Found: C, 21.14; H, 1.06.

By methylation with alkali and dimethyl sulfate, 3,4,6-tribromoveratrole was obtained, which crystallized from alcohol in needles of m.p. 69°.

Anal. Calc'd for C₈H,Br₈O₂: C, 25.6; H, 1.86; Br, 64.0; 20CH₃, 16.5.

Found: C, 25.65; H, 1.98; Br, 63.6; OCH₃, 16.63.

3,4,6-Tribroveratrole boils without appreciable decomposition at $315-317^{\circ} (uncorr.)/736$ mm. The distillate, crystallized from alcohol, melted at 69° .

3,4,6-Tribromocatechol diacetate. 3,4,6-Tribromocatechol was refluxed 5 hours with five times its weight of acetic anhydride. It was poured into water, filtered, and crystallized from alcohol; prismatic needles, m.p. 141°.

Anal. Calc'd for C₁₀H₇Br₃O₄: C, 27.84; H, 1.62.

Found: C, 28.17; H, 1.71.

4,5-Dibromoguaiacol (IV) from tetrabromoguaiacol (III). Ten grams of tetrabromoguaiacol (11) with 30 cc. of glacial acetic acid, 10 cc. of water, and 8 g. of zinc dust was refluxed for 5 minutes. On filtration into water, an oil separated, which solidified in a few hours. The solid was dried in a vacuum and recrystallized from ligroin with the use of charcoal; m.p. 94°.

Anal. Calc'd for C₇H₆Br₂O₂: C, 29.76; H, 2.12.

Found: C, 29.71; H, 2.49.

Methylation of the dibromoguai acol gave the known 4,5-dibromoveratrole (V) of m.p. 92°.

Anal. Cale'd for C8H8Br2O2: C, 32.43; H, 2.72; 2 OCH3, 20.9.

Found: C, 32.46; H, 2.74; OCH₃, 21.06.

4,6-Dibromoresorcinol from 2,4,6-tribromoresorcinol. Thirty grams of 2,4,6-tribromoresorcinol in 20 cc. of acetic acid with 30 cc. of water and 25 g. of zinc dust was refluxed for 12 minutes. It was filtered into water, and salted out with sodium chloride. The white needles were recrystallized from water, m.p. 112°. Methylation and recrystallization from alcohol gave 4,6-dibromoresorcinol dimethyl ether of m.p. 141°. Acetylation of 4,6-dibromoresorcinol gave the diacetate (from alcohol) of m.p. 94°.

5-Bromopyrogallol 1,3-dimethyl ether (VIII) from tribromopyrogallol 1,3-dimethyl ether (VII). Twenty grams of tribromopyrogallol 1,3-dimethyl ether in 35 cc. of acetic acid and 40 cc. of water with 20 g. of zinc dust was refluxed for 45 minutes. It was poured into water, and the oil which separated solidified after several hours in a freezing mixture. The product was recrystallized from boiling dilute acetic acid, dried in a vacuum, and recrystallized from ligroin; woolly needles of m.p. 106°.

Anal. Calc'd for C₈H₈BrO₃: C, 41.2; H, 3.86; Br, 34.33.

Found: C, 41.57; H, 3.89; Br, 34.02.

The benzoyl derivative crystallized from alcohol, m.p. 119°.

Anal. Calc'd for C₁₅H₁₃BrO₄: C, 53.4; H, 3.85; Br, 23.73.

Found: C, 53.33; H, 3.90; Br, 23.64.

5-Bromopyrogallol trimethyl ether (IX). On methylation of 5-bromopyrogallol 1,3-dimethyl ether, an oil separated, which became solid when shaken. After dilution with water, it was recrystallized from dilute alcohol, then from petroleum ether; m.p. 78°.

Anal. Calc'd for C₉H₁₁BrO₃: C, 43.73; H, 4.42.

Found: C, 43.94; H, 4.61.

The substance boiled at 269–273° (uncorr.)/747 mm.; (the b.p. of tribromopyrogallol trimethyl ether is 341° (uncorr.)/759 mm.).

SUMMARY

1. The action of zinc dust and acetic acid on tetrabromocatechol gives 3,4,6-tribromocatechol through replacement of a bromine para to a hydroxyl by hydrogen.

2. Tetrabromoguaiacol, by replacement of two para situated bromine atoms, gives 4,5-dibromoguaiacol.

3. 2,4,6-Tribromoresorcinol suffers replacement of the bromine between the two hydroxyls, to give 4,6-dibromoresorcinol.

4. Tribromopyrogallol 1,3-dimethyl ether exchanges the two bromine atoms meta to the hydroxyl for hydrogen, giving 5-bromopyrogallol 1,3-dimethyl ether.

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