

Anal. Calcd. for $C_{14}H_6O_2I_2$: I, 55.21. Found: I, 55.0, 55.3.

1,2-Diiodoanthraquinone.—This was prepared in a manner similar to that used with the 2,3-isomer. It crystallized in orange-red plates from a benzene-toluene mixture and melted at 236–237°.

Anal. Calcd. for $C_{14}H_6O_2I_2$: I, 55.21. Found: I, 55.6, 55.6.

1,4-Diiodoanthraquinone.—From heating 2 g. of 2-benzoyl-3,6-diiodobenzoic acid with 75 g. of 100% sulfuric acid at 100° for two hours, was obtained 1.1 g. (60%) of the anthraquinone. After crystallizing from alcohol it melted at 218–219°.

Anal. Calcd. for $C_{14}H_6O_2I_2$: I, 55.21. Found: I, 55.4, 55.3, 55.7.

1,2,4-Triiodoanthraquinone.—A. Two grams of the high-melting benzoyltriiodobenzoic acid was added to 60 g. of 100% sulfuric acid kept at 105° over a thirty-minute period with stirring and the mixture heated and stirred for thirty minutes longer. It was then cooled and poured on ice and the resulting colloidal suspension coagulated by heating on the steam-bath. The precipitate was then treated with dilute sodium hydroxide. The red residue upon crystallization from acetic acid yielded 0.5 g. of

product melting at 202–204°. This is about 25% of the theoretical amount. Alterations in these conditions did not improve the yield.

B. From treatment of the low-melting benzoyltriiodobenzoic acid as in A was obtained 0.4 g. of the anthraquinone. After two crystallizations from acetic acid the m. p. was 202–203.5°.

Anal. Calcd. for $C_{14}H_6O_2I_3$: I, 64.84. Found: I, 64.9, 65.0.

Summary

1. The condensation of di- and triiodophthalic anhydrides with benzene and aluminum chloride gives good yields of the benzoylbenzoic acids.

2. Ring closure of benzoyldiiodobenzoic acids is readily effected by treatment with 100% sulfuric acid. The triiodo compounds give smaller yields of the triiodoanthraquinones.

3. Veratrole and 4-chloroveratrole do not condense readily with iodinated phthalic anhydrides. Work upon the synthesis of iodinated hydroxyanthraquinones is being continued.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF EX-LAX, INC.]

3,3'-Dimethyl-4,4'-dihydroxybenzophenone

BY MAX H. HUBACHER

During the progress of some work being carried out recently, it became necessary to prepare a quantity of 3,3'-dimethyl-4,4'-dihydroxybenzophenone. This was done by a caustic potash fusion of *o*-cresolphthalein.¹

Since the properties of the compound prepared from *o*-cresolphthalein did not agree with those recorded by Doebner and Schroeder,² an investigation of this discrepancy was made in order to determine the true properties of this material. These chemists obtained a compound which they designated as dioxydimethylbenzophenone, melting at 138°, by caustic potash fusion of *o*-cresolbenzein. For an analysis they report, calculated for $C_{15}H_{14}O_3$: C, 78.51; found, 78.19. Evidently, an error was made in calculation as the value for carbon is 74.36.

A caustic potash fusion of *o*-cresolbenzein produced no trace of a compound melting at 138°. Instead, a product melting at 247° was obtained which was identical with that from *o*-cresol-

phthalein. That the compound of melting point 247° was the expected 3,3'-dimethyl-4,4'-dihydroxybenzophenone was confirmed by analysis and the preparation of the diacetyl derivative and the mono and dimethyl ethers. On prolonged fusion with caustic potash, the benzophenone was converted into *o*-cresol and 3-methyl-4-hydroxybenzoic acid.

Experimental³

3,3' - Dimethyl - 4,4' - dihydroxybenzophenone (I).—Seventy grams of potassium hydroxide was heated in a nickel crucible to 260–265° (oil-bath temperature) and 10 g. of *o*-cresolphthalein of m. p. 224–225° was stirred in. After ten minutes, the melt was poured into 1.5 liters of water and acidified with hydrochloric acid. The 6.60 g. of crude was crystallized from 75 cc. of glacial acetic acid; 4.85 g. (69.3%) of (I), melting at 246–247° was obtained. A second crystallization or a sublimation *in vacuo*⁴ at 180° gave a pure product, melting point 247.0–247.8°. It formed colorless needles from 20% ethanol and rectangular plates from acetic acid. It dissolved in both sodium hydroxide or concd. sulfuric acid with yellow color.

(3) All melting points are corrected.

(4) All the sublimations were done in a vacuum produced by a CenCO-HyvAC pump guaranteed to produce a vacuum of 0.3 micron.

(1) A. v. Baeyer, *Ann.*, **202**, 126 (1880); W. R. Orndorff and W. R. Barrett, *This Journal*, **46**, 2488 (1924).

(2) O. Doebner and G. Schroeder, *Ann.*, **257**, 74 (1890).

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 74.36; H, 5.82; mol. wt., 242. Found: C, 74.42; H, 5.95; mol. wt. (Rast, in camphor), 237, 241.

The aqueous mother liquor from the crude (I) yielded 1.09 g. of benzoic acid.

3,3'-Dimethyl-4,4'-diacetoxybenzophenone was prepared by refluxing 2.42 g. of (I), 3.1 g. of acetic anhydride, 10 cc. of acetic acid and one drop of concd. sulfuric acid; 3.11 g. (95%) was obtained. The pure compound formed thin plates from ethanol and melted at 106.8–107.2°.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 69.91; H, 5.56. Found: C, 70.21; H, 5.53.

3,3'-Dimethyl-4,4'-dimethoxybenzophenone (II).—To 2.42 g. of (I) in 60 cc. of normal sodium methylate was added 5.0 g. of dimethyl sulfate and the mixture refluxed for one hour. After the evaporation of the methanol and taking up in water, the alkali insoluble portion weighed 0.85 g. After sublimation *in vacuo* at 100°⁴ and crystallization from 50% ethanol, the dimethyl ether (II) melted at 113.7–114.2° (silky needles).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 75.52; H, 6.71. Found: C, 75.71; H, 6.83.

3,3'-Dimethyl-4,4'-dimethoxybenzophenoneoxime.—1.35 g. of (II) and 0.70 g. of hydroxylamine hydrochloride in 4 cc. of pyridine were heated for three hours to 90°. The oxime (1.41 g.) melted at 160.9–161.2° after crystallizations from ethanol.

Anal. Calcd. for $C_{17}H_{18}O_2N$: N, 4.91. Found: N, 5.14.

3,3'-Dimethyl-4-methoxy-4'-hydroxybenzophenone.—The alkali soluble portion from the methylation of (I) above weighed 1.61 g. After sublimation *in vacuo* at 180°⁴ followed by several crystallizations from ethanol, the pure monomethyl ether melted at 203.7–204.2°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.96; H, 6.29; OCH_3 , 12.11. Found: C, 74.77, 75.57; H, 5.91, 6.55; OCH_3 , 11.97.

Fusion of *o*-Cresolbenzein with Potassium Hydroxide.—Five grams of *o*-cresolbenzein² and 30 g. of potassium hydroxide were heated for ten minutes at 260–265° (oil-bath

temperature). The crude, after one crystallization from glacial acetic acid, weighed 2.31 g. (61%) and melted at 246.0–247.3°. Neither a mixture of this material with (I) nor a mixture of the diacetyl derivatives showed a depression of the melting points.

Fusion of (I) with Potassium Hydroxide.—Ten grams of (I) prepared from *o*-cresolphthalein and 50 g. of potassium hydroxide were heated for one hundred and ten minutes at 280°. The fusion was poured into water and saturated with carbon dioxide. The ether extract was distilled, the fraction boiling at 186–190°, weighing 3.77 g. The 2,4-dinitrophenyl ether prepared from this fraction melted at 88.4–88.8° and showed no depression when mixed with a known sample of 2,4-dinitrophenyl *o*-cresyl ether of m. p. 88.7–90.0°.

The aqueous solution was acidified and the precipitate purified by sublimation at 160° *in vacuo* (5.41 g.), a crystallization from water, followed by a second sublimation. The 3-methyl-4-hydroxybenzoic acid melted at 173.9–175.0°⁵. Neutralization equiv. calcd. 152, found 151.3. The methyl ether melted at 195.9–196.2°⁶ and the ethyl ester at 95.0–96.6°.⁷

Summary

3,3'-Dimethyl-4,4'-dihydroxybenzophenone was made by caustic potash fusion of *o*-cresolphthalein and of *o*-cresolbenzein. Its diacetyl derivative and the mono and dimethyl ethers were prepared. The structure was shown by its conversion into *o*-cresol and 3-methyl-4-hydroxybenzoic acid.

The 3,3'-dimethyl-4,4'-dihydroxybenzophenone reported by Doebner and Schroeder as melting at 138° is incorrect.

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(5) F. Tiemann and C. Schotten, *Ber.*, **11**, 777 (1878), gave a m. p. of 172–175° for 3-methyl-4-hydroxybenzoic acid.

(6) C. Schall, *ibid.*, **12**, 825 (1879), reported a m. p. of 192–193° for the 3-methyl-4-methoxybenzoic acid.

(7) K. Auwers, *ibid.*, **39**, 3174 (1906), gave a m. p. of 98–99° for the ethyl ester of 3-methyl-4-hydroxybenzoic acid.