

prepared in essential accordance with the three-stage procedure of Meldrum and Shah.¹²

The methyl ester was prepared from the acid with methanol and hydrogen chloride in 92% yield. After crystallization from dilute methanol, the ester melted at 62°.

Anal. Calcd. for C₈H₇O₃Br: Br, 34.6. Found: Br, 34.4.

In an attempt to prepare dibenzo-*p*-dioxin-1,6-dicarboxylic acid, there was added to a solution made up by dissolving one g. of sodium in 10 cc. of methanol, 9.2 g. (0.04 mole) of methyl 3-bromosalicylate. The methanol was removed at reduced pressure, and the residue was subjected to dry distillation. The material gradually charred and no product distilled when the bath temperature reached 300°.

(12) Meldrum and Shah, *J. Chem. Soc.*, **123**, 1990 (1923). We had no appreciable success in preparing the acid by the method of Sen and Ray, *J. Indian Chem. Soc.*, **9**, 173 (1932).

Summary

Metalation of thianthrene by *n*-butyllithium followed by carbonation and hydrolysis, gives 1-thianthrenecarboxylic acid, the structure of which was established by a ring-closure synthesis. Accordingly, the other thianthrenecarboxylic acid prepared by earlier workers by a modified Friedel-Crafts reaction must be the 2-acid. Incidentally, it was shown that sulfur with *n*-butyllithium gives *n*-butyl mercaptan, di-*n*-butyl sulfide, and di-*n*-butyl tetrasulfide.

Dibenzo-*p*-dioxin is mono-metated by methyl-lithium in the 1-position. With *n*-butyllithium, two dimetalation products are formed.

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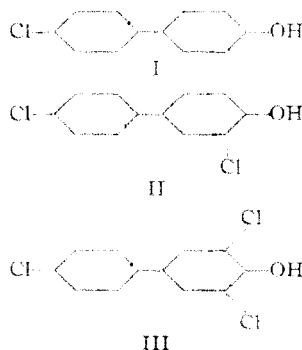
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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF TEXAS AND SOUTHWESTERN LOUISIANA INSTITUTE]

Studies in the Biphenyl Series. III. The Attempted Chlorination of the Acetate, Benzoate and Benzenesulfonate of 4-(4-Chlorophenyl)-phenol: 2-Chloro-4-(4-chlorophenyl)-phenol¹

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In connection with the study of the relationship of bactericidal activity² to structure of certain halogenated phenylphenols it was desirable to prepare 2-chloro-4-(4-chlorophenyl)-phenol (II). This was readily accomplished by chlorination of 4-(4-chlorophenyl)-phenol (I). Further chlorination gave rise to the known 2,6-dichloro-4-(4-chlorophenyl)-phenol (III), which incidentally served to prove the structure of II.



(1) The main portion of this investigation was the subject of a research course taken by Mrs. Savoy while working toward the degree of Master of Arts at the University of Texas. Present address: Department of Chemistry, Southwestern Louisiana Institute, Lafayette, Louisiana.

(2) Professor O. B. Williams of the Department of Bacteriology of the University of Texas is directing the testing of the phenol coefficients of these substances in an independent investigation.

In previous investigations,³ in this series it has been demonstrated that chlorination of the 4-phenylphenyl esters introduces chlorine in the 4'-position of the biphenyl nucleus. It was of interest to see if utilization of these same mild chlorinating conditions would introduce chlorine ortho to the ester linkage, if the 4'-position was already substituted with chlorine. Hence the acetate, benzoate and benzenesulfonate of II were subjected to the chlorination procedure, using iodine as the catalyst and carbon tetrachloride as the solvent. None of the anticipated esters resulted. This would lend support to the view that the ester linkage hinders the 3-position.

Although none of the 2-chloro-4-(4-chlorophenyl) esters were identified in the reaction products of the chlorination of the esters of II, these esters were readily prepared by respective acetylation, benzoylation and benzenesulfonation of I.

Acknowledgment.—The authors are indebted to the Research Institute of the University of Texas for a grant which made this investigation possible. We are indebted to Professor H. R. Henze for assistance during the progress of this investigation.

(3) Savoy and Abernethy, *THIS JOURNAL*, **64**, 2219, 2719 (1942).

Experimental

Attempted Chlorination of the Acetate, Benzoate and Benzenesulfonate of 4-(4-Chlorophenyl)-phenol.—The esters were dissolved in separate portions of carbon tetrachloride to which had been added a trace of iodine. A slight excess over the theoretical amount of chlorine dissolved in carbon tetrachloride was introduced dropwise into each of these esters over a period of two hours and the solution was stirred for an additional two hours. The solvent was removed under reduced pressure in each instance. Fractional crystallization of the acetate and benzoate did not yield any of the 2-chloro-4-(4-chlorophenyl)-phenyl esters, but a large quantity of original was obtained.

In the case of the benzenesulfonate, the oily product was distilled under reduced pressure (0.2–0.4 mm.). The distillate yielded a small quantity of the original ester along with an oily product. Attempts to isolate 2-chloro-4-(4-chlorophenyl)-phenyl benzenesulfonate were unsuccessful.

2-Chloro-4-(4-chlorophenyl)-phenol (XI).—A solution of 2.0 g. of chlorine in 35 cc. of carbon tetrachloride was added dropwise to 5.1 g. of 4-(4-chlorophenyl)-phenol in 25 cc. of carbon tetrachloride and the mixture was stirred for two hours. Approximately three-fourths of the solvent was removed under reduced pressure. The remaining solution was cooled and an equal volume of petroleum ether (b. p. 60–68°) was added. A white crystalline mass formed which weighed 5.9 g. and melted at 69°. This material was dissolved in hot chloroform, filtered and cooled. An equal volume of petroleum ether was added. A white precipitate formed which weighed 5.5 g. and melted at 71–72°. Further crystallization did not increase the melting point. This represented a 92% yield.

Anal. Calcd. for $C_{12}H_8OCl_2$: Cl, 29.67. Found: Cl, 29.82.

2,6-Dichloro-4-(4-chlorophenyl)-phenol.—(a) To five grams of 2-chloro-4-(4-chlorophenyl)-phenol in 25 cc. of carbon tetrachloride was added 1.7 g. of chlorine in 25 cc. of carbon tetrachloride. The resultant solution was allowed to stand overnight. Approximately three-fourths of the solvent was removed under reduced pressure. The remaining solution was cooled and an equal volume of petroleum ether was added. The resulting crystalline mass was recrystallized from a mixture of chloroform and petroleum ether. There resulted 3.7 g. (64% yield) of 2,6-dichloro-4-(4-chlorophenyl)-phenol, m. p. 144°. A mixed melting point with known 2,6-dichloro-4-(4-chlorophenyl)-phenol melted at 144°. Furthermore, when the substance was acetylated an ester, m. p. 79–79.5°, was formed which did not depress the melting point of the known acetate.

(b) To a solution of 5.1 g. of 4-(4-chlorophenyl)-phenol in 25 cc. of carbon tetrachloride was added 4 g. of chlorine in 50 cc. of carbon tetrachloride and the mixture was allowed to stand overnight. At the end of this time three-fourths of the solvent was removed under reduced pressure and petroleum ether (b. p. 60–68°) was added. The solid mass which separated was removed by filtration and was recrystallized from a mixture of chloroform and petroleum ether. The yield of crude 2,6-dichloro-4-(4-chlorophenyl)-phenol was 6.3 g. (m. p. 134–136°). Recrystallization

once more from the same solvent produced 4.2 g. (62% yield) of the pure material which melted at 144°.

2-Chloro-4-(4-chlorophenyl)-phenyl Acetate.—A mixture of 2 g. of 2-chloro-4-(4-chlorophenyl)-phenol and 10 cc. of acetic anhydride was refluxed for ten minutes, cooled and sufficient crushed ice to make a total volume of 50 cc. was added. A white solid formed immediately and it was removed by filtration, washed and crystallized from methanol. The resultant crystalline material weighed 1.5 g. and melted at 74.5–75°. This represented a 63% yield.

Anal. Calcd. for $C_{14}H_{10}O_2Cl_2$: Cl, 25.24. Found: Cl, 25.19.

2-Chloro-4-(4-chlorophenyl)-phenyl Benzoate.—To a suspension of 2 g. of 2-chloro-4-(4-chlorophenyl)-phenol in 20 cc. of 10% sodium hydroxide was added an excess of benzoyl chloride over a period of ten minutes. The resultant mixture was poured into 20 cc. of water and the solid material removed by filtration. The precipitate was washed with water and recrystallized from ethanol and then from a methanol-carbon tetrachloride mixture. The resultant crystalline material weighed 2.2 g. (76% yield) and melted at 125–126°.

Anal. Calcd. for $C_{16}H_{12}O_2Cl_2$: Cl, 20.67. Found: Cl, 20.65.

2-Chloro-4-(4-chlorophenyl)-phenyl Benzenesulfonate.—To a suspension of 2 g. of 2-chloro-4-(4-chlorophenyl)-phenol in 20 cc. of 10% sodium hydroxide was added an excess of benzenesulfonyl chloride over a period of ten minutes. The mixture was cooled and the solution decanted from the precipitate. Upon being twice recrystallized from ethanol, the resultant ester weighed 2.1 g. (66% yield) and melted at 100–101°.

Anal. Calcd. for $C_{18}H_{12}O_3Cl_2S$: S, 8.457. Found: S, 8.420.

Summary

Attempted chlorination of the acetate, benzoate and benzenesulfonate of 4-(4-chlorophenyl)-phenol did not introduce chlorine in an ortho position to the ester linkage.

2-Chloro-4-(4-chlorophenyl)-phenol has been prepared by the chlorination of 4-(4-chlorophenyl)phenol. Further chlorination yielded 2,6-dichloro-4-(4-chlorophenyl)-phenol.

The acetate, benzoate and benzenesulfonate of 2-chloro-4-(4-chlorophenyl)-phenol have been prepared by respective acetylation, benzoylation and benzenesulfonylation of 2-chloro-4-(4-chlorophenyl)-phenol.

The results of these experiments seem to confirm the conclusion that esterification of 4-phenylphenol hinders chlorination in the 3-position of the biphenyl nucleus and thereby promotes chlorination in the 4'-position.