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THE PREPARATION OF 1,4-DICHLORO-ANTHRAQUINONE FROM PHTHALIC ANHYDRIDE AND PARA-DICHLOROBENZENE

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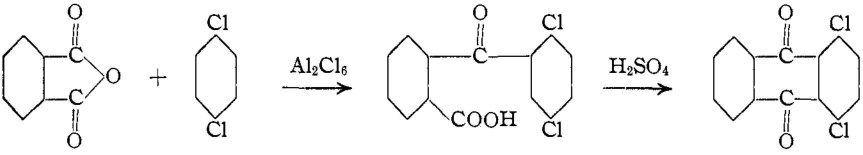
1,4-Dichloro-anthraquinone has been prepared by Graebe,[1] by Walsh and Weizmann[2] and by Ullmann and Billig.[3] The last-mentioned authors prepared it in a pure state by condensing 3,6-dichlorophthalic anhydride with benzene and anhydrous aluminum chloride into 3,6-dichloro-2-benzoylbenzoic acid and converting this into 1,4-dichloro-anthraquinone by dehydration with concd. sulfuric acid.

The present paper describes a method for preparing this dichloro-anthraquinone by condensing phthalic anhydride, *p*-dichlorobenzene and anhydrous aluminum chloride into 2′,5′-dichloro-2-benzoylbenzoic acid and the conversion of this into 1,4-dichloro-anthraquinone. The reactions involved in this synthesis may be depicted by the following structural formulas.



Phthalic anhydride

p-Dichlorobenzene

2′,5′-Dichloro-2-benzoylbenzoic acid

1,4-Dichloro-anthraquinone

Experimental Part

2′,5′-Dichloro-2-benzoylbenzoic Acid.—Fourteen and eight-tenths g. (0.1 mole) of phthalic anhydride, 73.5 g. (0.5 mole) of *p*-dichlorobenzene and 40 g. (0.15 mole) of anhydrous aluminum chloride were placed in a flask provided with an air condenser at the end of which was attached a calcium chloride tube. It was heated in an oil-bath maintained at 110–120° until there was no further evolution of hydrogen chloride (about four hours). The black, viscid reaction product, after being cooled to room temperature, was poured into ice water, 50 cc. of concd. hydrochloric acid was added and the mixture was steam-distilled to remove the excess of *p*-dichlorobenzene. The residue in the flask was washed with hot water and digested on the steam-bath with sodium carbonate solution. The digestion mixture was then boiled with animal charcoal and filtered, and the filtrate was made acid with dil. sulfuric acid. The dichlorobenzoylbenzoic acid was filtered off, washed with water and dried at 110°; yield, 15.48 g., or 27.2%. It was crystallized from benzol as colorless, prismatic crystals; m. p., 169° (corr.). It is soluble in ethyl alcohol, methyl alcohol, chloroform, ether and glacial acetic acid; it is insoluble in petroleum ether.

Anal. Subs., 0.1315: CO_2, 0.2748; H_2O, 0.0354. Subs., 0.1173, 0.0964: AgCl,

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[1] Graebe, *Ber.*, **33,** 2019 (1900).

[2] Walsh and Weizmann, *J. Chem. Soc.*, **97,** 685 (1910).

[3] Ullmann and Billig, *Ann.*, **381,** 11 (1911).

0.1136, 0.0940. Calcd. for $C_{14}H_8O_3Cl_2$: C, 56.96; H, 2.76; Cl, 24.03. Found: C, 56.98; H, 3.01; Cl, 23.95, 24.12.

1,4-Dichloro-anthraquinone.—Thirteen and six-tenths g. of 2′,5′-dichloro-2-benzoylbenzoic acid and 82 g. of sulfuric acid (d., 1.84) were heated together in an oil-bath at 150° for four hours. The reaction product, after being cooled to room temperature, was poured into ice water, filtered, washed with dil. sodium carbonate solution and then with water, and finally dried at 110°; yield, 10.63 g., or 83.0%. It was crystallized from glacial acetic acid as orange-colored needles; m. p., 187.5° (corr.). It was found to be identical with the 1,4-dichloro-anthraquinone of Ullmann and Billig.[3]

Anal. Subs., 0.1142, 0.1438: AgCl, 0.1175, 0.1477. Calcd. for $C_{14}H_6O_2Cl_2$: Cl, 25.60. Found: 25.45, 25.41.

Summary

1. 2′,5′-Dichloro-2-benzoylbenzoic acid has been prepared by condensing phathalic anhydride and *p*-dichlorobenzene, using anhydrous aluminum chloride as the condensing agent.
2. The 2′,5′-dichloro-2-benzoylbenzoic acid, when heated with sulfuric acid at 150°, was converted into 1,4-dichloro-anthraquinone.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACY OF THE UNIVERSITY OF FLORIDA]

THE EFFECT OF AMINO ACIDS AND OTHER COMPOUNDS UPON THE ACTIVITY OF UREASE[1]

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Rockwood and Husa[2] recorded the effect of 48 different compounds on the enzymic activity of urease and found that all compounds which had a promoter action contained both the amino and carboxyl groups. Furthermore, the promoter effect was dependent on the relative position of these two groups; thus, in the study of mono-amino-monocarboxylic acids it was found that the average promoter effect of 10 α-amino acids was 20%, of 3 β-amino acids 3%, while the only γ-amino acid available had a negative promoter effect, causing a decrease in enzymic activity of 1%. It was also demonstrated that in α-amino acids, replacement of one hydrogen atom of the amino group by benzoyl, or esterification of the carboxyl group, did not diminish the promoter action. These results have been extended in the present investigation by a study of the effect of certain amino acids and other compounds.

Experimental Procedure

The procedure previously described[2] was again employed with two exceptions as follows: (1) the reaction was carried out in a Freas large size

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[1] Presented before the Division of Biological Chemistry at the Seventy-second Meeting of the American Chemical Society, Philadelphia, September 6 to 11, 1926.

[2] Rockwood and Husa, THIS JOURNAL, **45**, 2678 (1923).