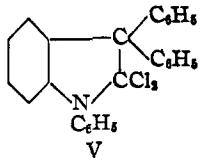

V

Experimental Part

1,3,3-Triphenyloxindole (II) and 1,2,3-Triphenylindoleoxide-2,3 (I).—N-phenylisatin (0.025 mole) was added slowly, over a period of one hour, to a solution of phenylmagnesium bromide (0.125 mole) in 150 ml. of dry ether. After addition of the last portion the mixture was heated at the boiling temperature for one hour and then poured into a mixture of ice and concentrated sulfuric acid. The ether layer was separated, dried over anhydrous sodium sulfate and the ether removed under reduced pressure. The yellow mass which was obtained was crystallized from ethyl alcohol. Repeated crystallization yielded 5.75 g. of colorless plates; m. p. 161°, and a small yield of yellow crystalline powder, m. p. 238°. The yellow compound exhibited marked fluorescence in solution.

Anal. of compound m. p. 161° (II). Calcd. for $C_{26}H_{19}ON$: N, 3.87. Found: N, 3.84, 3.67. *Anal.* of compound m. p. 238° (I). Calcd. for $C_{26}H_{19}ON$: N, 3.87. Found: N, 3.87.

Compound II. By the Friedel-Crafts Reaction.—Powdered anhydrous aluminum chloride (0.05 mole) was added slowly to a solution of 3,3-dichloro-1-phenyloxindole (0.01 mole) in 40 ml. dry benzene and the reaction mixture heated for one hour at 60°. The benzene was removed under reduced pressure and the residue treated with ice and hydrochloric acid. The entire reaction mixture was then extracted with ether and the ether removed under reduced pressure after decolorizing with charcoal and drying over anhydrous sodium sulfate. The product was purified by crystallization from ethyl alcohol from which it separated as colorless plates, m. p. 161°. Mixed melting points with samples of the colorless compound from the Grignard reaction showed no depression.

2,2-Dichloro-1,3,3-triphenyl-di-hydroindole (V).—A mixture of 2 g. of 1,3,3-triphenyloxindole (II) with 10 g. of phosphorus pentachloride was heated for four hours at 150°, the mixture cooled and water added, the residue collected and crystallized from ethyl alcohol from which it separated as colorless prisms; m. p. 200°.

Anal. Calcd. for $C_{26}H_{19}NCl_2$: N, 3.36. Found: N, 3.36, 3.33.

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DEPARTMENT OF CHEMISTRY
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The Preparation of *m*-Hydroxybenzoic Acid

BY H. E. UNGNADE AND A. S. HENICK

m-Hydroxybenzoic acid has been prepared by fusion of *m*-chlorobenzoic acid with alkali,[1] by diazotization of *m*-aminophenol, subsequent replacement with the cyano group and hydrolysis,[2] by alkaline fusion of the sodium *m*-sulfonate of benzoic acid,[3] and by action of nitrous acid on *m*-aminobenzoic acid, followed by hydrolysis of the diazonium salt.[4]

It has been found in this Laboratory that the acid can be prepared conveniently from methyl *m*-aminobenzoate. The ester is used rather than the acid since methyl *m*-nitrobenzoate is readily obtained in a pure state, is easily reduced, and is an intermediate in the preparation of *m*-nitrobenzoic acid.[5]

The reduction of methyl *m*-nitrobenzoate may be carried out catalytically with Raney nickel either under low pressure or more rapidly under high pressure and at a slightly elevated temperature. The yields in the reduction are 93–95%.

Diazotization and hydrolysis of methyl *m*-aminobenzoate give *m*-hydroxybenzoic acid directly in yields of 80–87%.

Experimental

Methyl *m*-Aminobenzoate.—Methyl *m*-nitrobenzoate (20 g.)[6] in ethyl acetate (100 cc.) was reduced with hydrogen at 50 lb. in the presence of Raney nickel (3 g.). The theoretical amount of hydrogen was absorbed in twelve hours. A 100-g. sample of the nitro compound in 100 cc. of methanol could be reduced at 50° in two and one-half hours at 2000–3000 lb. with Raney nickel (3 g.). After removal of catalyst and solvent the product was dried in ether solution. The ether was distilled off and the residual oil distilled under reduced pressure. The pure methyl *m*-aminobenzoate boiled at 152–153° (11 mm.); f. p. 37° (from the cooling curve); yield 93–95%.

Acetyl Derivative.—The acetyl derivative was obtained by refluxing the amine for twenty minutes with acetic anhydride. It melted at 136–137° after crystallization from water.

Anal. Calcd. for $C_{10}H_{11}O_3N$: C, 62.17; H, 5.70. Found: C, 62.16; H, 5.87.[7]

***m*-Hydroxybenzoic Acid.**—Methyl *m*-aminobenzoate (50 g.) was dissolved in a solution of 75 cc. of concentrated sulfuric acid and 150 g. of ice. The solution was then treated with 100 g. of ice, cooled to 0° and diazotized by the addition of 25 g. of sodium nitrite in 60 cc. of water. The resulting diazonium salt solution was added all at once to a hot solution of 100 g. of anhydrous sodium sulfate and 40 cc. of concentrated sulfuric acid in 400 cc. of water. The mixture was refluxed for three hours. Then the reaction mixture was boiled with norite, filtered, and allowed

(1) Dembey, *Ann.*, **148**, 222 (1868).

(2) Ahrens, *Ber.*, **20**, 2953 (1887).

(3) Offermann, *Ann.*, **280**, 6 (1894); Graebe and Kraft, *Ber.*, **39**, 2512 (1906).

(4) Fischer, *Ann.*, **127**, 148 (1863); Bryd, *Roczniki Chem.*, **7**, 436 (1927); *Chem. Abs.*, **22**, 2372 (1928).

(5) "Org. Syntheses," Coll. Vol. I, 2nd ed., 392 (1941).

(6) "Org. Syntheses," Coll. Vol. I, 2nd ed., 372 (1941).

(7) Semi-microanalysis by E. Milberger.

to crystallize. The acid was filtered with suction and dried *in vacuo;* yield 37–41 g. Recrystallization from water gave a nearly white product melting at 199–200°.

CHEMISTRY DEPARTMENT
UNIVERSITY OF MISSOURI
COLUMBIA, MISSOURI

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Identification of Amides through the Mercury Derivatives

BY JONATHAN W. WILLIAMS, WILLIAM T. RAINEY, JR., AND ROBERT S. LEOPOLD

In characterizing amides the most general procedure is hydrolysis, followed by identification of the two products. With unsubstituted amides, solid derivatives may be prepared directly by reaction with phthalyl chloride.[1] Another procedure, the use of which obviates hydrolysis, is the preparation of the mercury derivative. This procedure is simple and gives satisfactory derivatives for a large number of unsubstituted amides.

The reaction represented by the equation

$$2R{-}\underset{\underset{O}{\|}}{C}{-}NH_2 + HgO \longrightarrow (R{-}\underset{\underset{O}{\|}}{C}{-}NH)_2Hg + H_2O$$

was first reported in 1852 by Dessaignes,[2] who prepared the mercury derivatives of benzamide and acetamide. Mercury derivatives of several other amides have since been described.[3]

Two general procedures were investigated for the preparation of these mercury compounds. Procedure 1, patterned after the work of Dessaignes,[2] consisted of bringing a mixture of yellow mercuric oxide and excess amide to the melting point of the amide, maintaining that temperature and adding more mercuric oxide in small portions until no further reaction occurred, and then purifying the product by recrystallization from ethanol or by leaching with hot ethanol. This process is the more generally applicable one, and the one that must be used with aliphatic amides. Procedure 2, based on the process described by Mann and Saunders,[4] consisted of refluxing about 0.04 mole of amide with excess (around 0.025 mole) yellow mercuric oxide in 50 ml. of 95% ethanol for one hour, filtering while hot, cooling, removing the crystalline mercury derivative, and purifying by recrystallization or leaching.

(1) Evans and Dehn, THIS JOURNAL, **51**, 3651 (1929).

(2) Dessaignes, *Ann.*, **82**, 231 (1852).

(3) For summary and complete references, see Whitmore, "Organic Compounds of Mercury," Chemical Catalog Company (Reinhold Publishing Corporation), New York, N. Y., 1921, pp. 159–161.

(4) Mann and Saunders, "Practical Organic Chemistry," Longmans, Green and Company, London, 1938, p. 79.

In Table I are listed the melting points and mercury analyses[5–7] of the compounds successfully prepared. Due to low solubility in boiling ethanol, the purification of the mercury derivatives of *p*-anisamide and *m*-chlorobenzamide must be accomplished by leaching.

TABLE I

Amide	M. p., °C. (uncor.)	M. p. of mercury derivative, °C. (uncor.)	Mercury, % Calcd.	Found	
Acetamide	82	196–197	..	..	..
Propionamide	79	201	58.2	57.8	58.5
Butyramide	115	222–224	53.8	53.3	53.4
Benzamide	128	222	45.5	45.1	45.2
m-Chlorobenzamide	134	245	39.2	39.0	38.6
p-Chlorobenzamide	178	258	39.2	38.9	39.1
o-Bromobenzamide	155	242	33.5	33.5	..
m-Bromobenzamide	155	235	33.5	33.2	33.2
p-Bromobenzamide	191	266	33.5	33.1	33.5
o-Toluamide	158	196	42.6	42.4	42.5
m-Toluamide	94	200	42.6	43.1	42.3
p-Toluamide	166	260	42.6	42.5	..
o-Anisamide	128	241	40.1	39.8	40.3
p-Anisamide	167	222	40.1	39.9	40.3
Salicylamide	139	190	42.4	42.7	..

Unsuccessful attempts were made to prepare the mercury derivatives of isovaleramide, stearamide, *m*-anisamide and benzenesulfonamide. In the first two cases, decomposition occurred at the temperature used, making isolation of the mercury derivative impossible. With the latter two substances, reaction occurred readily, but the products obtained could not be rendered analytically pure.

Experimental

Procedure 1.—In a test-tube were placed 1.5 g. of the amide and 0.5 g. of yellow mercuric oxide. Using a small flame, the mixture was heated at the melting point of the amide until all mercuric oxide had reacted (disappearance of color) and the water vapor had been dispelled. More mercuric oxide was then added in small portions until no more would react. If an excess of mercuric oxide was obtained, enough of the amide to react with it was added and the yellow color removed completely. The melt was cooled somewhat, then taken up in the minimum amount of boiling ethanol and allowed to cool. The crystals were filtered and washed with cold ethanol or ether. Considerable variations were found in the solubilities of the mercury derivatives in alcohol. The derivatives of aliphatic amides were quite soluble, even in cold ethanol. On the other hand, the derivatives of *p*-anisamide, *m*-chlorobenzamide and benzenesulfonamide were quite insoluble in

(5) Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **10**, 331 (1938).

(6) Shriner, "Quantitative Analysis of Organic Compounds," Edwards Brothers, Ann Arbor, Mich., 1938, p. 31.

(7) Shukis and Tallman, *Ind. Eng. Chem., Anal. Ed.*, **12**, 123 (1940).