

other aldehydes to form dihydric alcohols.<sup>5,6</sup> Sodium hydroxide is a suitable catalyst for condensations with formaldehyde but for other condensations the only catalysts which have been used successfully have been mild alkalies<sup>7</sup> such as calcium hydroxide or sodium or potassium carbonates. A large excess of the aldehyde is used to force the reaction as nearly to completion as possible and this is subsequently removed by low temperature distillation.

### Procedure

**4-Nitro-3,5-heptanediol.**—The flask is charged with 61 g. (1 mole) of nitromethane, 50 ml. of 95% ethanol, and 3 g. of potassium carbonate. While stirring vigorously, 130 g. of propanal is added dropwise. External cooling is used to keep the temperature between 28–35°. A small amount of water is added to give a homogeneous solution which is left for four days at room temperature. The potassium carbonate is neutralized and the salt and aqueous layer removed. The solution is then stripped overnight with the water pump at room temperature to remove volatile substances. The salt, which precipitates, is removed by filtration and the stripping continued at room temperature at 1.5 mm. The residue is chilled to complete crystallization and then filtered (yield, about 50%) and finally recrystallized from a butanal-toluene mixture.

Unsymmetrical nitrodiols are prepared by first forming the nitroalcohol<sup>2,6</sup> from nitromethane and the more complex of the aldehydes and then treating this product with the second aldehyde in the presence of potassium carbonate as described above.

Nitrodiols are white, crystalline substances, soluble in water or alcohol, but insoluble in hydrocarbon solvents. Some data for three nitrodiols are listed in the table.

Compound	Melting point, °C.	Empirical formula	Carbon or nitrogen, %	
			Calcd.	Found
4-Nitro-3,5-heptanediol	97	C <sub>7</sub> H <sub>16</sub> NO <sub>4</sub>	47.46	47.30 <sup>a</sup>
3-Nitro-2,4-hexanediol	94	C <sub>6</sub> H <sub>12</sub> NO <sub>4</sub>	8.58	8.47 <sup>b</sup>
8-Nitro-7,9-pentadecanediol	66-67	C <sub>15</sub> H <sub>31</sub> NO <sub>4</sub>	4.87	4.74 <sup>b</sup>

<sup>a</sup> Percentage carbon by the "Wet Method," Pollard and Forsee, *Ind. Eng. Chem., Anal. Ed.*, **7**, 77 (1935).

<sup>b</sup> Percentage nitrogen by "Kjeldahl," Harte, *ibid.*, **7**, 432-3 (1935).

Because of the presence of three functional groups, these compounds are quite reactive and have unusual possibilities in organic synthesis.

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RECEIVED FEBRUARY 17, 1942

(5) Schmidt and Wilkendorf, *Ber.*, **55**, 316 (1922).

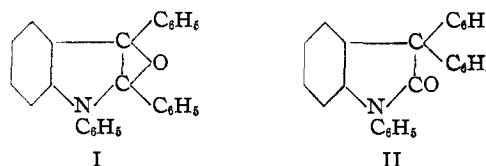
(6) Mousset, *Rec. trav. chim.*, **21**, 95 (1902).

(7) Hass and Vanderbilt, *Ind. Eng. Chem.*, **32**, 34 (1940).

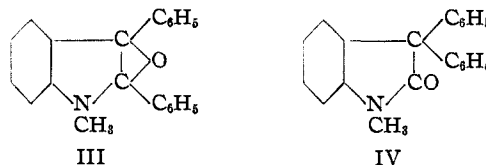
## The Reaction of Phenylmagnesium Bromide with N-Phenylisatin

BY WARD C. SUMPTER

Stollé<sup>1</sup> obtained two products from the reaction of N-phenylisatin with excess phenylmagnesium bromide: a colorless compound melting at 161° and a yellow compound melting at 238°. Stollé described the colorless compound as 1,2,3-triphenylindole-oxide-2,3 (I). No formula was assigned to the yellow compound.



Myers and Lindwall<sup>2</sup> found that 2,3-diphenyl-1-methylindole-oxide-2,3 (III) is a yellow compound exhibiting greenish fluorescence and that a second colorless compound (IV) is obtained along with III when N-methylisatin reacts with excess phenylmagnesium bromide.



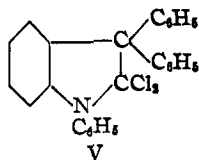
In the light of these facts it seemed likely that Stollé's characterization was in error and that the colorless compound (m. p. 161°) was compound II and that the yellow compound (m. p. 238°) was in reality compound I.

To test this conclusion the experimental work of Stollé has been repeated. Analyses of both compounds are in agreement with the formula C<sub>26</sub>H<sub>19</sub>ON. That the colorless compound (m. p. 161°) is in reality 1,3,3-triphenyloxindole (II) was confirmed by its synthesis from 3,3-dichloro-1-phenyloxindole, benzene and aluminum chloride. The yellow compound exhibits green fluorescence in solution and is analogous in color and fluorescence to compound III of Myers and Lindwall. Accordingly it seems reasonable to assign structure I to the yellow compound (m. p. 238°).

Treatment of compound II with phosphorus pentachloride yields 2,2-dichloro-1,3,3-triphenyl-di-hydroindole (V).

(1) Stollé, Hecht and Becker, *J. prakt. Chem.*, **135**, 358 (1932).

(2) Myers and Lindwall, *THIS JOURNAL*, **60**, 2153 (1938).



### Experimental Part

**1,3,3-Triphenyloxindole (II) and 1,2,3-Triphenylindole-oxide-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.

This work has been supported by a research grant (A.A.A.S.) received through the Kentucky Academy of Science.

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BOWLING GREEN, KY. RECEIVED MAY 11, 1942

### 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,<sup>1</sup> by

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

diazotization of *m*-aminophenol, subsequent replacement with the cyano group and hydrolysis,<sup>2</sup> by alkaline fusion of the sodium *m*-sulfonate of benzoic acid,<sup>3</sup> and by action of nitrous acid on *m*-aminobenzoic acid, followed by hydrolysis of the diazonium salt.<sup>4</sup>

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.<sup>5</sup>

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.)<sup>6</sup> 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  $C_{10}H_{11}O_2N$ : C, 62.17; H, 5.70. Found: C, 62.16; H, 5.87.<sup>7</sup>

***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

(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.