THE SYNTHESIS OF 2,2′-DIPHENYLBENZIDINE.

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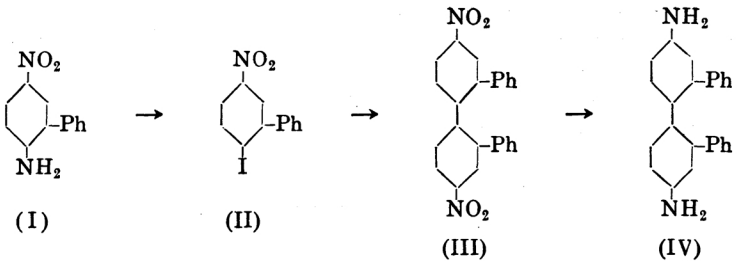
The synthesis of 2,2′-diphenylbenzidine has been carried out in connection with the other diamino-derivatives[1] of 2,2′-diphenyldiphenyl prepared in this laboratory. The starting substance employed for this synthesis is 2-amino-5-nitro-diphenyl (I) which has been obtained along with 2-amino-3-nitro-diphenyl in the nitration[2] of 2-acetamidodiphenyl. 2-Amino-5-nitro-diphenyl has been converted into 5-nitro-2-iododiphenyl (II) in the usual way, and the latter treated with copper powder to yield 4,4′-dinitro-2,2′-diphenyldiphenyl (III) which, on reduction, gives 2,2′-diphenylbenzidine (IV).



Experimental.

5-Nitro-2-iododiphenyl (II). 2-Amino-5-nitrodiphenyl (I) (21.4 g.) was dissolved in 120 c.c. of conc. H_2SO_4 at ordinary temperature with stirring. The vessel was surrounded by ice water and the solution diluted with 40 g. of ice. With vigorous stirring, 7.2 g. of sodium nitrite were added at once. After some time 60 g. of ice was added in three portions with an interval between each addition. It was finally diluted with a large quantity of ice, filtered, and treated with a solution of 19 g. of potassium iodide in the cold. The iodo-compound separated in an oil which solidified slowly. The crude product, 32 g., was dissolved in ether, and the solution filtered to remove some insoluble matter, shaken with a potassium hydroxide solution and dried. The ether was then evaporated off and the residue distilled under reduced pressure. It had b.p. 191–192°/4 mm. Recrystallized from MeOH it formed light-yellow, long needles melting at 114°C (Found: I, 38.73. Calc. for $C_{12}H_8O_2NI$: I, 39.05%). The yield of the pure substance was 26 g.

4,4′-Dinitro-2,2′-diphenyldiphenyl (III). To 63 g. of 5-nitro-2-iododiphenyl heated in an oil bath at 215–225° was added during 10 minutes 45 g. of copper powder prepared by the method of Piccard and Larsen[3] with stirring, and the mixture heated 20 minutes

(1) This Bulletin, **9** (1934), 70; **10** (1935), 585.
(2) This Bulletin, **9** (1934), 65.
(3) *J. Am. Chem. Soc.*, **39** (1917), 2007.

more. The cooled mass was extracted with a large quantity of boiling benzene. After the removal of benzene, the residue was purified by vacuum distillation. It boiled at 290°/4 mm. On crystallization from benzene, yellow crystals melting at 218–219°C. separated (Found: N, 7.4. Calc. for $C_{24}H_{16}O_4N_2$: N, 7.1%). The yield was 27 g. It is moderately soluble in boiling benzene, and difficultly soluble in cold benzene and hot acetone.

2,2′-Diphenylbenzidine (IV). A suspension of 22 g. of powdered 4,4′-dinitro-2,2′-diphenyldiphenyl (III) in a solution of 100 g. of stannous chloride in 290 c.c. of acetic acid containing dry HCl was heated on the water bath for 8 hours with frequent shaking, HCl being led in all the time. Frequent shaking was necessary because the unchanged dinitro-compound which subsided was apt to be covered by the reaction product which, being almost insoluble, began to separate soon after the start. When the reaction was over, the precipitated double salt was collected, dissolved in 1100 c.c. of water, and made alkaline with a solution of KOH (60 g.). The free base which solidified at once was filtered, dissolved in ether and the solution filtered. The solvent was then removed and the residue, 18 g., on two crystallizations from EtOH, gave large crystals melting at 151–152°C. (Found: N, 8.7. Calc. for $C_{24}H_{20}N_2$: N, 8.3%). The separation of the crystals from the alcoholic solution was very slow. Its solution darkens in colour fairly quickly.

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