196. *Improved Preparations of 3 : 3′-Dinitro- and 3 : 3′-Diaminodiphenylamine, together with Some Derivatives.*

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3 : 3′-Diaminodiphenylamine has been prepared for the first time in quantity, and in over 90% yield, by the neutral reduction of 3 : 3′-dinitrodiphenylamine with iron powder (cf. Hodgson and Marsden, *J.*, 1944, 398). The 3 : 3′-dinitro-compound has also been obtained in much improved yield. *N*-Benzoyl-3 : 3′-dinitrodiphenylamine has been successfully reduced by the iron powder method without removal of the benzoyl group.

3 : 3′-DINITRODIPHENYLAMINE has been obtained in 70% yield from 3-bromonitrobenzene and 3-nitroacetanilide by a modification of the conditions employed by Albert and Linnell (*J.*, 1936, 88) in the Goldberg synthesis for substituted diphenylamines (*Ber.*, 1907, **40**, 4541). The use of 3-chloro- instead of 3-bromo-nitrobenzene gave a reduced yield of a cruder product.

3 : 3′-Dinitrodiphenylamine was readily acetylated and benzoylated, but under the same conditions *p*-toluenesulphonyl chloride failed to react with it. Various thionating conditions were used in an unsuccessful attempt to cyclise the diphenylamine with a sulphur bridge, but without success; *viz.*, by heating the amine with sulphur alone, sulphur and aluminium chloride, thionyl chloride, and thionyl chloride with aluminium chloride, in the first two cases at temperatures up to 250°, and in the last two cases with excess of thionyl chloride at the boiling point; in all these reactions the initial compound was recovered unchanged.

In view of the ease with which 3 : 3′-diaminodiphenylamine is oxidised either when heated in air or in various reactions, the N-*benzoyl* derivative was made by benzoylation of 3 : 3′-dinitrodiphenylamine and reduction of the nitro-groups by the neutral iron powder method of Hodgson and Marsden (*J.*, 1944, 398), whereby an almost theoretical yield was obtained; it was identified by hydrolysis with 10% hydrochloric acid to benzoic acid and 3 : 3′-diaminodiphenylamine, and by bisdiazotisation and subsequent coupling with β-naphthol.

3 : 3′-Diaminodiphenylamine was prepared from the dinitro-compound in yields of over 90% by the neutral iron reduction method of Hodgson and Marsden (*loc. cit.*). Other attempts at reduction, including the method adopted by Albert and Linnell, who do not report yields and who worked with 0·2 g., and also that of reductive acetylation with zinc dust in acetic anhydride–glacial acetic acid–sodium acetate, afforded either very poor yields or produced tarry material which was difficult to resolve. Moreover, the colourless product obtained by the iron method was very stable in air and only slowly turned brown in the course of several months. The other properties reported by Albert and Linnell (*loc. cit.*) for the amine and the ease of resinification of the diacetyl derivative are confirmed. The diglycine [3 : 3′-*di*-(ω-*carboxymethylamino*)*diphenylamine*] was readily obtained by the action of sodium chloroacetate on 3 : 3′-diaminodiphenylamine, but attempts at decarboxylation to 3 : 3′-bismethylaminodiphenylamine (cf. Henesey, *J. Soc. Dyers and Col.*, 1938, **54**, 66) were unsuccessful.

EXPERIMENTAL.

Preparation of 3 : 3′-*Dinitrodiphenylamine*.—3-Bromonitrobenzene (40·4 g., 0·2 g.-mol.) and 3-nitroacetanilide (18 g., 0·1 g.-mol.) were refluxed in nitrobenzene solution (200 c.c.) for 16 hours in the presence of anhydrous potassium carbonate (14 g.) and cuprous bromide (0·5 g.), after which the nitrobenzene and unchanged 3-bromonitrobenzene were removed by steam. The tarry residue was solidified by keeping it at 0° for a short time, powdered, thoroughly washed with water at the pump, and extracted thrice with boiling ethanol (300 c.c. each time). The extract was filtered, concentrated to 300 c.c., refluxed for an hour after the addition of hydrochloric acid (45 c.c., *d* 1·18), and poured on ice (500 c.c.), and the precipitated crude reddish-brown 3 : 3′-dinitrodiphenylamine was filtered off after it had coagulated, and washed with hot water until the washings were clear; yield, 18·7 g., 72%. The compound separated from ethanol (charcoal) in small orange plates, m. p. 188° (Albert and Linnell, *loc. cit.*, give m. p. 186·5°) (Found: N, 16·5. Calc. for $C_{12}H_9O_4N_3$: N, 16·2%), which were readily soluble in cold pyridine and nitrobenzene, slightly so in cold chloroform, glacial acetic acid, ethanol, ether, and toluene, and insoluble in ligroin; in concentrated sulphuric acid, the solution had a slight greenish tint (which was emphasised by the addition of a drop of nitric acid), and on dilution with water it afforded a pale yellow suspension which had a slight green fluorescence. Attempts to prepare this compound by interaction of 3-nitroaniline and its hydrochloride were unsuccessful since at the point when reaction commenced (*ca.* 180°), as shown by the sublimation of ammonium chloride, more profound reactions also occurred, and at *ca.* 210° the mass began to evolve heat and decompose into a deep blue complex which could not be identified. After removal of unchanged 3-nitroaniline with hot dilute hydrochloric acid, even before the stage of vigorous decomposition, the blue substance of m. p. 200—230° (from glacial acetic acid) was an invariable product, and, from its colour and solubility in concentrated hydrochloric acid, it would appear to be of a diphenazine type; 3 : 3′-dinitrodiphenylamine was not isolated from any of the experiments.

N-*Acetyl*-3 : 3′-*dinitrodiphenylamine* was obtained when a mixture of 3 : 3′-dinitrodiphenylamine (1 g.), acetic anhydride (6 c.c.), and fused sodium acetate (2 g.) was refluxed for 3 hours and then poured into water. After the excess of acetic anhydride had hydrolysed, the precipitated acetyl compound was removed; it crystallised from ethanol (charcoal) in fine colourless needles, m. p. 181° (Found: N, 14·2. $C_{14}H_{11}O_5N_3$ requires N, 14·0%). N-*Benzoyl*-3 : 3′-*dinitrodiphenylamine* was formed when a mixture of 3 : 3′-dinitrodiphenylamine (13 g.), benzoyl chloride (15 c.c.), and pyridine (20 c.c.) was refluxed for 3 hours, cooled, and treated with cold 3% aqueous hydrochloric acid until the product had solidified; it was then removed, treated with hot aqueous sodium hydrogen carbonate, and washed with water; it recrystallised from ethanol (charcoal) in minute colourless needles, m. p. 145° (Found: N, 11·9. $C_{19}H_{13}O_5N_3$ requires N, 11·6%), which were readily soluble in the usual organic solvents except ligroin and readily hydrolysed by hot acids and alkalis; the ethanol solution afforded a yellow colour when treated with aqueous sodium hydroxide.

Neutral Reduction of N-*Benzoyl*-3 : 3′-*dinitrodiphenylamine*.—A mixture of the compound (7·2 g.)

with iron powder (26 g., pin dust), ferrous sulphate (2·6 g.), and water (150 c.c.) was refluxed for 6 hours, cooled, and filtered, the residue was extracted thrice with ethanol (50 c.c. per time), and the ethanol was removed from the filtered extract; the crude N-*benzoyl*-3 : 3′-*diaminodiphenylamine* (5·9 g., 98% yield) separated from ethanol (charcoal) in colourless plates, m. p. 205° (Found : N, 13·9. $C_{19}H_{17}ON_3$ requires N, 13·9%), which were readily soluble in the usual organic solvents and in dilute mineral acids, slightly soluble in hot water and in ligroin. This compound was readily hydrolysed with 10% aqueous hydrochloric acid, and an ether extract of the liquor afforded benzoic acid, m. p. and mixed m. p. with an authentic specimen 121°; an ether extract of the liquor after it had been made alkaline gave 3 : 3′-diaminodiphenylamine, m. p. and mixed m. p. with an authentic specimen 95°.

N-*Benzoyldiphenylamine*-3 : 3′-*bisazo*-β-*naphthol* was obtained when a solution of *N*-benzoyl-3 : 3′-diaminodiphenylamine (0·5 g.) in 3% hydrochloric acid (10 c.c.) was diazotised by addition below 5° of a solution of sodium nitrite (0·3 g.) in the minimum amount of water, and the clear solution stirred into 10% aqueous sodium hydroxide (10 c.c.) containing β-naphthol (1 g.). After 30 minutes the precipitate was coagulated by heat, removed, washed with hot water, and then dissolved in hot glacial acetic acid (charcoal), from which it separated on cooling in red microcrystals, m. p. 303° (Found : N, 11·7. $C_{39}H_{27}O_3N_5$ requires N, 11·4%), which gave a magenta-coloured solution in concentrated sulphuric acid, turning to pink on dilution.

3 : 3′-Dinitrodiphenylamine was reduced by refluxing it (13 g.) for 3 hours with iron powder (50 g.), ferrous sulphate (2 g.), and water (50 c.c.), after which charcoal was added and the boiling continued for a further 30 minutes. The mixture was filtered, while boiling, on to ice (100 g.), placed in the filtration flask, and the residue washed with boiling water (50 c.c.). On cooling, 3 : 3′-diaminodiphenylamine (9·2 g., 90%) separated in colourless hexagonal plates which on recrystallisation from hot water had m. p. 95° (Albert and Linnell, *loc. cit.*, give m. p. 95°) (Found : N, 21·3. Calc. for $C_{12}H_{13}N_3$: N, 21·1%) and were stable in air. The compound is readily soluble in the usual organic solvents, dilute acids, and hot water. When this amine (1 g.) was dissolved in ether (50 c.c.) and the solution stirred with acetic anhydride (2 c.c.), opalescence occurred after a few minutes, and addition of water followed by careful introduction of steam caused separation of 3 : 3′-diacetamidodiphenylamine which crystallised from ether in colourless micro-crystals, m. p. 211° (Albert and Linnell, *loc. cit.*, give m. p. 211°) (Found : N, 15·0. Calc. for $C_{16}H_{17}O_2N_3$: N, 14·8%), which form tar very readily and cannot be obtained from solutions which have been previously overheated.

3 : 3′-*Di*-(ω-*carboxymethylamino*)*diphenylamine*.—A mixture of 3 : 3′-diaminodiphenylamine (2·1 g., 0·01 g.-mol.), chloroacetic acid (1·9 g., 0·02 g.-mol.), sodium carbonate (1·06 g.), and water (1·5 c.c.) was heated on the water-bath for 4 hours, cooled, and made alkaline; complete dissolution then occurred. The filtered solution was acidified with dilute hydrochloric acid, and the yellow precipitate of the *diglycino*-compound (2 g., 66% yield) collected and crystallised from hot water; it separated in yellow micro-crystals which on heating became chocolate-brown at 100°, sintered at 100°, and decomposed at *ca.* 350° (Found : N, 13·5. $C_{16}H_{17}O_4N_3$ requires N, 13·3%), and were readily soluble in cold dilute alkali, less so in cold dilute acids, but more soluble on heating, also soluble in cold pyridine, hot glacial acetic acid, and ethanol, but insoluble in chloroform, toluene, ether, and ligroin. The solutions were yellow when dilute but brown when more concentrated, and exhibited a slight green fluorescence.

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