CCXXXII.—*Studies in the Diphenyl Series. Part I. The Isomeric* 4 : 4′-*Dichloro*-3 : 3′(2 : 3′ ?)- *and* 3 : 5′-*dinitrodiphenyls.*

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The isomeric *o*-dinitrobenzidines were studied by Cain, Coulthard, and Micklethwait (J., 1912, **101**, 2298; 1913, **103**, 2074), who found that the replacement of the amino-groups by chlorine, by means of copper bronze (Ullmann's process) ensued normally with 3 : 3′(2 : 3′ ?)-dinitrobenzidine, but that 3 : 5′-dinitrobenzidine gave mainly 4″ : 4‴-dichlorotetranitrobenzerythrene mixed with small but varying quantities of other compounds of higher nitrogen content. Benzerythrene formation likewise occurred during replacement by bromine, but all the products obtained from 3 : 3′(2 : 3′ ?)-dinitrobenzidine by means of either copper bronze or cuprous bromide were so impure that 4 : 4′-dibromo-3 : 3′(2 : 3′ ?)-dinitrodiphenyl had to be prepared by the Saunders perbromide process (*Amer. Chem. J.*, 1891, **13**, 486), which method also proved suitable for the isolation of the 3 : 5′-isomeride. Since substitution of iodine for the amino-groups proceeded normally, the presence of copper or its compounds appears to have been the cause of the complications encountered by those investigators.

In the present work the diazo-solutions were decomposed in the cold by adding them to vigorously stirred solutions of cuprous chloride in concentrated hydrochloric acid. From 3 : 3′(2 : 3′ ?)-dinitrobenzidine, 4 : 4′-dichloro-3 : 3′(2 : 3′ ?)-dinitrodiphenyl was obtained mixed with traces of highly coloured impurities (probably azo-compounds) which could not be removed by repeated crystallisation from boiling alcohol in the presence of charcoal; the m. p. of the compound, however, was thus raised to 129° (Cain, Coulthard, and Micklethwait, *loc. cit.*, give m. p. 111—112°). From 3 : 5′-dinitrobenzidine, Cain's 4″ : 4‴-dichlorotetranitrobenzerythrene (m. p. 203°) was obtained, but the residue left after its extraction with glacial acetic acid contained an isomeride, m. p. 300°, of unknown constitution and of much smaller solubility.

When the Sandmeyer procedure was reversed, *i.e.*, solid cuprous chloride was added to the diazo-solution, much greater complications ensued, and from the high chlorine content of the mixture of products obtained from 3 : 5′-dinitrobenzidine, their relatively great solubilities in alcohol, and their low m. p.'s, it would appear that nitro-groups had been displaced by chlorine.

In recording the preparation of 3 : 5′-dinitrobenzidine by the alkaline hydrolysis of its diacetyl derivative, neither Strakosch (*Ber.*, 1872, **5**, 236), nor Brunner and Witt (*Ber.*, 1887, **20**, 1024), nor Cain and his co-workers (*loc. cit.*) mentioned the extreme sensitiveness of 3 : 5′-dinitrodiacetylbenzidine to potassium hydroxide. Unless special care be exercised, the bulk of the hydrolysed product is soluble in alkalis; it appears to be 3 : 5′-dinitro-4′-amino-4-hydroxydiphenyl. Hot or cold concentrated sulphuric acid apparently does not hydrolyse the dinitrodiacetylbenzidine.

4 : 4′-*Dichloro*-3 : 5′-*dinitrodiphenyl* has been prepared by the addition of an acidified solution of cuprous chloride to a solution of

diazotised 4-chloro-3-nitroaniline, but it is mixed with a small quantity of an isomeride. This by-product, which is removed by taking advantage of its greater solubility in the usual solvents, can be only 4 : 4′-dichloro-2 : 2′ or 3 : 3′-dinitrodiphenyl from its mode of formation (the former would be produced from 4-chloro-2-nitroaniline if this were present as an impurity in the original substance). The m. p. (237°) and behaviour of 4 : 4′-dichloro-3 : 5′-dinitrodiphenyl correspond to those of 4 : 4′-dibromo- (m. p. 247°) and 4 : 4′-di-iodo-3 : 5′-dinitrodiphenyl (m. p. 252°) (Cain, Coulthard, and Micklethwait, *loc. cit.*).

Direct nitration of 4 : 4′-dichlorodiphenyl gives mainly 4 : 4′-dichloro-3 : 3′(2 : 3′ ?)-dinitrodiphenyl, the identity of which with the product obtained from 3 : 3′(2 : 3′ ?)-dinitrobenzidine is shown by the m. p. of a mixture of the two compounds and by the formation of the same 4-chloro-4′-aminodinitrodiphenyl when either is heated with an excess of alcoholic ammonia at a high temperature. Only one of the two chlorine atoms in 4 : 4′-dichloro-3 : 3′ (2 : 3′ ?)-dinitrodiphenyl is readily displaced by means of ammonia.

Since this paper was submitted for publication, Dennett and Turner (this vol., p. 476) have furnished evidence in favour of the constitutions 4 : 4′-dichloro- and 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl for the products of the dinitration of 4 : 4′-dichloro- and 4 : 4′-dibromo-diphenyl. The conclusion of Le Fèvre and Turner (see following paper), that Bandrowski's compound is mainly 2 : 3′-dinitrobenzidine, we had inferred from the results now presented, but we delayed publication in order to obtain more definite evidence in view of Cain's positive statement that both dinitrobenzidines give different tetra-aminodiphenyls which, however, form the same diquinoxaline on treatment with benzil (see also Brady and McHugh, J., 1923, **123**, 2053).

EXPERIMENTAL.

4 : 4′-*Dichloro*-3 : 3′-*dinitrodiphenyl*.—(*a*) *Preparation from* 3 : 3′-*dinitrobenzidine*. 3 : 3′-Dinitrobenzidine (5 g.; prepared from diphthalylbenzidine) was diazotised in concentrated sulphuric acid at 0° with 4 g. of solid sodium nitrite. Having been poured on to crushed ice and filtered, the solution was added slowly to a well-cooled solution of cuprous chloride (3 g.) in concentrated hydrochloric acid (30 c.c.) and, after 1 hour, the light orange solid was filtered off, washed, dried, and extracted several times with boiling alcohol. Most of it dissolved and from the cooled extracts orange-yellow crystals, m. p. 120°, of 4 : 4′-dichloro-3 : 3′-dinitrodiphenyl were deposited; these became pale yellow and had m. p. 129° after recrystallisation from hot alcohol in presence of animal charcoal (Found : N, 9·2; Cl, 22·5. Calc. : N, 8·95; Cl, 22·7%).

When a diazo-solution prepared as described above was saturated with sodium chloride, hydrochloric acid (100 c.c.) added, and the mixture treated with solid cuprous chloride so long as reaction occurred, a deep reddish-brown solid, m. p. 117°, was obtained which was separated by fractional crystallisation from alcohol into a small crop, m. p. *ca.* 164° (Found: Cl, 17·4%), and a second crop, m. p. 102° (Found: N, 12·6%). The latter, after several crystallisations from alcohol, had m. p. 122° (Found: N, 9·4%) (compare Cain, *loc. cit.*, p. 2081).

(*b*) *By direct nitration of* 4 : 4′-*dichlorodiphenyl.* Nitration was effected at 0°, the solution filtered on to ice, and the light reddish-brown solid obtained was crystallised several times from alcohol, separating in almost colourless parallelograms, which sintered at 133·5° and were completely molten at 140° (Found: N, 8·9; Cl, 22·6%). Schmidt and Schultz (*Annalen*, 1881, **207**, 340) and Dennett and Turner (*loc. cit.*) give m. p. 140°. A mixture of the two specimens obtained by methods (*a*) and (*b*) melted at 132°.

The nitration must be conducted as rapidly as possible to avoid tetranitration. In one experiment, the crude product, after crystallisation from ether, had m. p. 117—118° (Found: Cl, 19·3, N, 10·8%. A mixture of equal parts of dichlorodi- and tetranitrodiphenyls requires Cl, 19·8; N, 11·1%). An ethereal solution of a much over-nitrated product was kept in a beaker. The solid left by the evaporation of the liquor that had crept up the sides was the dinitro-compound and was continually removed; in this way, after complete evaporation of the ether, a resinous residue was obtained which slowly solidified and then melted below 100° (Found: N, 13·3. $C_{12}H_4O_8N_4Cl_2$ requires N, 13·8%).

4-*Chloro*-3 : 3′-*dinitro*-4′-*aminodiphenyl.*—Each of the 4 : 4′-dichloro-3 : 3′(2 : 3′ ?)-dinitrodiphenyls prepared by methods (*a*) or (*b*) above was heated in a sealed tube with excess of alcoholic ammonia at 160—170° for 5 hours. The cooled product deposited light orange needles, m. p. 218° after recrystallisation from alcohol [Found: (*a*) N, 14·0; Cl, 11·8. (*b*) N, 14·2; Cl, 11·9. $C_{12}H_8O_4N_3Cl$ requires N, 14·4; Cl, 12·1%]. The alcoholic filtrates, on dilution with water, gave yellowish-orange mixtures, m. p. 189—194°, of the above with unchanged material; by heating these at 230° with a large excess of ammonia, almost quantitative yields of 4-chloro-3 : 3′-dinitro-4′-aminodiphenyl were obtained.

Hydrolysis of 3 : 5′-*Dinitrodiacetylbenzidine.*—Strakosch's method (*loc. cit.*), which tended to get beyond control, gave a product almost the whole of which dissolved to form a dense brown solution, from which, on acidification, 3 : 5′-*dinitro*-4′-*amino*-4-*hydroxydiphenyl* was obtained; when dried, this was a reddish-brown, microcrystalline, infusible solid, decomp. 240—260° (Found: N, 14·9. $C_{12}H_9O_5N_3$ requires N, 15·2%).

The following procedure gave a much better result: A cold paste of 3 : 5′-dinitrodiacetylbenzidine (1 part) and a little alcohol was triturated with a solution of potassium hydroxide (1½ parts) in water (4½ parts). After 30 minutes, the mixture was diluted with water, and the deep red 3 : 5′-dinitrobenzidine filtered off. The substance in the filtrate was precipitated on acidification (yield about 40%) (Found: N, 15·0%).

The Diazo-reaction applied to 3 : 5′-*Dinitrobenzidine. The Isomeric Benzerythrenes.*—(*a*) Submitted to the process (*a*) (p. 1756), 3 : 5′-dinitrobenzidine gave an orange-red substance which was successively extracted with the following boiling solvents: (1) Ether removed a very small quantity of material, m. p. 170°; (2) from the cold alcoholic extract a crystalline substance, m. p. 170—180° (Found: Cl, 17·3%), separated in a quantity too small for further investigation; (3) glacial acetic acid removed a substance, m. p. 200° (203° after recrystallisation from glacial acetic acid), which was undoubtedly Cain's 4′′ : 4′′′-dichlorotetranitrobenzerythrene (Found: N, 10·2; Cl, 13·2. Calc.: N, 10·1; Cl, 12·8%); (4) from the benzene extract, on cooling, orange-red crystals, m. p. 300°, separated (Found: N, 10·0; Cl, 13·1. $C_{24}H_{12}O_8N_4Cl_2$ requires N, 10·1; Cl, 12·8%); (5) the acetone extract gave a product, m. p. 300°, identical with (4) (Found: Cl, 12·9%), which appears to be an isomeride of (3). It is less soluble than this in the above solvents, is somewhat lighter in colour, and is obtained in smaller quantity.

(*b*) Addition of solid cuprous chloride to diazotised 3 : 5′-dinitrobenzidine (compare p. 1757) led to orange-red products which were almost completely soluble in boiling alcohol. From the solutions, on cooling, mixtures were obtained of much higher chlorine content and lower m. p. than those isolated in method (*a*) above; *e.g.*, in four different experiments, 26·5% Cl (m. p. 102°), 21·8% Cl (m. p. 194°), 21·85% Cl (m. p. 210°), 19·7% Cl (m. p. 195°). From these mixtures pure compounds have not yet been isolated.

4 : 4′-*Dichloro*-3 : 5′-*dinitrodiphenyl.*—The paste obtained by cooling a mixture of 4-chloro-3-nitroaniline (3 g.; m. p. 103°), concentrated sulphuric acid (5 c.c.), and water (10 c.c.) to 0° was diazotised, and after 30 minutes the filtered solution was treated gradually with cuprous chloride (2 g.) dissolved in concentrated hydrochloric acid (10 c.c.). The brown solid produced was filtered off and distilled with steam, 2 : 5-dichloronitrobenzene (0·4 g.) passing over. The non-volatile residue was extracted, first with boiling alcohol, which removed a yellowish-white, crystalline substance (A), m. p. 160—170° (Found: N, 9·0; Cl, 22·3. $C_{12}H_6O_4N_2Cl_2$

requires N, 8·95; Cl, 22·7%), and then with boiling benzene or glacial acetic acid; this extract deposited colourless needles, m. p. 237°, of 4 : 4′-*dichloro*-3 : 5′-*dinitrodiphenyl* (Found: N, 9·1; Cl, 22·4. $C_{12}H_6O_4N_2Cl_2$ requires N, 8·95; Cl, 22·7%). This compound, in contrast to 4 : 4′-dichloro-3 : 3′(2 : 3′ ?)-dinitrodiphenyl, is only sparingly soluble in cold ether, acetone, or alcohol, but is more soluble in boiling alcohol, benzene, acetone, or glacial acetic acid.

Substance (A) appears to be a mixture of 4 : 4′-dichloro-3 : 3′(2 : 3′ ?)- or 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl (from 4-chloro-2-nitroaniline as impurity in the 4-chloro-3-nitroaniline) with 4 : 4′-dichloro-3 : 5′-dinitrodiphenyl.

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