153. *Derivatives of* 1 : 2 : 4 : 5-*Tetrachlorobenzene. Part III. The Amination of* 2 : 3 : 5 : 6-*Tetrachloro-nitrobenzene and* -4-*nitroaniline.*

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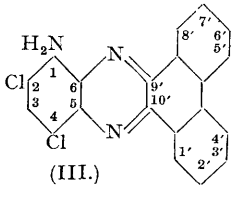
The nitro-group and, to a less extent, both chlorine atoms ortho to it in 2 : 3 : 5 : 6-tetrachloronitrobenzene are labile. Products of amination isolated were 2 : 3 : 5 : 6-tetrachloroaniline and 3 : 5-*dichloro*-1-*nitro*-2 : 6-*diaminobenzene* (II); the presence of 3 : 5 : 6-trichloro-1-nitro-2-aminobenzene (I) was shown by reduction and conversion into 1 : 2 : 4-*trichloro*-5 : 6 : 9′ : 10′-*phenanthraphenazine*. Only the two chlorine atoms ortho to the nitro-group in 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline (V) are labile; amination converted (V) into 3 : 5-*dichloro*-1-*nitro*-2 : 4 : 6-*triaminobenzene* (VI), and only a trace of 3 : 5 : 6-trichloro-1-nitro-2 : 4-diaminobenzene was detected by reduction and conversion into 1 : 2 : 4-*trichloro*-3-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine*.

It was anticipated that the nitro-group in 2 : 3 : 5 : 6-tetrachloronitrobenzene would be more labile than the chlorine atoms in positions 2 and 6 and that the probable products of heating it with excess of alcoholic ammonia at 200° would be mainly 2 : 3 : 5 : 6-tetrachloroaniline, together with some 3 : 5 : 6-trichloro-1-nitro-2-aminobenzene (I) and 3 : 5-*dichloro*-1-*nitro*-2 : 6-*diaminobenzene* (II). When the product was distilled with steam, the non-volatile (II) was isolated in small amount, 2 : 3 : 5 : 6-tetrachloroaniline was recovered as the chief volatile constituent, but no (I) was isolated. The presence of (I) was demonstrated by first reducing a portion of the volatile product and then condensing it with 9 : 10-phenanthraquinone in acetic acid, 1 : 2 : 4-*trichloro*-5 : 6 : 9′ : 10′-*phenanthraphenazine* being formed.

In confirmation of its constitution, (II) did not condense with 9 : 10-phenanthraquinone, so it is not 5 : 6-dichloro-1-nitro-2 : 3-diaminobenzene. Reduction gave a triamine which condensed with 9 : 10-phenanthraquinone to give (III), so (II) is not 2 : 6-dichloro-1-nitro-3 : 5-diaminobenzene. Consequently, this triamine must be either 4 : 6-dichloro-1 : 2 : 3-triaminobenzene or 3 : 6-dichloro-1 : 2 : 5-triaminobenzene. Synthesis of the former *via* 3 : 5-dichloro-1 : 2 : 6-trinitrobenzene failed, because 3 : 5-dichloro-1 : 2-dinitrobenzene (Blanksma, *Rec. Trav. chim.*, 1908, **27**, 46) was recovered unaltered even after heating with potassium nitrate and 25% oleum at 130—160°. On the other hand, 2 : 5-dichloro-4 : 6-dinitroaniline was reduced by aqueous-alcoholic sodium hydrosulphite to 3 : 6-dichloro-1 : 2 : 5-triaminobenzene, which condensed with 9 : 10-phenanthraquinone to give 1 : 4-*dichloro*-2-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine* (IV). The phenanthraphenazine (III) was isomeric and not identical with (IV). Compound (II), therefore, is 3 : 5-dichloro-1-nitro-2 : 6-diaminobenzene and (III) is 2 : 4-*dichloro*-1-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine*.



(III.)

Amination of 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline (V) furnished as main product the very stable 3 : 5-*dichloro*-1-*nitro*-2 : 4 : 6-*triaminobenzene* (VI) (the constitution of which is confirmed by the fact that it does not condense with 9 : 10-phenanthraquinone), only a trace of 3 : 5 : 6-trichloro-1-nitro-2 : 4-diaminobenzene being formed. Although the latter was not isolated, its presence was demonstrated, after separation of (VI), by reducing the residue, which consisted mainly of unaltered (V), and condensing the product with 9 : 10-phenanthraquinone, a little 1 : 2 : 4-*trichloro*-3-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine* thus being obtained.

Experimental.

Microanalyses were carried out by Dr. G. Weiler and Dr. F. B. Strauss, of Oxford.

Amination of 2 : 3 : 5 : 6-*Tetrachloronitrobenzene: Formation of* 2 : 3 : 5 : 6-*Tetrachloroaniline*, 3 : 5 : 6-*Trichloro*-1-*nitro*-2-*aminobenzene* (I), *and* 3 : 5-*Dichloro*-1-*nitro*-2 : 6-*diaminobenzene* (II).—2 : 3 : 5 : 6-Tetrachloronitrobenzene (8·3 g.) and 2·94N-alcoholic ammonia (30 c.c.) were heated in a sealed tube at 200° for 10 hours, and the mixture distilled with steam. The reddish solid (6·4 g.) from the distillate was reduced with boiling aqueous-alcoholic sodium hydrosulphite, the mixture cooled and diluted, and the almost colourless precipitate collected, dissolved in acetic acid, and boiled with 9 : 10-phenanthraquinone in acetic acid for several minutes. The resulting precipitate (A) of 1 : 2 : 4-*trichloro*-5 : 6 : 9′ : 10′-*phenanthraphenazine* crystallised from amyl alcohol in pale yellow, fibrous needles, m. p. 262—263° [yield, 1·15 g., corresponding to a yield of 0·75 g. or 9·7% of (I)] (Found: N, 7·6; Cl, 26·8. $C_{20}H_9N_2Cl_3$ requires N, 7·3; Cl, 27·8%). The filtrate from (A) was diluted, and the precipitate collected; after removal of the phenanthraquinone with sodium bisulphite, 2 : 3 : 5 : 6-tetrachloroaniline crystallised from alcohol in colourless needles, m. p. and mixed m. p. 107—108° (yield, 4·5 g.; 61·2%). The non-volatile residue was crystallised from ligroin; 3 : 5-*dichloro*-1-*nitro*-2 : 6-*diaminobenzene* separated in fine, deep red needles, or scarlet leaflets, m. p. 172—173° (yield, 0·4 g.; 5·6%) (Found: C, 32·6; H, 2·2; N, 18·1; Cl, 31·5. $C_6H_5O_2N_3Cl_2$ requires C, 32·4; H, 2·25; N, 18·9; Cl, 31·9%). Its *diacetyl* derivative crystallised from acetic acid in colourless prisms, darkening at 295° and melting at 315° (decomp.) (Found: C, 39·4; H, 3·2; Cl, 23·2. $C_{10}H_9O_4N_3Cl_2$ requires C, 39·2; H, 2·9; Cl, 23·2%).

3 : 5-*Dichloro*-1 : 2 : 6-*triaminobenzene*.—3 : 5-Dichloro-1-nitro-2 : 6-diaminobenzene (0·35 g.) was boiled with alcohol (30 c.c.), and aqueous sodium hydrosulphite added until completely decolorised. The mixture was concentrated, cooled, and extracted with ether, and removal of ether gave a residue which crystallised from alcohol in clusters of colourless needles, m. p. 121—122° (decomp.) (yield, 0·17 g.; 56%). The triamine (0·09 g.) was boiled with 9 : 10-phenanthraquinone in acetic acid and gave 2 : 4-*dichloro*-1-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine* (III), which crystallised from amyl alcohol in fine, orange needles, m. p. 265° (yield, 0·11 g.; 64·7%) (Found: C, 66·0; H, 3·1; N, 11·65; Cl, 19·2. $C_{20}H_{11}N_3Cl_2$ requires C, 65·9; H, 3·0; N, 11·55; Cl, 19·5%).

2 : 5-*Dichloro*-4 : 6-*dinitroaniline* (cf. Chem. Fabr. vorm. Sandoz; E.P. 457,518).—A mixture (6·3 g.) of equal parts of nitric acid (*d* 1·52) and 100% sulphuric acid was added to 2 : 5-dichloro-4-nitroaniline (10·4 g.) in 100% sulphuric acid (50 g.) at −5°, and stirred at 0° for 1 hour. After pouring on ice, the precipitate was collected, washed with cold dilute sodium hydroxide solution, and crystallised from alcohol, forming orange-yellow needles, m. p. 170—171° (yield, 6·7 g.; 53%).

3 : 6-*Dichloro*-1 : 2 : 5-*triaminobenzene*.—2 : 5-Dichloro-4 : 6-dinitroaniline (1·3 g.) in 50% aqueous alcohol (80 c.c.)

was reduced by adding sodium hydrosulphite until decolorised. The solution was cooled, diluted, and extracted with ether, ether removed, and the triamine crystallised from aqueous alcohol, forming fawn needles (yield, 0·15 g.; 16%), which were immediately condensed with 9 : 10-phenanthraquinone in acetic acid. 1 : 4-*Dichloro*-2-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine* (IV) crystallised from amyl alcohol in small yellow needles, m. p. *ca.* 322° (yield, 0·25 g.; 83%) (Found : C, 66·2; H, 3·3; N, 11·5; Cl, 19·0. $C_{20}H_{11}N_3Cl_2$ requires C, 65·9; H, 3·0; N, 11·5; Cl, 19·5%).

Amination of 2 : 3 : 5 : 6-*Tetrachloro*-4-*nitroaniline* (V) : *Formation of* 3 : 5-*Dichloro*-2 : 4 : 6-*triaminobenzene* (VI) *and* 3 : 5 : 6-*Trichloro*-1-*nitro*-2 : 4-*diaminobenzene*.—2 : 3 : 5 : 6-Tetrachloro-4-nitroaniline (2·76 g.) and 2·94N-alcoholic ammonia (15 c.c.) were heated in a sealed tube at 200° for 22 hours. The contents of the tube were crystallised from alcohol; the solution deposited red needles (1·13 g.), m. p. 256—257° (decomp.). A further amount (0·2 g.) was obtained by diluting the alcoholic filtrate with water, collecting the precipitate, extracting it with hot concentrated hydrochloric acid, and diluting the acid extract with water. 3 : 5-*Dichloro*-1-*nitro*-2 : 4 : 6-*triaminobenzene* crystallised from alcohol in red needles, m. p. 256—257° (decomp.) (yield, 56%) (Found : C, 30·0; H, 2·9; N, 23·3; Cl, 30·5. $C_6H_6O_2N_4Cl_2$ requires C, 30·4; H, 2·5; N, 23·6; Cl, 29·9%). The yellow residue insoluble in hot concentrated hydrochloric acid consisted mainly of 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline, but the presence of a trace of 3 : 5 : 6-trichloro-1-nitro-2 : 4-diaminobenzene was demonstrated by reduction with aqueous-alcoholic sodium hydrosulphite, dilution with water, and boiling of the resulting precipitate with 9 : 10-phenanthraquinone in acetic acid. 1 : 2 : 4-*Trichloro*-3-*amino*-5 : 6 : 9′ : 10′-*phenanthraphenazine* crystallised from acetic acid in clusters of light yellow needles, darkening at 280°, m. p. > 330° (yield, 1%) (Found : N, 10·9. $C_{20}H_{10}N_3Cl_3$ requires N, 10·55%).

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