96. *Derivatives of* 1 : 2 : 4 : 5-*Tetrachlorobenzene. Part II.* N-*Nitroamino-compounds.*

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Nitration of 2 : 3 : 5 : 6-tetrachloroacetanilide gave solely 2 : 3 : 5 : 6-*tetrachloro*-N-*nitroacetanilide* (I), hydrolysed to 2 : 3 : 5 : 6-*tetrachloro*-N-*nitroaniline* (II), whereas nitration of 2 : 3 : 5 : 6-tetrachloroaniline gave (II) and 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline. Excess of nitric acid converts 2 : 3 : 5 : 6-tetrachloroaniline or (II) into 2 : 3 : 5 : 6-*tetrachloro*-4-*nitro*-N-*nitroaniline* (III). Reactions of (I), (II), and (III), involving elimination or replacement of the substituted amino-group, are described. Both (II) and (III) form N-*methyl* derivatives with alkaline methyl sulphate.

In attempts to prepare 2 : 3 : 5 : 6-tetrachloro-4-nitroacetanilide by nitrating 2 : 3 : 5 : 6-tetrachloroacetanilide, the sole nitration product melted with vigorous evolution of oxides of nitrogen, and was partly decomposed in boiling alcohol or benzene, but crystallisation from ligroin gave 2 : 3 : 5 : 6-*tetrachloro*-N-*nitroacetanilide* (I) quantitatively. On boiling with xylene, (I) was converted into 2 : 3 : 5 : 6-tetrachloroacetanilide, 1 : 2 : 4 : 5-tetrachlorobenzene, and a little chloranil, whilst boiling toluene afforded the last two substances and some pentachlorobenzene. The *N*-nitroacetamido-group in (I) was replaced by chlorine or bromine, and halogen also introduced in position 4, by heating with hydrochloric or hydrobromic acid in acetic acid and gave hexachlorobenzene or 2 : 3 : 5 : 6-tetrachloro-1 : 4-dibromobenzene, respectively, but heating (I) with hydriodic acid in acetic acid gave 2 : 3 : 5 : 6-tetrachloroaniline. Orton (J., 1902, **81**, 501) found no evidence of *N*-nitration by the action of nitric acid on *s*-trihalogenoacetanilides. Hydrolysis of (I) with aqueous sodium hydroxide or alcoholic hydrochloric acid gave 2 : 3 : 5 : 6-*tetrachloro*-N-*nitroaniline* (II), which was also obtained, together with 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline, by nitrating 2 : 3 : 5 : 6-tetrachloroaniline. Attempted acetylation of (II) by acetyl chloride resulted in the formation of a mixture of penta- and hexa-chlorobenzene, probably due to formation and decomposition of (I). On the other hand, Macciotta (*Gazzetta*, 1930, **60**, 408) prepared 2 : 3 : 4 : 6-tetranitro-*N*-nitroacetanilide by the action of acetyl chloride on 2 : 3 : 4 : 6-tetranitro-*N*-nitroaniline. The nitro-group in (II) migrates on boiling with acetic acid and 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline is formed to a small extent.

Nitration of 2 : 3 : 5 : 6-tetrachloroaniline with excess of nitric acid gave 2 : 3 : 5 : 6-*tetrachloro*-4-*nitro*-N-*nitroaniline* (III), which was also obtained less readily from 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline.

Both (II) and (III) were decomposed by hydrochloric or hydrobromic acid in acetic acid to give hexachlorobenzene or 2 : 3 : 5 : 6-tetrachloro-1 : 4-dibromobenzene, respectively, and nitrous acid converted both (II) and (III) into diazonium salts to a slight extent as was demonstrated qualitatively by coupling and isolating derived azo-dyes. Methylating (II) and (III) with alkaline methyl sulphate gave 2 : 3 : 5 : 6-*tetrachloro*-N-*nitromethylaniline* and its 4-*nitro*-derivative, respectively.

Experimental.

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

2 : 3 : 5 : 6-*Tetrachloro*-N-*nitroacetanilide* (I).—2 : 3 : 5 : 6-Tetrachloroacetanilide (10 g.), acetic anhydride (60 c.c.), and nitric acid (*d* 1·5; 4 c.c.) were gradually warmed to 50°, and the mixture poured on ice. The N-*nitro*-compound crystallised from ligroin in small, brittle, fawn needles, m. p. 131° (vigorous decomp. with evolution of oxides of nitrogen) (yield, 11·6 g.; 100%) (Found: C, 30·7; H, 1·45; N, 9·0; Cl, 44·6. $C_8H_4O_3N_2Cl_4$ requires C, 30·2; H, 1·3; N, 8·8; Cl, 44·65%).

Reactions of 2 : 3 : 5 : 6-*Tetrachloro*-N-*nitroacetanilide.*—(*a*) 2 : 3 : 5 : 6-Tetrachloro-*N*-nitroacetanilide (6·4 g.) was refluxed with toluene (10 c.c.) for 20 minutes; a vigorous reaction was accompanied by evolution of oxides of nitrogen. On distilling with steam, the toluene was followed by an aqueous distillate containing a yellow solid; extraction of the total aqueous and solid distillate with ether, removal of the ether, and fractional crystallisation of the residue from alcohol gave 1 : 2 : 4 : 5-tetrachlorobenzene, m. p. and mixed m. p. 137—139°, pentachlorobenzene, m. p. and mixed m. p. 84°, and a little chloranil. When xylene was used in place of toluene, 2 : 3 : 5 : 6-tetrachloroacetanilide (0·4 g.), m. p. and mixed m. p. 213—214°, was obtained in addition to 1 : 2 : 4 : 5-tetrachlorobenzene and chloranil.

(*b*) Compound (I) (5 g.), acetic acid (130 c.c.), and hydrochloric acid (50 c.c.) were refluxed for 1 hour. The crystals which separated were recrystallised from acetic acid, forming colourless needles, m. p. and mixed m. p. with hexachlorobenzene, 226—227° (with sublimation) (Found: Cl, 74·7. Calc. for C_6Cl_6: Cl, 74·7%).

(*c*) Compound (I) (2 g.), acetic acid (50 c.c.), and 60% hydrobromic acid (10 c.c.) were refluxed for 15 minutes and

cooled; 2 : 3 : 5 : 6-tetrachloro-1 : 4-dibromobenzene crystallised from acetic acid in fine colourless needles, m. p. 246—247° (with sublimation) (yield, 1·2 g.; 51%), identical with that obtained by brominating 1 : 2 : 4 : 5-tetrachlorobenzene (cf. Mouneyrat and Pouret, *Compt. rend.*, 1899, **129**, 605).

(*d*) Compound (I) (2 g.), acetic acid (50 c.c.), and hydriodic acid (*d* 1·7; 10 c.c.) were refluxed for 45 minutes, and the mixture diluted with water. 2 : 3 : 5 : 6-Tetrachloroaniline crystallised from alcohol in cream-coloured needles, m. p. and mixed m. p. 107—108°.

2 : 3 : 5 : 6-*Tetrachloro*-N-*nitroaniline* (II).—(*a*) 2 : 3 : 5 : 6-Tetrachloro-*N*-nitroacetanilide (4 g.) was refluxed with 3% aqueous sodium hydroxide (100 c.c.) for 5 minutes, and the mixture filtered hot (charcoal). On cooling, colourless leaflets of a sodium salt separated, which decomposed vigorously at *ca.* 290°; the mixture was acidified with hydrochloric acid, and the precipitate of 2 : 3 : 5 : 6-*tetrachloro*-N-*nitroaniline* crystallised from aqueous alcohol, forming colourless prisms or leaflets, m. p. 145—146° (vigorous decomp.) (yield, 3 g.; 86·7%) (Found: C, 26·3; H, 1·0; N, 10·35; Cl, 51·7. $C_6H_2O_2N_2Cl_4$ requires C, 26·1; H, 0·7; N, 10·1; Cl, 51·45%). Hydrolysis was also effected with alcoholic hydrochloric acid (yield, 75%).

(*b*) A mixture of 2 : 3 : 5 : 6-tetrachloroaniline (10 g.), nitric acid (*d* 1·5; 20 c.c.), and acetic acid (50 c.c.) was slowly heated to 60°, kept at this temperature for 5 minutes, and poured on ice. Extraction of the precipitate with hot dilute sodium carbonate solution gave an insoluble residue of 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline (yield, 3·6 g.; 31·6%) and an extract which on acidification with acetic acid afforded 2 : 3 : 5 : 6-tetrachloro-*N*-nitroaniline, m. p. and mixed m. p. with the product from (*a*), 145—146° (decomp.) (yield, 6·9 g.; 57·8%).

Reactions of 2 : 3 : 5 : 6-*Tetrachloro*-N-*nitroaniline*.—(*a*) Compound (II) (5·5 g.) was refluxed with acetyl chloride (20 c.c.) for 30 minutes, the excess of acetyl chloride removed under reduced pressure, and the residue dissolved in alcohol and added to water; the product (4·7 g.) was fractionally crystallised from alcohol, giving colourless needles, m. p. 226—227° (with sublimation), of hexachlorobenzene, and more soluble colourless needles, m. p. 84—85°, of pentachlorobenzene.

(*b*) Compound (II) (1·5 g.) was boiled with acetic acid (3 c.c.) for 2 minutes; 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline, m. p. and mixed m. p. 216° (yield, 0·15 g.; 10%), separated.

(*c*) Compound (II) (1·4 g.) in acetic acid (20 c.c.) was refluxed with hydrochloric acid (5 c.c.) or 60% hydrobromic acid (5 c.c.) for 20 minutes, and gave hexachlorobenzene, m. p. 226—227° (yield, 0·6 g.; 41%), or 2 : 3 : 5 : 6-tetrachloro-1 : 4-dibromobenzene, m. p. 246—247° (yield, 1·3 g.; 68·4%), respectively.

2 : 3 : 5 : 6-*Tetrachloro*-4-*nitro*-N-*nitroaniline* (III).—2 : 3 : 5 : 6-Tetrachloroaniline (3 g.) was added to acetic acid (15 c.c.) and nitric acid (*d* 1·5; 10 c.c.), and the mixture gradually warmed to 50°, kept at this temperature for 3 minutes, and poured on ice. The precipitate was extracted with hot aqueous sodium carbonate, the extract acidified with hydrochloric acid, the precipitate dissolved in ether, and excess of ligroin added, whereupon 2 : 3 : 5 : 6-*tetrachloro*-4-*nitro*-N-*nitroaniline* crystallised in small brownish needles, m. p. 88—95° according to the rate of heating (yield, 3·9 g.; 93·3%) (Found: C, 23·3; H, 0·8; N, 12·9; Cl, 44·4. $C_6HO_4N_3Cl_4$ requires C, 22·4; H, 0·3; N, 13·1; Cl, 44·2%), which were rapidly turned yellow by light or heat. It was also obtained when 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline (5·5 g.) was added to nitric acid (*d* 1·5; 20 c.c.) at 0°, and the mixture poured on ice.

On refluxing compound (III) (1 g.) in acetic acid (20 c.c.) with addition of hydrochloric acid (5 c.c.) or 60% hydrobromic acid (5 c.c.) for 10 minutes, hexachlorobenzene or 2 : 3 : 5 : 6-tetrachloro-1 : 4-dibromobenzene, respectively, was obtained.

Action of Nitrous Acid on Compounds (II) *and* (III).—2 : 3 : 5 : 6-Tetrachloro-*N*-nitroaniline (0·28 g.) or its 4-nitro-derivative (0·32 g.), sodium nitrite (0·07 g.), and 2-hydroxy-3-naphthanilide (0·13 g.) were dissolved in a hot solution of sodium hydroxide (0·4 g.) in water (200 c.c.) and added to boiling 70% aqueous acetic acid (200 c.c.); the corresponding azo-compounds were formed in small amounts. 2 : 3 : 5 : 6-Tetrachlorobenzeneazo-2′-hydroxy-3′-naphthanilide crystallised from acetic acid in red needles, m. p. and mixed m. p. with a specimen prepared from 2 : 3 : 5 : 6-tetrachloroaniline 260° (decomp.), and its 4-nitro-derivative separated from amyl alcohol in deep red needles, m. p. and mixed m. p. 296° (decomp.) (cf. this vol., p. 234).

2 : 3 : 5 : 6-*Tetrachloro*-N-*nitromethylaniline*.—Methyl sulphate (3·3 c.c.) and 10% aqueous sodium hydroxide (10 c.c.) were added gradually to 2 : 3 : 5 : 6-tetrachloro-*N*-nitroaniline (2·8 g.) in 5% aqueous sodium hydroxide (10 c.c.), the mixture raised slowly to the b. p., boiled for 2 minutes, and cooled, and the product extracted with ether. 2 : 3 : 5 : 6-*Tetrachloro*-N-*nitromethylaniline* crystallised from alcohol in colourless, lustrous plates, m. p. 138—139° (yield, 1·9 g.; 65·5%) (Found: C, 29·2; H, 1·7; N, 9·8; Cl, 48·9. $C_7H_4O_2N_2Cl_4$ requires C, 29·0; H, 1·4; N, 9·65; Cl, 48·9%).

2 : 3 : 5 : 6-*Tetrachloro*-4-*nitro*-N-*nitromethylaniline*.—2 : 3 : 5 : 6-Tetrachloro-4-nitro-*N*-nitroaniline (3·2 g.) in 4% aqueous sodium hydroxide (25 c.c.) with methyl sulphate (4·5 c.c.) at 50° for 20 minutes gave the N-*methyl* derivative, which separated from alcohol in fine, almost colourless needles, becoming yellow at 110°, and melting at 171—175° (decomp.) (yield, 1 g.; 30%) (Found: C, 26·0; H, 1·2; N, 13·0; Cl, 41·6. $C_7H_3O_4N_3Cl_4$ requires C, 25·1; H, 0·9; N, 12·5; Cl, 42·4%).

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