58. *Derivatives of* 1 : 2 : 4 : 5-*Tetrachlorobenzene. Part I. Nitro- and Amino-compounds.*

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2 : 3 : 5 : 6-*Tetrachloro*-4-*nitroaniline* (IV), prepared from 2 : 3 : 5 : 6-tetrachloro-1 : 4-dinitrobenzene (III) by reduction with sodium hydrosulphite or by amination with alcoholic ammonia, is diazotisable with nitrosylsulphuric acid at 60—70° and then couples to form azo-dyes. 2 : 3 : 5 : 6-Tetrachloro-aniline, -1 : 4-diaminobenzene, and -4-aminoanisole were also examined as intermediates for azo-dyes. 2 : 3 : 5 : 6-*Tetrachloro*-4-*nitrophenol* (V), best prepared by nitrating 2 : 3 : 5 : 6-tetrachlorophenol, was also a by-product of the preparation of (IV) and 2 : 3 : 5 : 6-tetrachloro-4-nitroanisole from (III) by amination and the action of sodium methoxide, respectively. Replacement of chlorine or demethylation occurred when 2 : 3 : 5 : 6-*tetrachlorobenzenediazonium sulphate* or its 4-methoxy-derivative was decomposed in aqueous sodium acetate, giving 3 : 4 : 6-*trichlorobenzene*-2-*diazo*-1-*oxide* or 2 : 3 : 5 : 6-*tetrachlorobenzene*-4-*diazo*-1-*oxide*, respectively.

We have studied the chemistry of 1 : 2 : 4 : 5-tetrachlorobenzene with special reference to derivatives which may be used as intermediates for azo-dyes. The preparation of 2 : 3 : 5 : 6-tetrachloroaniline (I) (Holleman, *Rec. Trav. chim.*, 1920, **39**, 736; Dyson, George, and Hunter, J., 1926, 304) has been improved. Compound (I) was diazotised satisfactorily with nitrosylsulphuric acid at 60° and then coupled normally to form azo-dyes. On the other hand, when the diazonium solution from (I) was kept in aqueous sodium acetate at room temperature for several days, partial replacement of the 2-chloro-atom occurred with formation of 3 : 4 : 6-*trichlorobenzene*-2-*diazo*-1-*oxide*, identical with that obtained from 3 : 4 : 6-trichloro-*o*-anisidine (see Harrison, Peters, and Rowe, following paper).

2 : 3 : 5 : 6-Tetrachloro-1 : 4-diaminobenzene (II), prepared by Krause (*Ber.*, 1879, **12**, 51) from 1 : 4-dichlorodi-iminobenzoquinone and fuming hydrochloric acid, was readily obtained by reducing 2 : 3 : 5 : 6-tetrachloro-1 : 4-dinitrobenzene (III) with tin and hydrochloric acid in alcohol, and formed only *mono*- and *tetra-acetyl* derivatives. Diazotisation of the monoacetyl compound with nitrosylsulphuric acid led to hydrolysis of the acetyl group, so that, on coupling with alkaline β-naphthol, 2 : 3 : 5 : 6-*tetrachloro*-4-*aminobenzeneazo*-β-*naphthol* was obtained.

2 : 3 : 5 : 6-*Tetrachloro*-4-*nitroaniline* (IV) was prepared conveniently by reducing compound (III) with aqueous-alcoholic sodium hydrosulphite, and, owing to the liability of the 1-nitro-group in (III), was also obtained equally well by aminating it with alcoholic ammonia at 110—120°, but nitrating (I) gave (IV) in much lower yield. The nitroamine (IV) gave a *mono*- and a *di-acetyl* derivative, the latter being reduced to 2 : 3 : 5 : 6-*tetrachloro*-4-*aminodiacetanilide*, which could not be obtained directly from (II), and converted by further acetylation into 2 : 3 : 5 : 6-tetrachloro-1 : 4-tetra-acetyldiaminobenzene. Diazotisation of (IV) required the use of nitrosylsulphuric acid at 60—70° and azo-compounds were prepared from the resulting solution.

Nitration of 2 : 3 : 5 : 6-tetrachloroanisole gave 2 : 3 : 5 : 6-tetrachloro-4-nitroanisole in excellent yield and, although, owing to the lability of the 1-nitro-group in compound (III), it was also readily obtained from (III) and sodium methoxide, a little 2 : 3 : 5 : 6-*tetrachloro*-4-*nitrophenol* (V) was formed at the same time in the latter case. Compound (V) was also obtained as a by-product during amination of (III), but was best prepared by nitrating 2 : 3 : 5 : 6-tetrachlorophenol (cf. Holleman, *loc. cit.*). 2 : 3 : 5 : 6-Tetrachloro-4-aminoanisole (cf. Bureš and Hutter, *Časopis Československ. Lék.*, 1931, **11**, 29), readily obtained by reducing the corresponding nitro-compound with aqueous-alcoholic sodium hydrosulphite, was diazotisable with warm nitrosylsulphuric acid and then coupled with β-naphthol in acetic acid to form 2 : 3 : 5 : 6-*tetrachloro*-4-*methoxybenzeneazo*-β-*naphthol*. On the other hand, 2 : 3 : 5 : 6-tetrachloro-4-methoxybenzenediazonium sulphate was readily convertible at room temperature into 2 : 3 : 5 : 6-*tetrachlorobenzene*-4-*diazo*-1-*oxide* (VI), which coupled with alkaline β-naphthol to form 2 : 3 : 5 : 6-*tetrachloro*-4-*hydroxybenzeneazo*-β-*naphthol* (VII). The azo-dye (VII) was also obtained when the crude diazo-oxide from 2 : 3 : 5 : 6-tetrachloro-4-nitrobenzenediazonium sulphate and aqueous sodium acetate was treated with alkaline β-naphthol, indicating the replacement of the 4-nitro-group and not the 2-chloro-atom with formation of some (VI) in the latter case.

2 : 3 : 5 : 6-*Tetrachloro*-, 2 : 3 : 5 : 6-*tetrachloro*-4-*nitro*-, and 2 : 3 : 5 : 6-*tetrachloro*-4-*methoxy*-2′-*hydroxy*-3′-*naphthanilide* were best prepared from the respective amines and 2-hydroxy-3-naphthoyl chloride in nitrobenzene.

EXPERIMENTAL.

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

2 : 3 : 5 : 6-*Tetrachloroaniline* (I) *and its Derivatives* (Lesimple, *Z. Chem.*, 1868, 227; cf. Holleman; Dyson, George, and Hunter, *locc. cit.*).—2 : 3 : 5 : 6-Tetrachloronitrobenzene (39 g.), m. p. 99·5—100·5°, was added during 30 minutes to a stirred, boiling mixture of alcohol (300 c.c.), hydrochloric acid (6 c.c.) and iron powder (40 g.). After refluxing and stirring for 6 hours, excess of sodium carbonate was added, the mixture filtered hot, and the filtrate diluted with water. The precipitate was collected, boiled with hydrochloric acid, washed with water, and crystallised from alcohol, forming long colourless needles, m. p. 107—108° (yield, 32·5 g.; 94·2%) (Dyson, George, and Hunter, *loc. cit.*, gave m. p. 90°). 2 : 3 : 5 : 6-Tetrachloroaniline forms an unstable hydrochloride with dry hydrogen chloride in benzene, but is insoluble in concentrated hydrochloric acid. The base (46·2 g.) was refluxed with acetic acid (100 c.c.) and acetic anhydride (20 g.) for 24 hours to give the *monoacetyl* derivative, which crystallised from alcohol in lustrous, colourless needles, m. p. 213—214° (yield, 39·6 g.; 72·5%) (Found: C, 35·35; H, 1·8; N, 4·7; Cl, 52·4. $C_8H_5ONCl_4$ requires C, 35·2; H, 1·8; N, 5·1; Cl, 52·0%). On refluxing the base (2 g.) with acetic anhydride (10 c.c.) or acetyl chloride (50 c.c.) for 8 hours, the *diacetyl* derivative was obtained, which crystallised from alcohol in long, colourless needles, m. p. 175—176° (yield,

2·4 g., 88·2%, or 2·6 g., 95·6%, respectively) (Found : C, 38·45; H, 2·3; N, 4·9; Cl, 45·4. $C_{10}H_7O_2NCl_4$ requires C, 38·1; H, 2·2; N, 4·4; Cl, 45·1%). 2 : 3 : 5 : 6-Tetrachlorobenzenediazonium sulphate can be isolated as a cream powder by diazotising the base in sulphuric acid and precipitating the product with alcohol at −3°; on solution in water and addition of a 50% solution of zinc chloride in hydrochloric acid at 0°, yellow needles of the *zinc chloride* double salt separated (Found : 64% of diazonium salt by coupling with β-naphthol. $C_6HCl_4N_2Cl,ZnCl_2$ requires 67·1%). 2 : 3 : 5 : 6-Tetrachloroaniline (1·1 g.) was diazotised with nitrosylsulphuric acid (prepared from 0·35 g. of sodium nitrite and 3 c.c. of sulphuric acid) at 60° and coupled with alkaline β-naphthol; 2 : 3 : 5 : 6-*tetrachlorobenzeneazo-β-naphthol* crystallised from toluene or acetic acid in fine, red needles, m. p. 212° (yield, 1·7 g.; 93%) (Found : N, 7·4. $C_{16}H_8ON_2Cl_4$ requires N, 7·25%).

2 : 3 : 5 : 6-*Tetrachloro-2′-hydroxy-3′-naphthanilide*.—2 : 3 : 5 : 6-Tetrachloroaniline (7·7 g.), 2-hydroxy-3-naphthoyl chloride (7 g.), and nitrobenzene (20 c.c.) were refluxed for 2 hours. Excess of sodium carbonate was added, and the mixture distilled with steam. The residue was extracted with 10% sodium hydroxide solution, the extract acidified, and the precipitate crystallised from acetic acid, forming brownish-yellow, irregular prisms, m. p. 232° (yield, 8·5 g.; 64·6%) (Found : C, 50·6; H, 2·55; Cl, 34·15. $C_{17}H_9O_2NCl_4$ requires C, 50·9; H, 2·25; Cl, 35·4%).

3 : 4 : 6-*Trichlorobenzene-2-diazo-1-oxide*.—2 : 3 : 5 : 6-Tetrachloroaniline (2·3 g.) was diazotised, and the solution poured on ice (200 g.) and sodium acetate (16 g.); after 4 days, the precipitate was collected and crystallised from dilute sulphuric acid, forming orange-yellow needles, m. p. 117—118° (decomp.) (yield, 0·56 g.; 25%). The diazo-oxide was identical with that prepared from 3 : 4 : 6-trichloro-*o*-anisidine (see Harrison, Peters, and Rowe, *loc. cit.*).

2 : 3 : 5 : 6-*Tetrachloro-1 : 4-diaminobenzene* (II) *and its Derivatives*.—(*a*) 2 : 3 : 5 : 6-Tetrachloro-1 : 4-dinitrobenzene (5 g.), m. p. 232° with sublimation (prepared in 60% yield by the method of Berckmans and Holleman, *Rec. Trav. chim.*, 1925, **44**, 851, but the monohydrate being used in place of 20% oleum), was refluxed with tin (10 g.), alcohol (150 c.c.), and hydrochloric acid (50 c.c.) for 1 hour, and the crystals which separated on cooling were ground with aqueous sodium hydroxide. The diamine crystallised from toluene in lustrous, colourless needles, m. p. 222—223° (yield, 3·4 g.; 85%) (Found : C, 29·85; H, 1·6; N, 11·5. Calc. for $C_6H_4N_2Cl_4$: C, 29·3; H, 1·6; N, 11·4%). (*b*) Compound (III) (3 g.) was refluxed with alcohol (200 c.c.) and sodium hydrosulphite (12 g.), water (100 c.c.) being gradually added and boiling continued until the solution was colourless. After filtration, the diamine was precipitated from the filtrate with water (yield, 2 g.; 81%).

The diamine (2 g.) was boiled with acetic anhydride (10 c.c.) for 3 minutes; the *monoacetyl* derivative crystallised from acetic acid in small, colourless rhombohedra, m. p. 276° (yield, 2·3 g.; 100%) (Found : C, 33·7; H, 2·2; N, 9·75. $C_8H_6ON_2Cl_4$ requires C, 33·3; H, 2·1; N, 9·7%). Refluxing (II) (4 g.) with acetic anhydride (20 c.c.) for 20 hours gave the *tetra-acetyl* derivative, which separated from acetic acid in large, colourless prisms, m. p. 205—209° (yield, 6 g.; 89·4%) (Found : C, 40·3; H, 2·85; N, 7·05; Cl, 34·4. $C_{14}H_{12}O_4N_2Cl_4$ requires C, 40·6; H, 2·9; N, 6·7; Cl, 34·3%).

The monoacetyl derivative (7·2 g.) was warmed on the water-bath with nitrosylsulphuric acid for 1 hour. The diazonium solution coupled with alkaline β-naphthol to give 2 : 3 : 5 : 6-*tetrachloro-4-aminobenzeneazo-β-naphthol*, which crystallised from toluene in deep red needles, m. p. 257—258° (decomp.) (yield, 6 g.; 60%) (Found : C, 47·9; H, 2·25; Cl, 35·4. $C_{16}H_9ON_3Cl_4$ requires C, 47·9; H, 2·2; Cl, 35·4%).

2 : 3 : 5 : 6-*Tetrachloro-4-nitroaniline* (IV) *and its Derivatives*.—(*a*) Sodium hydrosulphite (5·5 g.) in water (50 c.c.) was added to 2 : 3 : 5 : 6-tetrachloro-1 : 4-dinitrobenzene (3 g.) in boiling alcohol (180 c.c.) and, after refluxing for 20 minutes, the mixture was cooled. The precipitate crystallised from alcohol in fine, yellow needles, m. p. 216—217°, turning brown on the surface in air (yield, 1·8 g.; 65·2%) (Found : C, 26·8; H, 1·0; Cl, 51·8. $C_6H_2O_2N_2Cl_4$ requires C, 26·1; H, 0·7; Cl, 51·5%). (*b*) 2 : 3 : 5 : 6-Tetrachloro-1 : 4-dinitrobenzene (1·7 g.) was heated with 2·8N-alcoholic ammonia (8 c.c.) at 110—120° for 8 hours in a sealed tube, and the product precipitated by water (yield, 1 g.; 65·4%).

2 : 3 : 5 : 6-*Tetrachloro-4-nitroaniline* is insoluble in hydrochloric acid and does not form a hydrochloride with hydrogen chloride in chloroform. Heating it (5·5 g.) with acetyl chloride (2 c.c.) in toluene (20 c.c.) at 110—120° for 3 hours in a sealed tube gave the *monoacetyl* derivative, which crystallised from alcohol in fine, colourless needles, m. p. 252—253° (yield, 4·4 g.; 69·1%) (Found : C, 30·3; H, 1·3; N, 8·65; Cl, 45·0. $C_8H_4O_3N_2Cl_4$ requires C, 30·2; H, 1·3; N, 8·8; Cl, 44·65%). The *diacetyl* derivative, obtained when (IV) (5 g.) was refluxed with acetic anhydride (20 c.c.) and a drop of sulphuric acid, crystallised from alcohol in fern-like clusters of colourless needles, m. p. 168—169° (yield, 6·1 g.; 93·5%) (Found : C, 33·5; H, 1·7; N, 7·4; Cl, 40·0. $C_{10}H_6O_4N_2Cl_4$ requires C, 33·3; H, 1·7; N, 7·7; Cl, 39·4%). Reduction of the diacetyl derivative (2·4 g.) by refluxing with sodium hydrosulphite (5 g.), water (25 c.c.), and alcohol (55 c.c.) for 15 minutes, followed by precipitation with water, gave 2 : 3 : 5 : 6-*tetrachloro-4-aminodiacetanilide*, which crystallised from aqueous alcohol in long, colourless, rectangular plates, m. p. 194—195° (yield, 1·6 g.; 72·8%) (Found : C, 36·55; H, 2·7; N, 8·4; Cl, 42·8. $C_{10}H_8O_2N_2Cl_4$ requires C, 36·4; H, 2·4; N, 8·5; Cl, 43·0%), converted by boiling acetic anhydride and a little sulphuric acid into 2 : 3 : 5 : 6-tetrachloro-1 : 4-tetra-acetyldiaminobenzene, m. p. and mixed m. p. 205—209°.

2 : 3 : 5 : 6-Tetrachloro-4-nitroaniline (5·5 g.), diazotised with nitrosylsulphuric acid at 60—70°, was added to an aqueous solution of excess of sodium β-naphthol-1-sulphonate, the precipitated diazosulphonate ground with sodium carbonate solution, and the mixture acidified. 2 : 3 : 5 : 6-*Tetrachloro-4-nitrobenzeneazo-β-naphthol* crystallised from toluene in small red needles, with a bronze lustre, m. p. 282—284° (decomp.) (yield, 6 g.; 70%) (Found : N, 9·7; Cl, 33·2. $C_{16}H_7O_3N_3Cl_4$ requires N, 9·7; Cl, 32·9%). 2 : 3 : 5 : 6-Tetrachloro-4-nitroaniline (5·5 g.) was diazotised and coupled with 2-hydroxy-3-naphthanilide in acetic acid at 70°; 2 : 3 : 5 : 6-*tetrachloro-4-nitrobenzeneazo-2′-hydroxy-3′-naphthanilide* crystallised from acetic anhydride in small, red needles, m. p. 296° (decomp.) (yield, 6·6 g.; 60%) (Found : N, 10·2; Cl, 25·7. $C_{23}H_{12}O_4N_4Cl_4$ requires N, 10·2; Cl, 25·8%).

2 : 3 : 5 : 6-*Tetrachloro-4-nitro-2′-hydroxy-3′-naphthanilide*, prepared similarly to the unnitrated analogue, crystallised from acetic acid in faintly yellow plates, m. p. 269—270° (yield, 40%) (Found : C, 45·8; H, 2·0; Cl, 31·7. $C_{17}H_8O_4N_2Cl_4$ requires C, 45·7; H, 1·8; Cl, 31·8%).

2 : 3 : 5 : 6-*Tetrachloro-4-nitroanisole* (cf. Berckmans and Holleman, *loc. cit.*).—(*a*) 2 : 3 : 5 : 6-Tetrachloroanisole (4 g.) was added to nitric acid (*d* 1·5, 12 c.c.) at 0°. The mixture was poured on ice, and the precipitate crystallised from aqueous alcohol, forming long, colourless needles, m. p. 112—113° (yield, 4·5 g.; 95%) (Berckmans and Holleman gave m. p. 105—106°). (*b*) 2 : 3 : 5 : 6-Tetrachloro-1 : 4-dinitrobenzene (15·3 g.) was heated with 0·2N-sodium methoxide (250 c.c.) on the water-bath for 30 minutes, cooled, and diluted with water (yield, 13·4 g.; 92·1%). After the 2 : 3 : 5 : 6-tetrachloro-4-nitroanisole had been collected, the filtrate was evaporated to a small bulk and acidified with nitric acid; a little 2 : 3 : 5 : 6-tetrachloro-4-nitrophenol, m. p. and mixed m p. 148—149° (decomp.), was then obtained.

2 : 3 : 5 : 6-*Tetrachloro-4-aminoanisole and its Derivatives* (cf. Bureš and Hutter, *loc. cit.*).—2 : 3 : 5 : 6-Tetrachloro-4-nitroanisole (14·5 g.) was refluxed with sodium hydrosulphite (50 g.), alcohol (400 c.c.), and water (200 c.c.) for 30 minutes; after concentration and cooling, the amine separated and was crystallised from alcohol, forming faintly pink, long needles, m. p. 107—108° (yield, 12·5 g.; 96·1%) (diacetyl derivatives, m. p. 105—106°; Bureš and Hutter gave m. p. 101°). The base (4 g.) was diazotised in warm nitrosylsulphuric acid and coupled with β-naphthol in acetic acid; 2 : 3 : 5 : 6-*tetrachloro-4-methoxybenzeneazo-β-naphthol* crystallised from acetic acid in clusters of red needles, m. p. 204—205° (yield, 5·2 g.; 91·2%) (Found : N, 7·3; Cl, 34·2. $C_{17}H_{10}O_2N_2Cl_4$ requires N, 6·7; Cl, 34·1%). 2 : 3 : 5 : 6-*Tetra-*

chloro-4-methoxy-2′-hydroxy-3′-naphthanilide crystallised from acetic acid in colourless rhombs or needles, m. p. 208° (Found : C, 50·4; H, 2·65. $C_{18}H_{11}O_3NCl_4$ requires C, 50·1; H, 2·55%).

2 : 3 : 5 : 6-*Tetrachloro-4-nitrophenol* (V).—2 : 3 : 5 : 6-Tetrachlorophenol (2·3 g.) was added to nitric acid (*d* 1·5; 8 c.c.) and acetic acid (40 c.c.) at 10° and, after 1 hour, the mixture was poured on ice. The precipitate crystallised from aqueous acetic acid in colourless needles, m. p. 148—149° (decomp.) (yield, 1·8 g.; 65%) (Found : C, 26·5; H, 0·65; N, 5·1; Cl, 51·1. $C_6HO_3NCl_4$ requires C, 26·0; H, 0·4; N, 5·0; Cl, 51·2%). Concentration of the filtrate obtained after separation of 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline prepared by amination of 2 : 3 : 5 : 6-tetrachloro-1 : 4-dinitrobenzene (see p. 234), followed by extraction with benzene, gave 2 : 3 : 5 : 6-tetrachloro-4-nitrophenol (yield, 5%), m. p. and mixed m. p. 148—149° (decomp.), and the latter was also isolated in small quantity as a by-product in the preparation of 2 : 3 : 5 : 6-tetrachloro-4-nitroanisole by method (*b*) (*q.v.*). The *acetate*, prepared by boiling 2 : 3 : 5 : 6-tetrachloro-4-nitrophenol (0·3 g.) with acetic anhydride (2 c.c.) and a drop of sulphuric acid for 5 minutes, crystallised from aqueous alcohol in long, colourless needles, m. p. 113—114° (yield, 0·3 g.; 87·5%) (Found : C, 30·7; H, 1·4; Cl, 44·45. $C_8H_3O_4NCl_4$ requires C, 30·1; H, 0·9; Cl, 44·5%).

2 : 3 : 5 : 6-*Tetrachlorobenzene-4-diazo-1-oxide* (VI).—2 : 3 : 5 : 6-Tetrachloro-4-aminoanisole (4 g.) was diazotised with warm nitrosylsulphuric acid and diluted (500 c.c.) with addition of sodium acetate; after 4 hours, the *diazo-oxide* was collected and crystallised from ligroin, forming yellow needles, darkening at 120° and exploding at 131° (yield, 3·3 g.; 83%) (Found : N, 11·45; Cl, 55·1. $C_6ON_2Cl_4$ requires N, 10·85; Cl, 55·0%). On boiling the diazo-oxide (4 g.) with acetic anhydride (45 c.c.) for 1 minute, colourless needles of 2 : 3 : 5 : 6-tetrachloro-1 : 4-diacetoxybenzene separated, which were recrystallised from acetic acid, forming colourless needles, m. p. 251° (with sublimation) (yield, 1·6 g.; 33·6%) (Found : C, 36·4; H, 1·9; Cl, 42·4. Calc. for $C_{10}H_6O_4Cl_4$: C, 36·1; H, 1·8; Cl, 42·8%), not depressed on admixture with the product obtained by acetylation of tetrachloroquinol (Graebe, *Annalen*, 1891, **263**, 29). On coupling the diazo-oxide with β-naphthol in 1% sodium hydroxide solution, a brown solution was obtained; acidification with acetic acid gave 2 : 3 : 5 : 6-*tetrachloro-4-hydroxybenzeneazo-β-naphthol* (VII), which crystallised from toluene in fine, red needles, m. p. 264—265° (decomp.) (Found : C, 47·95; H, 2·2; N, 7·2; Cl, 35·3. $C_{16}H_8O_2N_2Cl_4$ requires C, 47·8; H, 2·0; N, 7·0; Cl 35·3%). Compound (VII) was also formed when diazotised 2 : 3 : 5 : 6-tetrachloro-4-nitroaniline was added to aqueous sodium acetate at 0° and, after 1 hour, the resulting yellow precipitate of crude diazo-oxide coupled with alkaline β-naphthol.

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