

59. Polyhalogeno-*o*-anisidines and their Derivatives.

By W. S. W. HARRISON, A. T. PETERS, and F. M. ROWE.

3 : 4 : 6-*Trichloro-2-nitroanisole* (IV), best prepared by nitrating 2 : 4 : 5-trichloroanisole (III), was reduced to 3 : 4 : 6-*trichloro-*o*-anisidine* (V), which with nitric acid (*d* 1.5) gave 2 : 3 : 5-*trichloro-4-nitro-6-methoxy-N-nitroaniline* (VI), converted by nitrous acid into the 1-diazonium compound or by acetic acid into 2 : 3 : 5-*trichloro-6-methoxy-p-benzoquinone*. Decomposition of 2 : 3 : 5-trichloro-6-methoxybenzenediazonium sulphate in presence of aqueous sodium acetate was accompanied by demethylation and gave 3 : 4 : 6-*trichlorobenzene-2-diazo-1-oxide*. Nitration of either *mono-* or *di-acetyl-3 : 4 : 6-trichloro-*o*-anisidine* gave *monoacetyl-3 : 4 : 6-trichloro-5-nitro-*o*-anisidine*, from which 3 : 4 : 6-*trichloro-5-nitro-*o*-anisidine* (VII) was obtained; the latter is convertible into (VI). Other compounds prepared include 3 : 4 : 6-*trichloro-5-amino-2-acetyl- or -diacetyl-aminoanisole*, 3 : 4 : 6-*trichloro-2 : 5-diaminoanisole*, and 3 : 4 : 6-*trichloro-5-bromo-*o*-anisidine*.

THE object of this work was to prepare tri- and tetra-chloro-*o*-anisidines which may be used as intermediates for azo-dyes. By the action of sodium methoxide on 1 : 2 : 4 : 5-tetrachlorobenzene (I), Holleman (*Rec. Trav. chim.*, 1920, **39**, 736) obtained 2 : 4 : 5-trichlorophenol (II) in addition to 2 : 4 : 5-trichloroanisole (III), but we prepared (II) as the sole product by heating (I) with methyl-alcoholic sodium hydroxide at 160° (cf. I.G. Farb. ; D.R.-P. 349,794) and (III) is best prepared by methylating (II). Methylation of 3 : 4 : 6-trichloro-2-nitrophenol (Kohn and Fink, *Monatsh.*, 1931, **58**, 73) with methyl sulphate in xylene-potassium carbonate at 140°, or with methyl toluene-*p*-sulphonate, gave only 10% yields of 3 : 4 : 6-*trichloro-2-nitroanisole* (IV), which was best prepared (66% yield) by nitrating (III). 3 : 4 : 6-*Trichloro-*o*-anisidine* (V), prepared by reducing (IV) with iron, alcohol, and aqueous acetic acid, was treated with nitric acid (*d* 1.5) in acetic acid below 10° and gave 2 : 3 : 5-*trichloro-4-nitro-6-methoxy-N-nitroaniline* (VI). It was converted into the 1-diazonium compound by nitrous acid, whereas refluxing (VI) with acetic acid gave 2 : 3 : 5-*trichloro-6-methoxy-p-benzoquinone*. Compound (V) was best diazotised with warm nitrosylsulphuric acid; on coupling with  $\beta$ -naphthol in sodium hydroxide or acetic acid solution, 2 : 3 : 5-*trichloro-6-methoxybenzeneazo- $\beta$ -naphthol* was formed. Decomposition of the diazonium sulphate or nitrite derived from (V) resulted in demethylation and gave 3 : 4 : 6-*trichlorobenzene-2-diazo-1-oxide*, also obtained from 2 : 3 : 5-6-tetrachlorobenzenediazonium sulphate (see Peters, Rowe, and Stead, preceding paper), and convertible into (II) by heating with alcohol at 150°. On adding the diazo-oxide to alkaline  $\beta$ -naphthol, a deep red solution (disodium salt) was formed; neutralisation gave a blue solution (monosodium salt), and acidification the insoluble red 2 : 3 : 5-*trichloro-6-hydroxybenzeneazo- $\beta$ -naphthol*. It is unusual for the decomposition of the diazonium salt of an *o*-anisidine to be accompanied by demethylation. We found that decomposition of the diazonium salt of 4-chloro-3 : 5-dibromo-*o*-anisidine is also accompanied by demethylation, giving 4-chloro-3 : 5-dibromobenzene-2-diazo-1-oxide, so that halogen in position 6 is not essential for such demethylation to occur.

Nitration of either *mono-* or *di-acetyl-3 : 4 : 6-trichloro-*o*-anisidine* gave *monoacetyl-3 : 4 : 6-trichloro-5-nitro-*o*-anisidine*, hydrolysed by acid to 3 : 4 : 6-*trichloro-5-nitro-*o*-anisidine* (VII), which is convertible into (VI). It is probable that, during the nitration of the above diacetyl compound, one acetyl group is replaced by a

nitro-group with formation of the *N*-nitro-*N*-acetyl derivative, followed by migration of the nitro-group to position 5. That the methoxy-group is removed in preparing 3 : 4 : 6-trichloro-5-nitrobenzene-2-diazo-1-oxide from (VII) was proved by coupling with 2-hydroxy-3-naphthylidene, 2 : 3 : 5-trichloro-4-nitro-6-hydroxybenzeneazo-2'-hydroxy-3'-naphthylidene (VIII) being formed. Diazotised 3 : 4 : 6-trichloro-5-nitro-*o*-anisidine with the same coupling component in acetic acid, or even in a mixture of acetic and sulphuric acids, gave 2 : 3 : 5-trichloro-4-nitro-6-methoxybenzeneazo-2'-hydroxy-3'-naphthylidene, together with a little (VIII).

3 : 4 : 6-Trichloro-5-nitro-*o*-anisidine (VII) was reduced with iron in alcohol and acetic acid to 3 : 4 : 6-trichloro-2 : 5-diaminoanisole, convertible into the 2 : 5-bisacetamido-derivative. 3 : 4 : 6-Trichloro-5-amino-2-acetyl- (IX) and -2-diacetyl-aminoanisole were obtained by reducing the mono- and di-acetyl derivative of compound (VII), respectively, and diazotisation of (IX) did not require the use of nitrosylsulphuric acid.

3 : 4 : 6-Trichloro-5-bromo-*o*-anisidine was readily prepared by brominating (V); it was diazotised with nitrosylsulphuric acid and then coupled normally to form azo-dyes. On the other hand, when the diazonium solution was kept for 1 day in presence of sodium acetate, the 2-diazo-1-oxide separated, and its constitution was proved by conversion into 2 : 3 : 5-trichloro-4-bromo-6-hydroxybenzeneazo-2'-hydroxy-3'-naphthylidene.

Bureš and Havlinova (*Časopis Českoslov. Lék.*, 1929, 9, 101, 129, 153) obtained 3 : 4 : 5 : 6-tetrachloro-*o*-anisidine by chlorinating acet-*o*-anisidine in acetic acid, followed by hydrolysis, but we prepared it readily by chlorinating 3 : 4 : 6-trichloro-*o*-anisidine in chloroform and diazotised it with nitrosylsulphuric acid.

#### EXPERIMENTAL.

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

2 : 4 : 5-Trichloro-phenol (II) and -anisole (III).—1 : 2 : 4 : 5-Tetrachlorobenzene (31 g.), sodium hydroxide (22.6 g.), and methyl alcohol (100 c.c.) were heated in an autoclave at 160° for 7 hours. After dilution to 500 c.c. with water, the mixture was acidified and distilled with steam. The distillate was cooled in ice and the 2 : 4 : 5-trichlorophenol, m. p. 63°, collected (yield, 24.2 g.; 84.9%). It crystallised from ligroin in colourless, feathery needles, m. p. 66°, b. p. 244—248°/746 mm. (cf. I. G. Farb., *loc. cit.*).

Methyl sulphate (9 c.c.) was added gradually to compound (II) (5 g.) in 20% aqueous sodium hydroxide (30 c.c.), the mixture refluxed for 3 hours and poured into water, and the product collected. 2 : 4 : 5-Trichloroanisole crystallised from alcohol in colourless needles, m. p. 75° (yield, 4.2 g.; 78.5%).

3 : 4 : 6-Trichloro-2-nitrophenol.—Nitric acid (*d* 1.43; 3.6 c.c.) in acetic acid (7 c.c.) was added to 2 : 4 : 5-trichlorophenol (6 g.) in acetic acid (7 c.c.) at <10°; after 30 minutes, the mixture, containing crystals, was added to ice, and the precipitate filtered off and crystallised from ligroin, forming pale yellow leaflets, m. p. 92—93° (Kohn and Fink, *loc. cit.*, recorded m. p. 81°) (yield, 6.8 g.; 90%).

3 : 4 : 6-Trichloro-2-nitroanisole (IV).—2 : 4 : 5-Trichloroanisole (30 g.) was added in small amounts to nitric acid (*d* 1.5; 80 c.c.) at 5—10°; after stirring for 40 minutes, the mixture was poured on ice (500 g.), and the product collected, dissolved in warm alcohol, and stirred at 0°; 3 : 4 : 6-trichloro-2-nitroanisole then crystallised in colourless needles, m. p. 19—21°; b. p. 288° (yield, 24.3 g.; 66.6%) (Found : C, 33.6; H, 1.5; N, 5.7; Cl, 41.4. C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>NCl<sub>3</sub> requires C, 32.8; H, 1.5; N, 5.5; Cl, 41.5%).

3 : 4 : 6-Trichloro-*o*-anisidine (V).—Iron powder (30 g.) was added gradually to the nitro-compound (IV) (20 g.) in acetic acid (50 c.c.), alcohol (60 c.c.), and water (40 c.c.), and, after refluxing for 1 hour, the mixture was filtered on ice; the precipitate crystallised from ligroin in almost colourless needles, m. p. 61—62° (yield, 14.1 g.; 79.8%) (Found : C, 36.8; H, 2.7; N, 6.6; Cl, 46.7. C<sub>7</sub>H<sub>4</sub>ONCl<sub>3</sub> requires C, 37.1; H, 2.65; N, 6.2; Cl, 47.0%). The base is readily soluble in most organic solvents, but is insoluble in concentrated hydrochloric acid, and is sparingly volatile with steam. The monoacetyl derivative separated after (V) (5 g.) had been refluxed with acetyl chloride (1.8 c.c.) in toluene (60 c.c.) for 1 hour and cooled; it crystallised from aqueous alcohol in colourless needles, m. p. 181—182° (yield, 4.5 g.; 76%) (Found : C, 40.7; H, 3.0; N, 5.0; Cl, 40.0. C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>NCl<sub>3</sub> requires C, 40.2; H, 3.0; N, 5.2; Cl, 39.7%). The diacetyl derivative, prepared by refluxing the base (V) (5 g.) with acetic anhydride (25 c.c.) and a drop of pyridine for 3 hours, crystallised from aqueous alcohol in colourless needles, m. p. 128—129° (yield, 5.8 g.; 84.5%) (Found : C, 43.2; H, 3.1; Cl, 34.4. C<sub>11</sub>H<sub>10</sub>O<sub>3</sub>NCl<sub>3</sub> requires C, 42.7; H, 3.2; Cl, 34.3%).

3 : 4 : 6-Trichloro-5-nitro-*o*-anisidine (VII).—Mono- (7 g.) or di-acetyl-3 : 4 : 6-trichloro-*o*-anisidine (7 g.) was added to nitric acid (*d* 1.5; 30 c.c.) at <10° and, after 30 minutes, the mixture was poured on ice; the monoacetyl-3 : 4 : 6-trichloro-5-nitro-*o*-anisidine crystallised from aqueous alcohol in colourless needles, m. p. 237° (yield, 7 g., 86%, or 5.5 g., 77.7%, respectively) (Found : C, 34.7; H, 2.3; N, 9.0; Cl, 33.9. C<sub>8</sub>H<sub>7</sub>O<sub>4</sub>N<sub>2</sub>Cl<sub>3</sub> requires C, 34.5; H, 2.4; N, 8.9; Cl, 34.0%). It (3.8 g.) was hydrolysed by warming with concentrated sulphuric acid (20 c.c.) on the water-bath for 1 hour and pouring on ice; the base (VII) crystallised from aqueous alcohol in golden-orange needles, m. p. 121—122° (yield, 2.7 g.; 82.3%) (Found : C, 31.3; H, 2.1; N, 10.1; Cl, 38.8. C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>N<sub>2</sub>Cl<sub>3</sub> requires C, 30.9; H, 1.8; N, 10.3; Cl, 39.2%). It was reconverted into its monoacetyl derivative by heating a toluene solution with an equimolecular proportion of acetyl chloride at 150° for 3 hours. The diacetyl derivative, obtained from the base (VII) (1 g.) or its monoacetyl derivative (1 g.) by heating with acetic anhydride (10 c.c.) at 150° for 3 hours in a sealed tube, crystallised from aqueous alcohol in colourless needles, m. p. 142—143° (yield, 80%) (Found : C, 37.5; H, 2.7; N, 8.3; Cl, 29.6. C<sub>11</sub>H<sub>9</sub>O<sub>5</sub>N<sub>2</sub>Cl<sub>3</sub> requires C, 37.1; H, 2.5; N, 7.9; Cl, 30.0%).

2 : 3 : 5-Trichloro-4-nitro-6-methoxy-*N*-nitroaniline (VI).—(a) Nitric acid (*d* 1.5; 30 c.c.) was added slowly to a stirred mixture of 3 : 4 : 6-trichloro-*o*-anisidine (5 g.) in acetic acid (20 c.c.) at <10° and the temperature kept at 10° for 1 hour. After addition to ice, the solid was filtered off, washed with water, dissolved in 20% aqueous sodium carbonate at 40°, and filtered. Acidification of the filtrate gave the *N*-nitroamine (VI), which crystallised from aqueous alcohol in colourless leaflets, m. p. 116—117° (decomp.) (yield, 4.8 g.; 69%) (Found : C, 26.8; H, 1.5; N, 13.0; Cl, 33.5. C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub> requires C, 26.6; H, 1.3; N, 13.3; Cl, 33.7%). (b) 3 : 4 : 5-Trichloro-5-nitro-*o*-anisidine (2 g.) in acetic acid (8 c.c.) and nitric acid (*d* 1.5; 20 c.c.) similarly gave the *N*-nitroamine (yield, 1.6 g.; 68.8%).

2 : 3 : 5-Trichloro-6-methoxy-*p*-benzoquinone.—Compound (VI) (4 g.) was refluxed with acetic acid (40 c.c.) for 2 hours, during which the almost colourless solution became deep red and oxides of nitrogen were evolved; after a further hour, nitrogen-free orange crystals separated from the cooled mixture; a further amount was obtained by concentrating the filtrate. The quinone crystallised from acetic acid in brilliant orange plates, m. p. 159° (yield, 1.8 g.; 59.4%) (Found : C, 34.4; H, 1.6; Cl, 43.9. C<sub>7</sub>H<sub>3</sub>O<sub>3</sub>Cl<sub>3</sub> requires C, 34.8; H, 1.2; Cl, 44.1%).

2 : 3 : 5-Trichloro-6-methoxybenzeneazo- $\beta$ -naphthol.—3 : 4 : 6-Trichloro-*o*-anisidine (6.8 g.) was heated with concentrated sulphuric acid (30 c.c.) and sodium nitrite (2.2 g.) on the water-bath until a drop of the solution gave no precipitate on dilution with water. The diluted diazo-solution was added to  $\beta$ -naphthol (4.4 g.) in 20% aqueous sodium hydroxide

(150 c.c.), or in acetic acid (250 c.c.), and the *azo*-dye was crystallised from toluene or acetic acid, forming orange-red needles, m. p. 166° (yield, 8.4 g., 73.5%, or 8.7 g., 76%, respectively) (Found: C, 52.9; H, 3.2; Cl, 27.6.  $C_{17}H_{11}O_2N_2Cl_3$  requires C, 53.5; H, 2.9; Cl, 27.9%).

3 : 4 : 6-Trichlorobenzene-2-diazo-1-oxide.—Dry hydrogen chloride was passed into a solution of 3 : 4 : 6-trichloro-*o*-anisidine (4.5 g.) in dry chloroform (80 c.c.); the hydrochloride separated in colourless needles (yield, 5.1 g.; 96.8%). The latter was diazotised by grinding with concentrated hydrochloric acid and excess of sodium nitrite dissolved in the minimum amount of water; after 24 hours at 0°, the crystals were collected and recrystallised from ligroin, forming orange needles, m. p. 118° (decomp.), of the *diazo*-oxide (yield, 2.2 g.; 51.8%) (Found: N, 12.0; Cl, 47.1.  $C_6HON_2Cl_3$  requires N, 12.5; Cl, 47.65%). The same compound was obtained when an aqueous solution of 3 : 4 : 6-trichloro-1-methoxybenzene-2-diazonium sulphate (from 4.5 g. of base) was heated on the water-bath (yield, 2 g.; 44.9%) or was neutralised with sodium acetate and kept overnight at 5–10° (yield, 2.2 g.; 49.3%). The *diazo*-oxide (1 g.) was heated with alcohol (20 c.c.) at 150° for 3 hours in a sealed tube, and the mixture added to water; 2 : 4 : 5-trichlorophenol separated in colourless needles, m. p. and mixed m. p. 63° (yield, 0.5 g.; 56.6%).

2 : 3 : 5-Trichloro-6-hydroxybenzeneazo- $\beta$ -naphthol.—3 : 4 : 6-Trichlorobenzene-2-diazo-1-oxide (2.2 g.) in acetic acid (10 c.c.) was added to  $\beta$ -naphthol (1.4 g.) in sodium hydroxide (10 g.) and water (60 c.c.). Addition of acetic acid changed the deep red colour to blue and acidification precipitated the *azo*-dye, which crystallised from toluene in deep crimson needles, m. p. 226–228° (yield, 2.4 g.; 66%) (Found: C, 51.85; H, 2.45; N, 7.7; Cl, 28.2.  $C_{16}H_9O_2N_2Cl_3$  requires C, 52.3; H, 2.45; N, 7.6; Cl, 29.0%).

3 : 4 : 6-Trichloro-5-nitrobenzene-2-diazo-1-oxide and 2 : 3 : 5-Trichloro-4-nitro-6-hydroxybenzeneazo-2'-hydroxy-3'-naphthanilide (VIII).—3 : 4 : 6-Trichloro-5-nitro-*o*-anisidine (2.7 g.) was diazotised with nitrosylsulphuric acid (prepared from 0.7 g. of sodium nitrite and 10 c.c. of sulphuric acid) on the water-bath, and the *diazo*-solution neutralised with sodium acetate. The *diazo*-oxide was collected after 6 hours (yield, 2 g.; 74.6%), dissolved in acetic acid (5 c.c.), and added to 2-hydroxy-3-naphthoic acid (2 g.) in aqueous sodium hydroxide; acidification with acetic acid gave the *azo*-dye, which crystallised from nitrobenzene in brownish-red plates with a bronze lustre, m. p. 285° (Found: C, 51.8; H, 2.5.  $C_{22}H_{13}O_5N_4Cl_3$  requires C, 51.9; H, 2.4%).

2 : 3 : 5-Trichloro-4-nitro-6-methoxybenzeneazo-2'-hydroxy-3'-naphthanilide.—3 : 4 : 6-Trichloro-5-nitro-*o*-anisidine (2.7 g.) was diazotised and coupled with 2-hydroxy-3-naphthanilide (2.7 g.) in acetic acid (150 c.c.) at 40–50°. After several crystallisations from toluene, the *azo*-dye formed red needles, m. p. 282° (yield, 3.2 g.; 58.7%) (Found: C, 53.1; H, 2.7.  $C_{22}H_{15}O_5N_4Cl_3$  requires C, 52.8; H, 2.75%). Some of the hydroxyazo-dye (VIII) was also formed.

3 : 4 : 6-Trichloro-2 : 5-diaminoanisole.—Iron powder (4 g.) was added to 3 : 4 : 6-trichloro-5-nitro-*o*-anisidine (3.8 g.) in acetic acid (20 c.c.), alcohol (30 c.c.), and water (15 c.c.) at 70°; after refluxing for 1 hour, the mixture was filtered on ice, and the solid collected. The *diamine* crystallised from aqueous alcohol in colourless needles, m. p. 121–122°, turning pink in air (yield, 2.8 g.; 83%) (Found: C, 35.1; H, 2.9; N, 11.35; Cl, 43.7.  $C_7H_7ON_2Cl_3$  requires C, 34.7; H, 2.8; N, 11.6; Cl, 44.1%). The 2-*diacetyl* derivative, obtained by refluxing the *diamine* (1 g.) with acetic anhydride (10 c.c.) for 4 hours, crystallised from aqueous alcohol in colourless needles, m. p. 342° (decomp.) (Found: C, 41.1; H, 3.5.  $C_{11}H_{11}O_3N_2Cl_3$  requires C, 40.6; H, 3.4%). The 2-*monoacetyl* derivative (IX) was obtained by refluxing acetyl-3 : 4 : 6-trichloro-5-nitro-*o*-anisidine (6.5 g.) with iron powder (4 g.) in acetic acid (50 c.c.), alcohol (60 c.c.) and water (40 c.c.) for 1 hour; it separated from aqueous acetic acid in colourless cubes, m. p. 202° (yield 3.8 g.; 64.4%) (Found: C, 37.4; H, 3.1; N, 10.3; Cl, 37.4.  $C_9H_5O_2N_2Cl_3$  requires C, 38.1; H, 3.2; N, 9.9; Cl, 37.6%). Compound (IX), dissolved in 50% acetic acid, was diazotised by pouring into water, hydrochloric acid and sodium nitrite, and coupled with alkaline  $\beta$ -naphthol; 2 : 3 : 6-trichloro-5-methoxy-4-acetamidobenzeneazo- $\beta$ -naphthol crystallised from toluene in orange needles, m. p. 267–268° (Found: C, 52.1; H, 3.3.  $C_{19}H_{14}O_3N_3Cl_3$  requires C, 52.0; H, 3.2%). 2-*Diacetyl*-3 : 4 : 6-trichloro-5-amino-*o*-anisidine, obtained by reducing the corresponding 5-nitro-compound (2 g.) under similar conditions to those used in making (IX), crystallised from aqueous acetic acid in colourless prismatic needles, m. p. 142° (yield, 1.2 g.; 69.6%) (Found: C, 40.3; H, 3.5; N, 8.5; Cl, 33.0.  $C_{11}H_{11}O_3N_2Cl_3$  requires C, 40.6; H, 3.4; N, 8.6; Cl, 32.7%).

3 : 4 : 6-Trichloro-5-bromo-*o*-anisidine.—Compound (V) (4.6 g.) was dissolved in acetic acid (10 c.c.) at 15°, and excess of bromine in acetic acid added gradually until crystals separated progressively; these were filtered off, warmed with concentrated sulphuric acid on the water-bath, and poured on ice. 3 : 4 : 6-Trichloro-5-bromo-*o*-anisidine crystallised from alcohol in colourless needles, m. p. 101° (yield, 6.1 g.; 98.4%) (Found: C, 27.9; H, 1.9; 6.412 mg. gave 13.600 mg. of AgCl + AgBr.  $C_7H_5ONCl_3Br$  requires C, 27.5; H, 1.6%; 13.140 mg. of AgCl + AgBr). The *monoacetyl* derivative crystallised from aqueous alcohol in colourless, prismatic needles, m. p. 236–237° (Found: C, 32.1; H, 2.4; 0.221 mg. gave 0.384 mg. of AgCl + AgBr.  $C_9H_7O_2NCl_3Br$  requires C, 31.4; H, 2.0%; 0.394 mg. of AgCl + AgBr). 2 : 3 : 5-Trichloro-4-bromo-6-methoxybenzeneazo- $\beta$ -naphthol, prepared by diazotising the base (6.1 g.) with nitrosylsulphuric acid (prepared from 1.4 g. of sodium nitrite and 20 c.c. of sulphuric acid) on the water-bath and coupling with alkaline  $\beta$ -naphthol, crystallised from toluene in bright red needles, m. p. 195° (yield, 6.8 g.; 73.9%) (Found: 0.204 mg. gave 0.275 mg. of AgCl + AgBr.  $C_{17}H_{10}O_2N_2Cl_3Br$  requires 0.276 mg. of AgCl + AgBr).

When 3 : 4 : 6-trichloro-5-bromo-*o*-anisidine (2.1 g.) was diazotised with nitrosylsulphuric acid, diluted, sodium acetate added, and the solution kept at room temperature for 1 day, the 2-diazo-1-oxide separated (yield, 1.8 g.; 85.7%); it coupled with 2-hydroxy-3-naphthanilide in aqueous sodium hydroxide, and acidification with acetic acid gave 2 : 3 : 5-trichloro-4-bromo-6-hydroxybenzeneazo-2'-hydroxy-3'-naphthanilide, which crystallised from acetic acid in reddish-brown plates with a bronze lustre, m. p. 274° (Found: N, 7.4; 3.842 mg. gave 3.810 mg. of AgCl + AgBr.  $C_{22}H_{13}O_5N_4Cl_3Br$  requires N, 7.4%; 4.202 mg. of AgCl + AgBr).

3 : 4 : 5-Tetrachloro-*o*-anisidine (cf. Bureš and Havlinova, *loc. cit.*).—Dry chlorine was introduced into 3 : 4 : 6-trichloro-*o*-anisidine (4.5 g.) in chloroform (80 c.c.). The colourless solid which soon separated was warmed with concentrated sulphuric acid on the water-bath until evolution of hydrogen chloride ceased, and the mixture poured on ice. Tetrachloro-*o*-anisidine crystallised from aqueous alcohol in colourless needles, m. p. 95° (yield, 4 g.; 76.9%) (Found: N, 5.3; Cl, 54.5. Calc. for  $C_7H_5ONCl_4$ : N, 5.4; Cl, 54.4%). The base (1.3 g.) was diazotised with nitrosylsulphuric acid (prepared from 0.35 g. of sodium nitrite and 6 c.c. of sulphuric acid) on the water-bath for 15 minutes and coupled with alkaline  $\beta$ -naphthol; 2 : 3 : 4 : 5-tetrachloro-6-methoxybenzeneazo- $\beta$ -naphthol crystallised from toluene in bright red needles, m. p. 204° (yield, 1.5 g.; 71.4%) (Found: N, 6.55; Cl, 33.9.  $C_{17}H_{10}O_2N_2Cl_4$  requires N, 6.7; Cl, 34.1%).

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