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

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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 β-naphthol in sodium hydroxide or acetic acid solution, 2 : 3 : 5-*trichloro*-6-*methoxybenzeneazo*-β-*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 β-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*-β-*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-naphthanilide, 2 : 3 : 5-*trichloro*-4-*nitro*-6-*hydroxybenzeneazo*-2′-*hydroxy*-3′-*naphthanilide* (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′-*naphthanilide*, 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′-*naphthanilide*.

Bureš and Havlinova (*Časopis Českoslov. Lék.*, 1929, **9**, 101, 129, 153) obtained 3 : 4 : 5 : 6-tetrachloro-*o*-anisidine by chlorinating acet-*o*-anisidide 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. $C_7H_4O_3NCl_3$ 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. $C_7H_6ONCl_3$ 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. $C_9H_8O_2NCl_3$ 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. $C_{11}H_{10}O_3NCl_3$ 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. $C_9H_7O_4N_2Cl_3$ 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. $C_7H_5O_3N_2Cl_3$ 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. $C_{11}H_9O_5N_2Cl_3$ 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. $C_7H_4O_5N_3Cl_3$ 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. $C_7H_3O_3Cl_3$ requires C, 34·8; H, 1·2; Cl, 44·1%).

2 : 3 : 5-*Trichloro*-6-*methoxybenzeneazo*-β-*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 β-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*-β-*naphthol*.—3 : 4 : 6-Trichlorobenzene-2-diazo-1-oxide (2·2 g.) in acetic acid (10 c.c.) was added to β-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. $C_{23}H_{13}O_5N_4Cl_3$ 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. $C_{24}H_{15}O_5N_4Cl_3$ 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 : 5-*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. $C_9H_9O_2N_2Cl_3$ 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 β-naphthol; 2 : 3 : 6-*trichloro*-5-*methoxy*-4-*acetamidobenzeneazo*-β-*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*-β-*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 β-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. $C_{23}H_{13}O_3N_3Cl_3Br$ requires N, 7·4%; 4·202 mg. of AgCl + AgBr).

3 : 4 : 5 : 6-*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 β-naphthol; 2 : 3 : 4 : 5-*tetrachloro*-6-*methoxybenzeneazo*-β-*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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