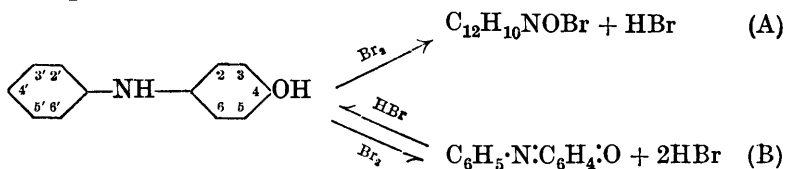


CCCLXXXII.—*The Halogenation of p-Hydroxydiphenylamine. Part II.*

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THE main reaction between bromine or chlorine and *p*-hydroxydiphenylamine and its derivatives (Smith and Orton, J., 1908, 93, 314) may follow one of two paths, leading either to a halogen-substituted *p*-hydroxydiphenylamine (A) or to a quinoneanil (benzoquinonephenylimine) (B). More drastic treatment leads to a disruption of the molecule.



The bromination of *p*-hydroxydiphenylamine, which is very rapid (*loc. cit.*), indicates that the imino-group is much more powerful as a directing group than the hydroxyl, the 2 : 2' : 4'-trisubstituted compound being the first isolable product. The influence of the imino-group is then diminished and bromine enters successively into positions 5 and 3, and, finally, positions 6 and 6' simultaneously. It is now found that, when the hydroxyl group is previously esterified by means of benzoyl chloride or *p*-toluenesulphonyl chloride, the 4'-bromo-, 2 : 2' : 4'-tribromo-, and, finally, 2 : 6 : 2' : 4' : 6'-pentabromo-compounds are successively obtained.

In acetic acid, the first main action of bromine on 2 : 6 : 2' : 4' : 6'-pentabromohydroxydiphenylamine is oxidation to the quinoneanil. The reaction is reversible and, provided the hydrogen bromide formed is not removed, an equilibrium is reached. The small amount of the hydroxy-compound present undergoes slow nuclear substitution (irreversible), displacing the equilibrium, and in time the whole is converted into the 2 : 3 : 5 : 6 : 2' : 4' : 6'-heptabromohydroxy-derivative, the original violet colour of the solution fading as the quinoneanil is reduced by the hydrogen bromide and brominated. If the hydrogen bromide be removed by the addition of sodium acetate, reduction and bromination are prevented.

Chlorine has a disruptive action on *p*-hydroxydiphenylamine; the benzoate or *p*-toluenesulphonate, however, may be chlorinated by the chloroamine method (Orton and King, J., 1911, 99, 1185; Orton and Bradfield, this vol., p. 986), the reaction following a similar

course to that of bromination of the esters, yielding finally the 2 : 6 : 2' : 4' : 6'-pentachloro-compound. The rate of further substitution in 2 : 6 : 2' : 4' : 6'-pentachloro-*p*-hydroxydiphenylamine, obtained from the ester, has now become so diminished that when it is treated with chlorine, oxidation to the quinoneanil initially predominates. This is succeeded, however, by reduction and substitution as in the further bromination of pentabromohydroxydiphenylamine, yielding the 2 : 3 : 6 : 2' : 4' : 6'-hexachloro- and 2 : 3 : 5 : 6 : 2' : 4' : 6'-heptachloro-derivatives.

The action of hydrochloric acid on an acetic acid solution of the pentachloroquinoneanil obtained by oxidation of pentachlorohydroxydiphenylamine with chromic anhydride or mercuric oxide yields the same hexa- and hepta-chloro-compounds. This fact is entirely in harmony with the view of the course of the reaction of *p*-hydroxydiphenylamine derivatives with halogens which has been put forward above; in so far as it relates to the production of halogenated derivatives from the quinoneanil, it closely resembles the scheme first advanced by Wichelhaus (*Ber.*, 1879, 12, 1500) to explain the action of hydrochloric acid on quinone.

Several mixed chlorobromo-*p*-hydroxydiphenylamine derivatives have been prepared.

Amongst the properties of the halogen derivatives of *p*-hydroxydiphenylamine, certain anomalies appear for which at present no explanation can be offered. These are :

(1) The majority of the compounds are, as would be expected, soluble in aqueous alkali; but the following are not, although they are soluble in alcoholic potash : 2 : 2' : 4'-trichloro-5 : 6'-dibromo-, 2 : 5 : 2' : 4'-tetrabromo-, 2 : 2' : 4'-trichloro-3 : 5 : 6 : 6'-tetrabromo-, 2 : 3 : 5 : 2' : 4' - pentabromo -, 2 : 3 : 5 : 2' : 4' : 6' - hexabromo-, 2 : 3 : 5 : 2' : 4' : 6'-hexachloro- and heptabromo-*p*-hydroxydiphenylamine.

Further, these same compounds have resisted all attempts at sulphonylation with *p*-toluenesulphonyl chloride, not only by the Schotten-Baumann procedure, but in pyridine or quinoline, in which they are soluble, indicating that the phenomenon, although concomitant, is not attributable simply to insolubility.

(2) Although 2 : 5 : 2' : 4'-tetrabromo- and 2 : 3 : 5 : 2' : 4'-pentabromo-*p*-hydroxydiphenylamine react with bromine, the benzoyloxy-derivatives prepared from them react very slowly or not at all under the conditions usually successful, in spite of the fact that positions ortho to the imino-group remain vacant, *i.e.*, esterification not only retards substitution in the ortho-position to the hydroxyl group, but greatly diminishes the reactivity of the molecule as a whole, even transmitting the effect through nitrogen to an attached

benzene ring. It is hoped to study this observation, which appears to be unique, in greater detail.

EXPERIMENTAL.

In the preparation of *p*-hydroxydiphenylamine by Calm's method (*Ber.*, 1883, 16, 2786; 1884, 17, 2431) the yield is much improved by the employment of crude aniline, and both yield and purity are enhanced if pure aniline to which a drop of sulphuric acid has been added is used. The product, after distillation in superheated steam and then under 12 mm. pressure, melts at 73°.

The *p*-toluenesulphonyl derivative, prepared from *p*-toluenesulphonyl chloride (210 g.), *p*-hydroxydiphenylamine (185 g.), benzene (900 c.c.), and aqueous sodium hydroxide, crystallises from alcohol in thin plates, m. p. 126·5°, soluble in benzene and chloroform, less soluble in alcohol, petroleum, and acetic acid (Found : S, 9·5. $C_{19}H_{17}O_3NS$ requires S, 9·5%).

The acetic acid used as a medium for halogenation was purified by Orton and Bradfield's method (this vol., p. 983).

Chloro-compounds.

The following chloro-4-acyloxydiphenylamines were prepared by chlorination by the chloroamine (*N*:2:4-trichloroacetanilide or dichloramine T) method and were usually precipitated on addition of water. They were hydrolysed by boiling alcoholic potassium hydroxide, and the hydroxy-compounds precipitated by addition of water to the acidified solutions. The anils were prepared by oxidising the corresponding chlorohydroxydiphenylamines in boiling benzene with yellow mercuric oxide or in boiling acetic acid with chromic acid; they were usually isolated by evaporation of the solvent and addition of petroleum in the former method and by addition of water in the latter. Fission of the anils was effected in acetic acid by addition of sulphuric acid; on dilution with water and basification, the expected chloroaniline was obtained in every case.

4'-Chloro-4-benzoyloxydiphenylamine is prepared from *p*-benzoyloxydiphenylamine; the reaction, initiated by the addition of one drop of hydrochloric acid, is completed in 15 minutes. The product (yield, 30%) crystallises from petroleum or 98% acetic acid in silvery plates, m. p. 148·5°. The presence of isomerides is indicated (Found : Cl, 10·6. $C_{19}H_{14}O_2NCl$ requires Cl, 11·0%).

4'-Chloro-4-hydroxydiphenylamine forms pale green leaflets (yield, 72%), m. p. 91° (Found : Cl, 15·9. $C_{12}H_{10}ONCl$ requires Cl, 16·2%). The *p*-toluenesulphonate has m. p. 93—94° (Found : Cl, 9·3. $C_{19}H_{16}O_3NClS$ requires Cl, 9·5%).

4'-Chlorobenzoquinoneanil crystallises in dark red, massive prisms,

m. p. 83.5°, insoluble in water, sparingly soluble in alcohol, hot or cold, and in cold petroleum and acetic acid, readily soluble in chloroform and benzene (Found : Cl, 16.0. $C_{12}H_8ONCl$ requires Cl, 16.3%).

2 : 2' : 4'-*Trichloro-4-benzoyloxy-* and *-4-p-toluenesulphonyloxy-diphenylamines* are prepared at 50—55° from the 4-acyloxy-compounds or their monochloro-derivatives and separate on cooling. The *benzoyloxy*-compound has m. p. 114° (Found : Cl, 27.3. $C_{19}H_{12}O_2NCl_3$ requires Cl, 27.1%); the *toluenesulphonyloxy*-compound crystallises from hot benzene-petroleum or from acetic acid in prisms, m. p. 130.5° (Found : Cl, 24.3. $C_{19}H_{14}O_3NCl_3S$ requires Cl, 24.1%).

2 : 2' : 4' - *Trichloro-4-hydroxydiphenylamine*, crystallised from glacial acetic acid and then from petroleum, forms prisms, never quite colourless, m. p. 128° (Found : Cl, 36.7. $C_{12}H_8ONCl_3$ requires Cl, 36.9%).

2 : 2' : 4' - *Trichlorobenzoquinoneanil* separates from petroleum (b. p. 40—60°), containing a very little benzene, in long, bronzy needles, m. p. 72.5°. It is readily soluble in all organic solvents except light petroleum (Found : Cl, 37.1. $C_{12}H_6ONCl_3$ requires Cl, 37.2%).

2 : 6 : 2' : 4' - *Tetrachloro-4-p-toluenesulphonyloxydiphenylamine* is obtained from the trichlorotoluenesulphonyloxydiphenylamine at 45—50°, and is separated from the other isomerides produced only by a tedious series of fractional precipitations from chloroform and light petroleum. It is much more soluble in common solvents than the tri- and penta-chloro-derivatives, and crystallises from acetic acid, chloroform, and petroleum (b. p. 110°) in prisms, m. p. 126° (Found : Cl, 30.1. $C_{19}H_{13}O_3NCl_4S$ requires Cl, 29.8%).

The *tetrachlorohydroxy*-compound solidifies with difficulty, but after being thoroughly washed and dried it may be obtained crystalline by the addition of petroleum, b. p. 40—60°, to a solution in petroleum, b. p. 110°; it then melts at 113° (Found : Cl, 44.3. $C_{12}H_7ONCl_4$ requires Cl, 44.0%). The *tetrachlorobenzoyloxy*-compound is obtained by benzoylating the tetrachlorohydroxy-compound in pyridine; after crystallisation from petroleum (b. p. 60—85°) it melts at 114.5° (Found : Cl, 33.1. $C_{19}H_{11}O_2NCl_4$ requires Cl, 33.3%).

2 : 6 : 2' : 4' - *Tetrachlorobenzoquinoneanil* separates from ethyl acetate in violet crystals, m. p. 143° (Found : Cl, 44.5. $C_{12}H_5ONCl_4$ requires Cl, 44.2%).

2 : 6 : 2' : 4' : 6' - *Pentachloro-4-benzoyloxydiphenylamine* is prepared from the mono- or trichloro-derivative; after crystallisation from alcohol (yield, 62%) it melts at 133—134° (Found : Cl, 38.0. $C_{19}H_{10}O_2NCl_5$ requires Cl, 38.4%). The *toluenesulphonyloxy*-compound is prepared from the trichlorosulphonyloxy-compound

at 55°; on cooling, it separates in quantitative yield, in prisms, m. p. 156·5°, unaltered by crystallisation from acetic acid. It is also obtained by passing chlorine into a hot acetic acid solution of 4-*p*-toluenesulphonyloxydiphenylamine in presence of anhydrous sodium acetate. It is soluble in chloroform, but sparingly soluble in other solvents (Found: Cl, 34·7. $C_{19}H_{12}O_3NCl_5S$ requires Cl, 34·7%). The *pentachlorohydroxy*-compound crystallises from petroleum in clear brown prisms, m. p. 156° (Found: Cl, 49·2. $C_{12}H_6ONCl_5$ requires Cl, 49·6%). The *monoacetyl* derivative, obtained by treating the hydroxy-compound in acetic acid with acetic anhydride in the presence of sodium acetate, has m. p. 126°. It is insoluble in alkali, very soluble in benzene, petroleum, and chloroform, and sparingly soluble in acetic acid (Found: Cl, 44·0. $C_{14}H_8O_2NCl_5$ requires Cl, 44·4%).

2 : 6 : 2' : 4' : 6'-*Pentachlorobenzoquinoneanil* (prepared by the chromic acid method) forms fine, bronzy-red needles with a metallic lustre, m. p. 163° (Found: Cl, 49·5. $C_{12}H_4ONCl_5$ requires Cl, 49·9%).

All attempts to chlorinate further *p*-benzoyloxy- and 4-*p*-toluenesulphonyloxy-diphenylamine have been unsuccessful, as is to be expected.

2 : 3 : 6 : 2' : 4' : 6'-*Hexachloro-4-hydroxydiphenylamine* is prepared from pentachlorohydroxydiphenylamine and forms hemispherical nodules, m. p. 114° (Found: Cl, 53·6. $C_{12}H_5ONCl_6$ requires Cl, 54·3%). Benzoylation in pyridine gives the *benzoyloxy*-derivative, which, crystallised from alcohol and then from petroleum, forms small clusters of hard, glistening, brown prisms, m. p. 125° (Found: Cl, 42·5. $C_{19}H_9O_2NCl_6$ requires Cl, 42·9%). The *toluenesulphonyloxy*-derivative crystallises from glacial acetic acid in white prisms, m. p. 141° (Found: Cl, 39·0. $C_{19}H_{11}O_3NCl_6S$ requires Cl, 39·0%).

2 : 3 : 6 : 2' : 4' : 6'-*Hexachlorobenzoquinoneanil** is obtained by the

* The synthesis of this compound establishes the hitherto uncertain constitution of the isomeride yielding the same fission products which was obtained by Orton and Smith (J., 1905, 87, 389) as a product of the transformation of *s*-trichlorophenylnitroamine, as the 2 : 3 : 5 : 2' : 4' : 6'-compound. Similarly, the preparation of 2 : 6 : 2' : 4' : 6'-pentabromobenzoquinoneanil (p. 2861) establishes the constitution of the isomeride produced by transformation of *s*-tribromophenylnitroamine (Orton and Smith, J., 1907, 91, 146) as the 3 : 5 : 2' : 4' : 6'-pentabromo-compound. It is regretted that, owing to a clerical error, the melting points of the penta- and hexa-bromobenzoquinoneanils given in that paper have become interchanged. Further examination has shown that the hexabromoquinoneanil then obtained was not completely pure. The following corrected melting points are given to avoid ambiguity :

3 : 5 : 2' : 4' : 6'-Pentabromo-4-hydroxydiphenylamine, m. p. 157°.

3 : 5 : 2' : 4' : 6'-Pentabromobenzoquinoneanil, m. p. 150·5°.

2 : 3 : 5 : 2' : 4' : 6'-Hexabromo-4-hydroxydiphenylamine, m. p. 216°.

2 : 3 : 5 : 2' : 4' : 6'-Hexabromobenzoquinoneanil, m. p. 171°.

chromic acid method as a black, crystalline solid, m. p. 114° after recrystallisation from alcohol. It dissolves in ordinary solvents, except alcohol, to give violet solutions (Found: Cl, 54.2. $C_{12}H_3ONCl_6$ requires Cl, 54.65%). On treatment of the red-brown solution in sulphuric acid (1 in 100) with water, the colour changes to light yellow and a mixture of yellow plates and red needles separates. The mixture is collected and digested with a little cold alcohol; the yellow trichlorobenzoquinone remaining undissolved melts, after crystallisation from hot alcohol, at 162—163°. Careful dilution of the alcoholic extract gave *s*-trichloroaniline, m. p. 77.5° (acetyl derivative, m. p. 204°).

Heptachloro-4-hydroxydiphenylamine.—The pentachlorohydroxydiphenylamine (5 g.; 1 mol.) in 15 c.c. of acetic acid is treated with a solution of *N*-chloroacetamide (1.35 g.; 1 mol.) in 5 c.c. of the same solvent, together with two drops of 20% hydrochloric acid, the mixture becoming at once deep violet. After 1 hour, a like amount of chloroamine is added. No chlorine remains after 18 hours. The solution is decolorised by heating with zinc dust and the boiling suspension is filtered at once. White needles (55%) separate on cooling, m. p. 158—159°, unchanged on recrystallisation from petroleum or slightly diluted acetic acid (Found: Cl, 58.05. $C_{12}H_4ONCl_7$ requires Cl, 58.3%).

The *benzoyloxy*-derivative crystallises from glacial acetic acid in massive, white plates, m. p. 164° (Found: Cl, 46.5. $C_{19}H_8O_2NCl_7$ requires Cl, 46.8%). The sulphonylation of the heptachlorohydroxy-derivative is characterised by its slowness, due no doubt to the presence of two ortho-substituents. After 45 minutes' shaking, a violet solid has separated; after being washed with water and with benzene, it crystallises from glacial acetic acid in white needles, m. p. 141.5° (Found: Cl, 42.4. $C_{19}H_{10}O_3NCl_7S$ requires Cl, 42.8%).

Heptachlorobenzoquinoneanil separates from alcohol in small, black crystals, m. p. 114°. Its solutions are violet. Fission by dilute sulphuric acid (1 in 50) and addition of water gives successively tetrachlorobenzoquinone (which sublimes in pale yellow, iridescent plates, not molten at 260°) and *s*-trichloroaniline, m. p. 77.5°.

Action of Hydrochloric Acid on 2 : 6 : 2' : 4' : 6'-Pentachlorobenzoquinoneanil.—Concentrated hydrochloric acid (2 c.c.) was added to the quinoneanil (1.5 g.) in glacial acetic acid (100 c.c.). After 18 hours, the bluish-green solution was treated with zinc dust to remove the excess of hydrochloric acid, filtered, and diluted with 300—400 c.c. of water. Hexachlorohydroxydiphenylamine separated as white, crystalline crusts, m. p. 114° after recrystallisation. The action of hydrochloric acid on 2 : 3 : 6 : 2' : 4' : 6'-hexachlorobenzo-

quinoneanil in a similar manner yielded heptachlorohydroxydiphenylamine.

Bromo-compounds.

4'-Bromo-4-benzoyloxydiphenylamine. — *p*-Benzoyloxydiphenylamine (5 g.; 1 mol.) and anhydrous sodium acetate (2 mols.), dissolved in 250 c.c. of acetic acid, were treated with a solution of bromine (0.865 c.c.; 1 mol.) in 125 c.c. of acetic acid. After $\frac{1}{2}$ hour, dilution to 75% caused slow separation of white, fibrous needles, which, after crystallisation from alcohol or benzene–ligroin, melted at 150.5°: yield, 33% (Found: Br, 21.2. $C_{19}H_{14}O_2NBr$ requires Br, 21.7%).

By hydrolysis of the above, the *hydroxy*-compound was obtained as thin laminæ, m. p. 108°, in 75% yield (Found: Br, 29.7. $C_{12}H_{10}ONBr$ requires Br, 30.3%).

4'-Bromobenzoquinoneanil was obtained by oxidation of the *hydroxy*-compound with excess of yellow mercuric oxide. The solution was evaporated to a small volume and the quinoneanil then separated in scarlet crystals, m. p. 100–104°. The melting point of this substance, which appears to be dimorphic, is not sharp and depends on the nature and temperature of the solvent (Found: Br, 29.8. $C_{12}H_8ONBr$ requires Br, 30.5%). Fission gave *p*-bromoaniline, but no trace of *p*-benzoquinone was found.

2 : 2' : 4'-Tribromo-4-p-toluenesulphonyloxydiphenylamine was prepared, by the method described above, from *4-p*-toluenesulphonyloxydiphenylamine at 50°, and crystallised from benzene–petroleum, acetone, or glacial acetic acid (Found: Br, 41.7; S, 5.6. $C_{19}H_{14}O_3NBr_3S$ requires Br, 41.7; S, 5.5%). The tribromo-4-benzoyloxy-compound obtained by Smith and Orton (*loc. cit.*) is produced in better yield by the Schotten–Baumann method or by bromination of *p*-benzoyloxydiphenylamine. Both esters are sparingly soluble in common organic media, and give on hydrolysis the tribromohydroxydiphenylamine described by Smith and Orton (*loc. cit.*), this synthesis providing the further evidence required to establish it as *2 : 2' : 4'-tribromo-4-hydroxydiphenylamine*.

The low solubility of tribromoacyloxydiphenylamines necessitated the following procedure: Finely powdered tribromo-4-*p*-toluenesulphonyloxydiphenylamine was exposed to the vapour of bromine in the presence of anhydrous sodium phosphate or sodium borate, and after 20 hours the absorbed bromine was removed by evacuation. Extraction with boiling benzene gave a quantitative yield of white, prismatic crystals of the sparingly soluble *2 : 6 : 2' : 4' : 6'-penta-bromo-4-p-toluenesulphonyloxydiphenylamine*, m. p. 210° (Found: Br, 54.1. $C_{19}H_{12}O_3NBr_5S$ requires Br, 54.5%).

The *hydroxy*-compound (yield, 60%) crystallised from ligroin containing 5% of benzene, or from 75% alcohol, in massive, brown prisms, m. p. 206—207° (Found: Br, 68·5. $C_{12}H_6ONBr_5$ requires Br, 69·0%). The *benzoyloxy*-derivative, prepared by benzoylation in pyridine, separated after 24 hours and was precipitated from benzene solution by light petroleum in white needles, m. p. 141—142° (Found: Br, 58·6. $C_{19}H_{10}O_2NBr_5$ requires Br, 58·5%).

2 : 6 : 2' : 4' : 6'-*Pentabromobenzoquinoneanil*, prepared by the chromic acid method, has m. p. 184—185° (Found: Br, 68·7. $C_{12}H_4ONBr_5$ requires Br, 69·2%). Fission gave *s*-tribromoaniline and 2 : 6-dibromobenzoquinone.

Pentabromo-4-hydroxydiphenylamine with bromine in acetic acid solution in the absence of an absorbent for hydrogen bromide, yielded heptabromohydroxydiphenylamine (Smith and Orton, *loc. cit.*), but in the presence of sodium acetate oxidation to the violet quinoneanil occurred. An attempt to sulphonylate the heptabromohydroxy-compound by the Schotten-Baumann method gave a *substance*, m. p. 188°, soluble in 5% alcoholic potash, which was neither the initial material nor the desired sulphonyloxy-compound (Found: Br, 70·4%).

All attempts to sulphonylate 2 : 5 : 2' : 4'-tetrabromo- and 2 : 3 : 5 : 2' : 4'-pentabromo-4-hydroxydiphenylamine (Smith and Orton, *loc. cit.*) by the Schotten-Baumann procedure and the various modifications of Einhorn's method (compare Fischer and Pfaehler, *Ber.*, 1920, **53**, 1642; Ohle, *Ber.*, 1924, **57**, 409; Ohle and Dickhäuser, *Ber.*, 1925, **58**, 2593) failed.

In general, the sulphonyloxy-compounds are brominated more smoothly than the benzoyloxy-compounds, but the failure to sulphonylate the two hydroxy-compounds above led us to investigate the effect of bromine on the corresponding benzoyloxydiphenylamines. Although two positions ortho to the powerfully directing imino-group are present in 2 : 5 : 2' : 4'-tetrabromo-4-benzoyloxydiphenylamine, this substance brominates too slowly to permit isolation of higher derivatives. Prolonged refluxing with bromine in carbon tetrachloride solution is followed by recovery of initial material. More drastic conditions such as the gaseous bromine-sodium phosphate method, or in chloroform in the presence of ferric chloride, lead to complete disruption of the molecule. Somewhat similar results followed from the work on 2 : 3 : 5 : 2' : 4'-pentabromo-4-benzoyloxydiphenylamine, but gaseous bromine converted it into a viscous, dark liquid from which a small amount of heptabromobenzoxyloxydiphenylamine was isolated.

Chlorobromo-compounds.

6 : 6'-Dichloro-2 : 2' : 4'-tribromo-4-p-toluenesulphonyloxy- and -4-benzoyloxy-diphenylamines.—Because of low solubility, the tri-bromo-4-acyloxydiphenylamines were chlorinated in suspension in acetic acid solutions of dichloramine T (100% excess); after 18 hours, 2 equivalents of chlorine had disappeared, a quantitative yield of pentahalogenated derivative having separated.

The *sulphonyloxy*-compound melted, after crystallisation from petroleum, at 185° (Found: * Hals., 131.2; AgCl, 111.6. $C_{19}H_{12}O_3NCl_2Br_3S$ requires Hals., 131.9; AgCl, 111.3). The *benzoyloxy*-compound, after crystallisation from acetic acid, melted at 153° (Found: Hals., 140.9; AgCl, 119. $C_{19}H_{10}O_2NCl_2Br_3$ requires Hals., 143; AgCl, 120.6). Both esters are very sparingly soluble in all solvents. Hydrolysis of these gave the *hydroxy*-compound in small, brown prisms which, after twice crystallising from petroleum, melted at 166° (Found: Hals., 171.6; AgCl, 145.1. $C_{12}H_6ONCl_2Br_3$ requires Hals., 173.1; AgCl, 146.1).

6 : 6'-Dichloro-2 : 2' : 4'-tribromobenzoquinoneanil, obtained by the chromic acid method, crystallised from acetic acid in deep purple, irregular prisms, m. p. 150° (Found: Hals., 173.1; AgCl, 147.8. $C_{12}H_4ONCl_2Br_3$ requires Hals., 174.0; AgCl, 146.6). By careful dilution of its solution in concentrated sulphuric acid, 2-chloro-4 : 6-dibromoaniline was obtained.

2 : 2' : 4'-Trichloro-6 : 6'-dibromo-4-p-toluenesulphonyloxydiphenylamine.—Trichlorosulphonyloxydiphenylamine was brominated by the bromine vapour-sodium borate (phosphate) method. After crystallisation from benzene, chloroform, or petroleum, the product melted at 174°. Yield, quantitative (Found: Hals., 133.5; AgCl, 120.1. $C_{19}H_{12}O_3NCl_3Br_2S$ requires Hals., 134.3; AgCl, 119.5). The *benzoyloxy*-compound, prepared similarly, formed a sticky magma, which was suspended in acetic acid and freed from bromine by passage of sulphur dioxide. On warming, the material dissolved, and then separated in colourless prisms, m. p. 134° (Found: Hals., 149.6; AgCl, 133.8. $C_{19}H_{10}ONCl_3Br_2$ requires Hals., 146.5; AgCl, 130.8). The *hydroxy*-compound, after repeated crystallisation from 75% acetic acid, formed irregular prisms, m. p. 180°, readily soluble in all other organic solvents (Found: Hals., 176.5; AgCl, 157.8. $C_{12}H_6ONCl_3Br_2$ requires Hals., 180.5; AgCl, 160.9).

* For the Carius estimation of some of the substances here described, prolonged heating at 300° was required. In such cases, Robertson's method (J., 1915, **107**, 902) frequently proved of service. For the analysis of the chlorobromo-compounds, the mixture of silver halides (the weight of which, obtained from 100 parts of the substance, is denoted by "Hals.") obtained was usually converted into silver chloride by warming in a current of chlorine.

By the chromic acid method 2 : 2' : 4'-trichloro-6 : 6'-dibromobenzoquinoneanil was obtained in massive, black prisms, m. p. 170° after crystallisation from chloroform (Found : Hals., 181·8; AgCl, 162·5. $C_{12}H_4ONCl_3Br_2$ requires Hals., 181·4; AgCl, 161·6). The fission of this quinoneanil requires care : a solution of 0·25 g. in 25 c.c. of concentrated sulphuric acid was slowly diluted with water to 20%. A small quantity of solid (unexamined) separated, and ether extraction then removed 2 : 4-dichloro-6-bromoaniline, m. p. 78° (acetyl derivative, m. p. 217°). Chattaway and Orton (J., 1901, 79, 816) give m. p. 83° and 218°, respectively.

2 : 2' : 4'-Trichloro-5-bromo-4-hydroxydiphenylamine.—Trichlorohydroxydiphenylamine in acetic acid solution containing sodium acetate was oxidised by bromine, giving quinhydrone-like complexes, but their formation was avoided when 1·85 c.c. of bromine in 25 c.c. of chloroform were added to 10 g. of the amine in 100 c.c. of boiling chloroform during 1 hour; evolution of hydrogen bromide ceased after 2·5 hours. The solution, concentrated to 25—30 c.c., deposited matted needles which, after crystallisation from petroleum, melted at 127—128° (yield, 5·9 g.); a further 2 g. were recovered from the mother-liquor (combined yields, 60%). The compound is easily soluble in aqueous caustic soda (Found : Hals., 165·0; AgCl, 152·8. $C_{12}H_7ONCl_3Br$ requires Hals., 167·4; AgCl, 155·3). The benzoyloxy-compound separated from pyridine; m. p. 186° (Found : Hals., 129·4; AgCl, 120·0. $C_{19}H_{11}O_2NCl_3Br$ requires Hals., 131·2; AgCl, 121·7).

When the above hydroxy-compound was sulphonylated in the usual way, and the reaction product kept for 2 hours in a freezing-mixture, a red, crystalline solid separated. Following washing with water and with light petroleum, crystallisation from slightly diluted acetic acid gave colourless prisms of 2 : 2' : 4'-trichloro-5-bromo-4-sulphonyloxydiphenylamine, m. p. 114° (Found : Hals., 117·9; AgCl, 109·5. $C_{19}H_{13}O_3NCl_3BrS$ requires Hals., 119·0; AgCl, 110·1).

2 : 2' : 4' - Trichloro - 5 - bromobenzoquinoneanil (mercuric oxide method) crystallised from benzene or petroleum, or a mixture of the two, in hemispherical nodules of red, spear-shaped needles, m. p. 115°. Fission by solution in 45 volumes of concentrated sulphuric acid and slow dilution to 25% strength, followed by steam distillation, gave a yellow quinone, m. p. 172°, reduction of which by sulphur dioxide in aqueous-alcoholic solution gave a colourless quinol, m. p. 169° (2-chloro-5-bromobenzoquinone and 2-chloro-5-bromoquinol both melt at 172°). Neutralisation of the acid liquor, followed by distillation in steam, gave 2 : 4-dichloroaniline, m. p. 61° (acetyl derivative, m. p. 145°).

2 : 2' : 4' - Trichloro - 5 : 6' - dibromo - 4 - hydroxydiphenylamine, prepared

by refluxing trichlorobromohydroxydiphenylamine (10 g.) and bromine (1 mol.) in 80 c.c. of chloroform for 90 minutes, separated, on cooling, in white needles, m. p. 189° after two crystallisations from chloroform (Found: Hals., 176·9; AgCl, 160·5. $C_{12}H_6ONCl_3Br_2$ requires Hals., 180·5; AgCl, 160·9). Fractions obtained from the chloroform mother-liquor appeared to contain isomerides. Attempts to sulphonylate and benzoylete this substance failed.

2 : 2' : 4'-Trichloro-5 : 6'-dibromobenzoquinoneanil (chromic acid method) formed small, vermilion, scintillating needles, m. p. 133° (Found: Hals., 177·7; AgCl, 159·1. $C_{12}H_4ONCl_3Br_2$ requires Hals., 181·4; AgCl, 161·4). Fission gave golden-yellow plates, m. p. 165° (2-chloro-5-bromobenzoquinone melts at 172°), and on dilution to 20% strength 2 : 4-dichloro-6-bromoaniline was precipitated.

2 : 2' : 4'-Trichloro-3 : 5 : 6 : 6'-tetrabromo-4-hydroxydiphenylamine. —To a solution of 4 g. of trichlorohydroxydiphenylamine in 40 c.c. of chloroform boiling under reflux, 2·8 c.c. (4 mols.) of bromine in the same solvent were slowly added; hydrogen bromide was at first rapidly evolved. The mixture was then transferred to a silica flask, with excess of bromine, and exposed to sunlight for 3½ days, the solid that had separated after 12 hours being redissolved by gentle warming. The large, thin laminæ (3·9 g.) which separated were broken up, and freed from bromine and chloroform over charcoal and potash in a vacuum; m. p. 160°. Evaporation of the mother-liquor yielded a further 3·5 g. (combined yield, 89%) (Found: Hals., 194·5; AgCl, 165·1. $C_{12}H_4ONCl_3Br_4$ requires Hals., 195·7; AgCl, 166·2). The *benzoyloxy*-compound crystallised from chloroform-acetic acid in small, elongated prisms, m. p. 163° (Found: Hals., 169·8. $C_{19}H_8O_2NCl_3Br_4$ requires Hals., 169·7). Attempts to sulphonylate the hydroxy-compound failed.

2 : 2' : 4'-Trichloro-3 : 5 : 6 : 6'-tetrabromobenzoquinoneanil (chromic acid method) crystallised from acetic acid in slender, indigo needles, m. p. 136°. Fission and dilution gave a very sparingly soluble substance, m. p. 294°, and 2 : 4-dichloro-6-bromoaniline. The literature notes the insolubility of chlorotribromoquinone and records two values for its m. p., *viz.*, 292° and 303°.

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