II.—*Halogen Derivatives of Diphenyl and Dihydroxydiphenyl.*

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IN an investigation on the action of water on the diazonium salt prepared from 3 : 3′-dichlorobenzidine (Trans., 1903, **83**, 688), only a very small quantity of 3 : 3′-dichloro-4 : 4′-dihydroxydiphenyl was obtained, the chief product being of a quinonoid nature. It appeared, therefore, of interest to study the behaviour of this diazonium salt when subjected to the processes employed in replacing the diazo-groups by hydrogen, chlorine, bromine, iodine, cyanogen, and carboxyl radicles.

A very convenient method of preparing 3 : 3′-dichloro-4 : 4′-dihydroxydiphenyl has been devised, which consists in chlorinating 4 : 4′-dihydroxydiphenyl in glacial acetic acid solution with the calculated quantity of chlorine. In connection with this part of the work, both the monochloro- and the trichloro- derivatives were prepared, the limit of the chlorination being the tetrachloro-compound, which has already been described by Magatti (*Ber.*, 1880, **13**, 224).

EXPERIMENTAL.

3 : 3′-*Dichlorodiphenyl.*

3 : 3′-Dichlorobenzidine (25 grams) was dissolved in ethyl alcohol, a mixture of strong sulphuric acid and alcohol added, and then, after cooling, a slight excess of dry sodium nitrite. The alcoholic solution of the diazonium sulphate thus obtained was boiled for half an hour, the alcohol evaporated off, and the residue distilled in a current of steam. The easily fusible yellowish-white solid collecting in the distillate was recrystallised from dilute alcohol. The 3 : 3′-dichlorodiphenyl thus obtained crystallises from dilute alcohol in white needles and is easily soluble in ether, alcohol, and benzene; it melts at 29° and boils at 298°.

0·1789 gave 0·2308 AgCl. Cl = 31·9.

$C_{12}H_8Cl_2$ requires Cl = 31·8 per cent.

3 : 4 : 3′ : 4′-*Tetrachlorodiphenyl.*

3 : 3′-Dichlorobenzidine (12·7 grams) was dissolved in 90 c.c. of hydrochloric acid of sp. gr. 1·16, diluted with 45 c.c. of water, the solution being cooled and diazotised with 6·9 grams of sodium nitrite dissolved

in a very small quantity of water. The resulting brownish-yellow solution was filtered and added to copper powder (the "copper bronze" of commerce) which had been moistened with hydrochloric acid. Nitrogen was immediately evolved, and on the following day the mixture was filtered and extracted with ether. After evaporating off the solvent from the extract, the dry residue was distilled under diminished pressure, and by this means the tetrachlorodiphenyl was freed from a red by-product. The solid distillate was crystallised twice from glacial acetic acid, from which it separates in fine white needles, melting at 172° and boiling at 230° under 50 mm. pressure. The tetrachlorodiphenyl thus obtained dissolves easily in ether, alcohol, or benzene.

0·1392 gave 0·2741 AgCl. Cl = 48·70.
$C_{12}H_6Cl_4$ requires Cl = 48·58 per cent.

3 : 3′-*Dichloro*-4 : 4′-*dibromodiphenyl.*

3 : 3′-Dichlorobenzidine (12·7 grams) was diazotised as in the preceding case, except that sulphuric acid was used instead of the hydrochloric acid; the filtered solution was poured into a solution of 20 grams of potassium bromide, to which copper powder had been added. The mixture was left for a time, then filtered, and extracted with ether. The red residue obtained after removing the solvent was distilled under diminished pressure. The dichlorodibromodiphenyl, which is soluble in the ordinary organic solvents, on crystallisation from glacial acetic acid separated in white needles melting at 176—177°.

0·1784 gave 0·2969 AgCl + AgBr. Halogen = 60·89
$C_{12}H_6Cl_2Br_2$ requires Cl + Br = 60·60 per cent.

3 : 3′-*Dichloro*-4 : 4′-*di-iododiphenyl.*

A solution of the diazonium sulphate was added to 20 grams of potassium iodide dissolved in water. Nitrogen was at once evolved, and after about 12 hours the mass was filtered, boiled with water to expel traces of free iodine, dried, and distilled under diminished pressure. The product was recrystallised from glacial acetic acid and obtained in pale yellow, fern-like aggregates of needles, melting at 162° and boiling at 275° under 10 mm. pressure; it is easily soluble in the ordinary organic solvents.

0·1552 gave 0·2448 AgCl + AgI. Halogen = 67·69.
$C_{12}H_6Cl_2I_2$ requires Cl + I = 68·39 per cent.

The effect of metallic sodium on the two foregoing substances was studied in the hope of obtaining a new condensation product, for although Fittig has shown (*Annalen*, 1864, **132**, 205) that this metal has no action on 4 : 4′-dibromodiphenyl, yet a 4 : 4′-dibromo- or 4 : 4′-di-iodo-diphenyl which contained a chlorine atom immediately adjacent to each atom of bromine or iodine might conceivably be more easily decomposed. Experiments were made in both ethereal and benzene solutions, but no action could be detected either with the dichlorodibromodiphenyl or the di-iodo-compound. These substances can even be heated with copper powder considerably above their melting points without any condensation taking place.

The Nitrile of 3 : 3′-*Dichlorodiphenyl*-4 : 4′-*dicarboxylic Acid* (3 : 3′-*Dichloro*-4 : 4′-*dicyanodiphenyl*).

A solution of the diazonium salt was added to a boiling solution of cuprous cyanide. After some time, the nitrile was collected, a small portion extracted with ether, the ethereal solution evaporated, and the red residue distilled. The red by-product was not volatile, and the nitrile was thus obtained as a white substance which crystallised from alcohol in white, flocculent needles melting at 152—153°.

3 : 3′-*Dichlorodiphenyl*-4 : 4′-*dicarboxylic Acid.*

The bulk of the crude nitrile was saponified by boiling with dilute caustic soda for a few hours. On filtering and acidifying, the acid separated out and was filtered, dried, and crystallised, first from glacial acetic acid and then from alcohol. From the latter solvent, it separates in small needles melting at 287—288°.

The substance thus obtained is very sparingly soluble in water, but dissolves more easily in alcohol or ether.

0·1280 gave 0·11753 AgCl. Cl = 22·71.

$C_{14}H_8O_4Cl_2$ requires Cl = 22·80 per cent.

Chlorination of 4 : 4′-*Dihydroxydiphenyl.*

As already indicated, Magatti (*loc. cit.*) obtained a tetrachlorodiphenol by the complete chlorination of 4 : 4′-dihydroxydiphenyl (γ-diphenol) in acetic acid solution.

Schmidt and Schultz (*Annalen*, 1881, **207**, 334), by treating γ-diphenol with phosphorus pentachloride, obtained three substances, namely, (1) a chlorinated diphenol (m. p. 126°); (2) *p*-dichlorodiphenyl (m. p. 148°); (3) pentachlorodiphenyl (m. p. 179°).

I have already shown that the first product was most probably not a trichlorodiphenol as suggested by Schmidt and Schultz, but was identical with 3 : 3′-dichloro-4 : 4′-dihydroxydiphenyl (*loc. cit.*) These chemists, assuming that the first product is a trichloro-derivative, explain the formation of the third compound from it by the replacement of hydroxyl by chlorine.

By chlorinating γ-diphenol with bleaching powder solution in presence of acids, a deep violet coloration is produced, which was noticed by Schmidt and Schultz. If this operation is carried out quantitatively, the interesting fact is demonstrated that three molecular proportions of chlorine are absorbed by one of γ-diphenol.

The diphenol (1 gram) was dissolved in caustic soda, dilute sulphuric acid added to the solution, and a solution of bleaching powder introduced from a burette until a reaction was obtained with starch-iodide paper. The amount of chlorine used was 1·14 grams, this quantity being identical with that corresponding with three molecules of chlorine.

The reaction does not appear to go quite smoothly, as a pure substance could not be isolated from the product of chlorination, but analyses indicated that a trichlorodiphenyl had been formed.

The object of these experiments being to find a method of obtaining the dichlorophenol, the direct chlorination in acetic acid solution was studied, and it was found that the mono-, di-, and tri-chloro-derivatives could be prepared by taking calculated quantities of chlorine obtained by oxidising hydrochloric acid with a weighed amount of potassium dichromate.

3-*Chloro*-4 : 4′-*dihydroxydiphenyl.*

The diphenol (1·86 grams) was dissolved in glacial acetic acid, and a current of dry chlorine, obtained by warming 0·98 gram of potassium bichromate with hydrochloric acid, was passed into the solution at the ordinary temperature. The gas was at once absorbed, and at the conclusion of the experiment the solution was concentrated to a small bulk and poured into water. The monochloro-compound, which was obtained as a white precipitate, was recrystallised from dilute acetic acid; it forms white needles, soluble in ether, alcohol, or benzene, and melting at 215°.

0·1628 gave 0·10463 AgCl. Cl = 15·89.

$C_{12}H_9O_2Cl$ requires Cl = 16·08 per cent.

3 : 3′-*Dichloro*-4 : 4′-*dihydroxydiphenyl.*

The chlorination of the diphenol was carried out exactly as in the preceding case, except that twice the quantity of potassium dichromate was used.

The crude dichloro-compound was recrystallised from hot water and obtained in fine, white needles melting at 124°. Its properties were identical with those of the 3 : 3′-dichloro-4 : 4′-dihydroxydiphenyl (m. p. 124°), obtained by another method (*loc. cit.*), and a mixture of the two preparations melted exactly at 124°. This identity is, of course, a proof of the constitution of this and the preceding substance.

0·1827 gave 0·20763 AgCl. Cl = 28·09.

$C_{12}H_8O_2Cl_2$ requires Cl = 27·81 per cent.

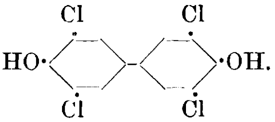
3 : 3′ : 5(?)-*Trichloro*-4 : 4′-*dihydroxydiphenyl.*

This trichloro-derivative, produced by using the appropriate amount of potassium dichromate, was obtained from dilute acetic acid in white needles ; it is soluble in ether, alcohol, or benzene, and melts at 179°.

0·0899 gave 0·13083 AgCl. Cl = 35·96.

$C_{12}H_7O_2Cl_3$ requires Cl = 36·75 per cent.

Although the orientation of the third atom of chlorine has not been absolutely demonstrated, yet there can be little doubt that the halogen occupies the position indicated by the notation used in naming the compound. The tetrachloro-compound, which was also prepared, and found to correspond exactly with the substance described by Magatti, has, in all probability, the following constitution :



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