

CCXII.—*The Action of Chlorine on m-Iodoaniline and on m-Bromoaniline.*

By HAMILTON McCOMBIE and PERCY JAMES WARD.

THE marked influence of the presence of a hydroxyl group in the benzene nucleus on the tervalency of the iodine atom, which has been studied by Brazier and McCombie (T., 1912, **101**, 948) and by King and McCombie (this vol., p. 220), led the authors to consider the influence which other groups (especially such as possess considerable partial valency) exert on the iodine atom, and the first group which was selected for this purpose was the amino-group.

The action of chlorine on aromatic iodo-compounds which contain the amino-group seems to have been studied only very slightly. Willgerodt and Simonis (*Ber.*, 1906, **39**, 273) found that 4-iodo-*m*-toluidine (Me=1), when acted on by chlorine in chloroform solution, yielded a very unstable iododichloride, together with other higher chlorination products. Hofmann (*Annalen*, 1848, **67**, 65) noticed that *p*-iodoaniline with chlorine gave 2:4:6-trichloroaniline very readily. This result has been confirmed by the authors, who have found that *p*-iodoaniline does not yield an iododichloride in any solvent, even when the solution is cooled in a freezing mixture—iodine is liberated immediately. The only statement which the authors have been able to find with reference to the action of chlorine on *m*-iodoaniline is one by Willgerodt and Wikander (*Ber.*, 1907, **40**, 4068), who considered that they had obtained an unstable iododichloride. On passing chlorine into a chloroform solution of *m*-iodoaniline, these experimenters obtained a dark red powder which, they state, decomposed rapidly, yielding

a product they were unable to analyse. By treatment with sodium hydroxide, *m*-iodoaniline was regenerated, from which fact they concluded that the original substance was an iododichloride. It seems probable from our work that these chemists had in their hands merely an impure specimen of *m*-iodoaniline hydrochloride.

When a 3 per cent. solution of *m*-iodoaniline in glacial acetic acid was subjected to the action of chlorine at the ordinary temperature, a quantitative yield of 2:4:6-trichloro-3-iodoaniline was obtained. On no occasion was the formation of an iododichloride observed. If concentrated acetic acid solutions were employed, some iodine was liberated, and a considerable quantity of *m*-iodoaniline hydrochloride was deposited. When carbon tetrachloride and chloroform were employed as solvents, it was impossible to prepare much of the chlorination product, owing to the precipitation of the hydrochloride of the original iodoaniline.

The constitution of 2:4:6-trichloro-3-iodoaniline was established by heating the substance on a water-bath with excess of alcoholic ethyl nitrite and a little concentrated hydrochloric acid. By this means the amino-group was replaced by hydrogen, and there resulted 2:4:6-trichloriodobenzene (Jackson and Gazzolo, *Amer. Chem. J.*, 1890, **22**, 52; Hantzsch, *Ber.*, 1897, **30**, 2354).

Analogous compounds to 2:4:6-trichloro-3-iodoaniline, produced by the chlorination of *m*-iodoaniline in this way, are obtained by the chlorination of the corresponding chloro- and bromo-compounds (see Beilstein and Kurbatoff, *Annalen*, 1877, **196**, 236; Orton and Reed, *T.*, 1907, **91**, 1552).

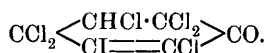
Some interesting examples of the influence of substituents on the course of a reaction were encountered in dealing with 2:4:6-trichloro-3-iodoaniline. It was found that no hydrochloride was produced by saturating an alcoholic solution with hydrogen chloride. Benzoylation in the presence of sodium hydroxide was without effect on the compound, but in the presence of pyridine the reaction proceeded quite smoothly. In this respect the behaviour is very similar to that of the halogen substituted phenols prepared by Brazier and McCombie (*loc. cit.*). Orton and Reed (*loc. cit.*) obtained some unexpected results when acetylating 2:4:6-trichloro-3-bromoaniline. When this substance was heated with acetic anhydride for several hours, a diacetyl derivative was obtained. When, however, the acetylation was conducted by warming the compound with acetyl chloride in a sealed tube, the monoacetyl derivative was produced. Similar results have been obtained in the case of 2:4:6-trichloro-3-iodoaniline.

When *m*-iodoaniline is converted into acyl derivatives, the partial valency of the amino-group is neutralised to a certain extent, and

these acyl derivatives show tendencies for the iodine to become tervalent. In these cases iododichlorides are produced, but they prove to be very unstable. Willgerodt and Wikander (*loc. cit.*) have described the chlorination of *m*-iodoacetanilide in an ice-cold chloroform solution, and state that an iododichloride was formed, but the figures they obtained in the analysis of this compound were very high. On repeating this work, the authors have found that an iododichloride was precipitated, but that it was very unstable, and decomposed with evolution of hydrogen chloride. When chlorine was passed into a hot glacial acetic acid solution of *m*-iodoacetanilide, 2:4:6-trichloro-3-iodoacetanilide was obtained. The constitution of this compound was confirmed by its identity with the substance produced on acetylating 2:4:6-trichloro-3-iodoaniline.

Somewhat similar results were obtained in dealing with the benzoyl derivative of *m*-iodoaniline. In a cold solution an unstable iododichloride was produced, whilst in a warm solution benzoyl-2:4-dichloro-5-iodoaniline resulted.

If, at ordinary room temperature, chlorine is passed into an acetic acid solution of *m*-iodoaniline for several hours, the 2:4:6-trichloro-5-iodoaniline, which is at first precipitated, disappears slowly, and a clear, yellow liquid is obtained, which deposits a quantity of ammonium chloride. When the acetic acid is removed, there is obtained a crystalline substance mixed with a dark red oil. This crystalline substance, on further examination, is found to be 2:2:3:4:4:6-hexachloro-5-iodo- Δ^5 -cyclohexenone,



This same compound may be obtained also by chlorinating a suspension of *m*-iodoaniline hydrochloride in acetic acid or by chlorinating *m*-iodoaniline in acetic acid at the temperature of the water-bath. It is interesting to notice that in the formation of the compound the action of the chlorine has been to remove the amino-group, but the iodine atom is left untouched. Considering that in the case of *p*-iodoaniline the first action of chlorine, even in a cold solution, is to displace the iodine, it is readily seen that the position of the iodine atom in the aniline molecule is of great importance in relation to the strength of its union to the carbon atom.

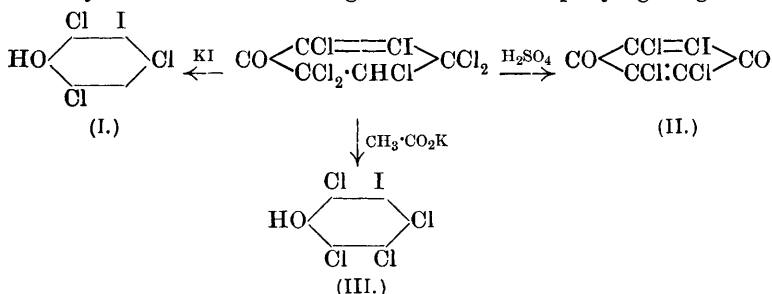
The constitution to be assigned to this ultimate chlorination product of *m*-iodoaniline is based on the following experimental facts: (1) Analyses show that there are six chlorine atoms and one iodine. As the compound is produced by the chlorination of 2:4:6-trichloro-3-iodoaniline, there must be chlorine atoms in

position 2, 4, and 6, and an iodine atom in position 3. Further, there must be one double bond in the molecule. (2) The compound, when heated with concentrated sulphuric acid on the water-bath, yielded 2:3:6-trichloro-5-iodo-*p*-benzoquinone (II). (3) The substance liberated iodine from potassium iodide, with the formation of 2:4:6-trichloro-3-iodophenol (I), and the reaction was found to proceed according to the following equation:

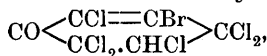


From this reaction it follows that there must be a hydrogen atom in the molecule of the substance, and this hydrogen atom must be in the meta-position with respect to the iodine atom.

(4) 2:3:4:6-Tetrachloro-5-iodophenol (III) was produced by boiling the substance with potassium acetate in the presence of acetic acid. From this reaction it follows that there must be a chlorine atom in position 3, as well as a hydrogen atom. A summary of these reactions is given in the accompanying diagram:



2:2:3:4:4:6-Hexachloro-5-bromo- Δ^5 -cyclohexenone,



was obtained in exactly the same way by the chlorination of *m*-bromoaniline, and its rearrangements with the same reagents as are employed for the iodo-compound show that it is constituted similarly to that substance. Thus, this bromo-compound, when acted on by concentrated sulphuric acid, yielded 2:3:6-trichloro-5-bromo-*p*-benzoquinone; with potassium iodide there resulted 2:4:6-trichloro-3-bromophenol, and treatment with potassium acetate in presence of acetic acid resulted in the formation of 2:3:4:6-tetrachloro-5-bromophenol.

It is interesting to note, also, that very similar results were obtained by Zincke and Shaum (*Ber.*, 1894, **27**, 548) by the action of chlorine on *m*-chloroaniline.

These chemists obtained two products in this reaction, namely, 2:3:4:4:5:6:6-heptachloro- Δ^2 -cyclohexenone and 2:2:3:4:5:6:6-heptachloro- Δ^3 -cyclohexenone.

EXPERIMENTAL.

The *m*-iodoaniline used in these experiments was prepared from *m*-nitroaniline according to the method described by Baeyer (*Ber.*, 1905, **38**, 2761), but this method was modified in the second stage of the reaction, namely, the conversion of the *m*-iodonitrobenzene into *m*-iodoaniline. This reduction was effected by Baeyer in the presence of methylated spirit, and it was found that after neutralisation and steam distillation, considerable quantities of *m*-iodoaniline were dissolved in the methylated spirit, and could not be recovered by dilution with water. Our modification consisted in distilling off the methylated spirit before neutralising the solution.

m-Iodoaniline Hydrochloride, $C_6H_4I \cdot NH_2 \cdot HCl$.

This compound was prepared by passing a stream of dry hydrogen chloride into a solution of *m*-iodoaniline in ethyl alcohol. Most of the solvent was then allowed to evaporate, and the hydrochloride was obtained in large, white leaflets, which melted at 260° :

0.1000 gave 0.1488 $AgCl + AgI$.

$C_6H_5NI \cdot HCl$ requires $AgCl + AgI = 0.1481$.

A suspension of *m*-iodoaniline hydrochloride in glacial acetic acid was chlorinated for about an hour. The hydrochloride gradually disappeared, hydrogen chloride was evolved, and the solution was found to contain 2:3:3:4:4:6-hexachloro-5-iodo- Δ^5 -cyclohexenone, melting at 104° .

Action of Chlorine on m-Iodoacetanilide: Preparation of 2:4:6-Trichloro-3-iodoacetanilide.

m-Iodoacetanilide, which was prepared by heating *m*-iodoaniline with acetic anhydride and a drop of acetyl chloride, was dissolved in glacial acetic acid, and the solution heated to the boiling point. A stream of chlorine was passed through the solution, and, when the evolution of hydrogen chloride had ceased, the liquid was concentrated to a small bulk. The white crystals which appeared were separated and recrystallised from a mixture of acetic acid and water, when they consisted of short needles, melting at 204° :

0.0941 gave 0.1715 $AgCl + AgI$.

$C_8H_5ONCl_3I$ requires $AgCl + AgI = 0.1718$.

2:4:6-Trichloro-3-iodoacetanilide is moderately soluble in acetic acid or light petroleum, very soluble in ethyl alcohol, and only sparingly so in acetone.

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Benzoyl-m-iodoaniline, $C_6H_4I \cdot NHBz$.

This compound was prepared by benzylation in presence of sodium hydroxide. When recrystallised twice from methylated spirit, it separated in slender, white needles, melting at $156-157^\circ$:

0.1000 gave 0.0719 AgI. $I = 38.85$.

$C_{13}H_{10}ONI$ requires $I = 39.32$ per cent.

Action of Chlorine on Benzoyl-m-iodoaniline: Preparation of Benzoyl-2:4-dichloro-5-iodoaniline.

On passing chlorine into a solution of benzoyl-*m*-iodoaniline in glacial acetic acid, an unstable iododichloride was at first precipitated. On boiling the solution, this unstable compound dissolved, and the passage of chlorine through the hot solution was continued. The solution was concentrated, and the short, white needles which appeared were separated and recrystallised from a mixture of glacial acetic acid and water, when the product was found to melt at 142° :

0.0708 gave 0.0932 AgCl + AgI.

$C_{13}H_8ONCl_2I$ requires AgCl + AgI = 0.0943.

Action of Chlorine on m-Iodoaniline: Preparation of 2:4:6-Trichloro-3-iodoaniline.

Ten grams of powdered *m*-iodoaniline were dissolved in 350 c.c. of glacial acetic acid, and a stream of chlorine was led into the solution. After a few minutes the liquid became dark green, then the colour changed to pale yellow, and fine, white crystals began to separate, accompanied by a rapid evolution of hydrogen chloride. The solution was then cooled, and the contents of the beaker were found to be almost solid. The crystals were separated, and the liquid subjected to the further action of chlorine, which process was continued until no more solid separated. The crude solid was washed with dilute sodium carbonate solution, and was found to weigh 12-13 grams. It was recrystallised from methyl alcohol, and separated in short, slender needles, melting at 88° :

0.1380 gave 0.2837 AgCl + AgI.

$C_6H_3NCl_3I$ requires AgCl + AgI = 0.2847.

2:4:6-Trichloro-3-iodoaniline is sparingly soluble in acetic acid, methyl alcohol, or light petroleum, and readily so in ethyl alcohol or acetone. The crystals assume a pink tinge after being kept for a short period. When subjected to the action of chlorine for a long time at the ordinary temperature or a shorter time

at the temperature of the water-bath, this compound yields 2:2:3:4:4:6-hexachloro-5-iodo- Δ^5 -cyclohexenone. 2:4:6-Trichloro-3-iodoaniline was boiled on the water-bath with an excess of alcoholic ethyl nitrite and a little concentrated hydrochloric acid; the alcohol was distilled off, and the residue was recrystallised from a mixture of glacial acetic acid and water, when a compound melting at 55° was obtained. This substance proved to be 2:4:6-trichloriodobenzene, previously described by Jackson and Gazzolo (*loc. cit.*) and by Hantzsch (*loc. cit.*). This reaction establishes the constitution of this chlorination product of *m*-iodoaniline.

Benzoyl-2:4:6-trichloro-3-iodoaniline.

It was found that 2:4:6-trichloro-3-iodoaniline could not be converted into the benzoyl derivative by the action of benzoyl chloride in the presence of sodium hydroxide, so that recourse was had to the pyridine method of benzoylation.

One gram of 2:4:6-trichloro-3-iodoaniline was dissolved in pyridine, and 0.5 gram of pure benzoyl chloride was added carefully. The solution was allowed to remain overnight, and was then poured into dilute hydrochloric acid. After several hours the precipitated product solidified, and, after separation, was washed with warm methyl alcohol, in which it is only sparingly soluble; after three recrystallisations from ethyl alcohol the benzoyl derivative was obtained in glistening, white leaflets, which melted at 229° :

0.0910 gave 0.1408 $\text{AgCl} + \text{AgI}$.

$\text{C}_{13}\text{H}_7\text{ONCl}_3\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.1420$.

Benzoyl-2:4:6-trichloro-3-iodoaniline is only sparingly soluble in acetone, but is moderately so in acetic acid; it is quite insoluble in benzene.

Preparation of 2:4:6-Trichloro-3-iodoacetanilide from 2:4:6-Trichloro-3-iodoaniline.

This compound was prepared by heating 2:4:6-trichloro-3-iodoaniline with an excess of acetyl chloride in a sealed tube on the water-bath. After being heated for fifteen minutes the tube was opened, the excess of acetyl chloride removed in a current of air, and the residue when recrystallised from a mixture of acetic acid and water proved identical with the product obtained by the chlorination of *m*-iodoacetanilide.

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Chlorination of a Hot Solution of m-Iodoaniline: Preparation of 2:2:3:4:4:6-Hexachloro-5-iodo- Δ^5 -cyclohexenone.

Ten grams of *m*-iodoaniline were dissolved in 350 c.c. of glacial acetic acid, the solution was warmed for a few minutes on a water-bath, and a stream of chlorine was passed through the solution. After a short time hydrogen chloride was evolved readily, and white crystals of ammonium chloride were deposited. When the chlorination had proceeded for about two hours, the evolution of hydrogen chloride had practically ceased, and the solution was then evaporated to dryness. The residue was washed with water to remove the ammonium chloride produced in the reaction, and there resulted about 18 grams of a crude oily product, with an odour strongly resembling that of camphor. This product, when recrystallised from glacial acetic acid, separated in large, transparent prisms, which melted at 104° :

0.1023 gave 0.2631 AgCl + AgI.

$C_6HOC l_6 I$ requires AgCl + AgI = 0.2614.

2:2:3:4:4:6-Hexachloro-5-iodo- Δ^5 -cyclohexenone is moderately soluble in methyl and ethyl alcohols, sparingly so in glacial acetic acid, and very soluble in acetone.

The method of preparation described above was not always satisfactory. In some cases the reaction proceeded too vigorously, resulting in the liberation of a large amount of iodine, probably producing a fair quantity of 2:3:4:4:5:6:6-heptachloro- Δ^2 -cyclohexenone, from which it is a matter of great difficulty to separate the iodo-compound.

If the chlorination was conducted in a cold solution, no iodine was liberated. Under these conditions the reaction required two days for completion, and a considerable quantity of the oily by-product was obtained.

When this compound was treated with concentrated sulphuric acid, it yielded trichloriodobenzoquinone; with potassium iodide, it yielded trichloriodophenol; and with potassium acetate, tetrachloriodophenol. These reactions established its constitution.

2:4:6-Trichloro-3-iodophenol.

Five grams of 2:2:3:4:4:6-hexachloro-5-iodo- Δ^5 -cyclohexenone were dissolved in warm glacial acetic acid, and 10 grams of powdered potassium iodide were added. Liberation of iodine commenced immediately, and when the mixture had been warmed on the water-bath for half an hour, the reaction was complete. The iodine was removed by the addition of sodium hydrogen

sulphite, and the phenol was separated and recrystallised from a mixture of glacial acetic acid and water. It crystallised in white, silky needles, melting at 102° :

0.0879 gave $0.1826 \text{ AgCl} + \text{AgI}$.

$\text{C}_6\text{H}_2\text{OCl}_3\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.1808$.

2:4:6-Trichloro-3-iodophenol is moderately soluble in ethyl and methyl alcohols, and readily so in acetic acid.

The *acetyl* derivative, $\text{C}_6\text{H}_2\text{Cl}_3\text{I}\cdot\text{OAc}$, was prepared by the action of acetic anhydride on 2:4:6-trichloro-3-iodophenol. It crystallises from a concentrated alcoholic solution in small leaflets, melting at 87° :

0.0555 gave $0.1034 \text{ AgCl} + \text{AgI}$.

$\text{C}_8\text{H}_4\text{O}_2\text{Cl}_3\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.1010$.

The *benzoyl* derivative, $\text{C}_6\text{H}_2\text{Cl}_3\text{I}\cdot\text{OBz}$, was prepared by the pyridine method, and when recrystallised from ethyl alcohol separated in small needles, which melted at $136\text{--}138^{\circ}$:

0.0620 gave $0.0967 \text{ AgCl} + \text{AgI}$.

$\text{C}_{13}\text{H}_6\text{O}_2\text{Cl}_3\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.0965$.

This derivative is readily soluble in acetone, and sparingly so in ethyl and methyl alcohols.

2:3:6-Trichloro-5-iodo-p-benzoquinone.

This compound was prepared by heating hexachloroiodocyclohexenone cautiously with concentrated sulphuric acid on a water-bath for about four hours. The solution was poured into water; the product, after separation, was washed first with water, and then with methyl alcohol:

0.0460 gave $0.0920 \text{ AgCl} + \text{AgI}$.

$\text{C}_6\text{O}_2\text{Cl}_3\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.0907$.

2:3:6-Trichloro-5-iodo-p-benzoquinone possesses a deep reddish-yellow colour, and can be sublimed at about 150° ; it melts indefinitely at about 280° . When attempts were made to recrystallise it from methyl alcohol it was found that decomposition took place. In other organic solvents it was practically insoluble.

2:3:4:6-Tetrachloro-5-iodophenol.

Four grams (1 mol.) of hexachloroiodocyclohexenone were heated on the water-bath with three grams (3 mols.) of potassium acetate in the presence of acetic acid. After two hours the mixture was poured into water, the phenol was separated, and the residue washed well with water, and then recrystallised three times from

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light petroleum, in which it is only sparingly soluble. It was obtained in long, white needles, melting at 169° :

0.0596 gave $0.1359 \text{ AgCl} + \text{AgI}$.

$\text{C}_6\text{HOCl}_4\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.1347$.

2 : 3 : 4 : 6-*Tetrachloro-5-iodophenol* is moderately soluble in acetic acid, and also in methyl and ethyl alcohols.

The *acetyl* derivative, $\text{C}_6\text{HCl}_4\text{I} \cdot \text{OAc}$, was prepared by heating tetrachloroiodophenol with acetic anhydride. It was crystallised from ethyl alcohol, from which it separated in glistening, short needles, melting at $140\text{--}141^{\circ}$:

0.0477 gave $0.0967 \text{ AgCl} + \text{AgI}$.

$\text{C}_8\text{H}_3\text{O}_2\text{Cl}_4\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.0964$.

The *acetyl* derivative is sparingly soluble in ethyl alcohol, and moderately so in methyl alcohol.

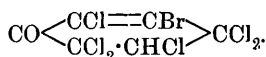
The *benzoyl* derivative, $\text{C}_6\text{HCl}_4\text{I} \cdot \text{OBz}$, was prepared by the pyridine method, and when recrystallised from ethyl alcohol separated in small, white prisms, melting at $175\text{--}176^{\circ}$:

0.0609 gave $0.1060 \text{ AgCl} + \text{AgI}$.

$\text{C}_{13}\text{H}_5\text{O}_2\text{Cl}_4\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.1066$.

This compound is only sparingly soluble in methyl and ethyl alcohols, insoluble in light petroleum, and readily soluble in acetone.

Chlorination of a Hot Solution of m-Bromoaniline: Preparation of
2 : 2 : 3 : 4 : 4 : 6-*Hexachloro-5-bromo- Δ^5 -cyclohexenone*.



This compound was prepared in a manner similar to that employed for the corresponding iodo-compound. When crystallised from glacial acetic acid, it forms transparent prisms, melting at 106° :

0.0923 gave $0.2558 \text{ AgCl} + \text{AgBr}$.

$\text{C}_6\text{HOCl}_6\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.2534$.

The solubilities of this bromo-compound were of the same order as those of the iodo-compound, thus, it is moderately soluble in methyl and ethyl alcohols, and sparingly so in glacial acetic acid.

2 : 4 : 6-*Trichloro-3-bromophenol*.

Two grams of hexachlorobromocyclohexenone were treated with 6 grams of powdered potassium iodide in the presence of acetic acid by the method used for the preparation of trichloroiodophenol. The product was crystallised from a mixture of acetic acid and

water, from which it separated in white, silky needles, melting at 61° :

0.0936 gave $0.2115 \text{ AgCl} + \text{AgBr}$.

$\text{C}_6\text{H}_2\text{OCl}_3\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.2095$.

2 : 4 : 6-*Trichloro-3-bromophenol* is moderately soluble in methyl and ethyl alcohols and in glacial acetic acid.

The *acetyl* derivative, $\text{C}_6\text{HCl}_3\text{Br}\cdot\text{OAc}$, was obtained by the action of acetic anhydride and crystallised in small leaflets, melting at 70° :

0.0644 gave $0.1266 \text{ AgCl} + \text{AgBr}$.

$\text{C}_8\text{H}_4\text{O}_2\text{Cl}_3\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.1252$.

The *benzoyl* derivative, $\text{C}_6\text{HCl}_3\text{Br}\cdot\text{OBz}$, was prepared in pyridine solution, and when recrystallised from ethyl alcohol melted at 102° :

0.0447 gave $0.0732 \text{ AgCl} + \text{AgBr}$.

$\text{C}_{13}\text{H}_6\text{O}_2\text{Cl}_3\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.0727$.

2 : 3 : 6-*Trichloro-5-bromo-p-benzoquinone*.

This was prepared by heating hexachlorobromocyclohexenone with concentrated sulphuric acid for three hours on a water-bath. The acid liquid was poured into water, and the yellow product was crystallised from much methyl alcohol, in which it is only sparingly soluble. It was obtained in bright yellow leaflets, melting at 292° (Found, $\text{AgCl} + \text{AgBr} = 0.1798$. Calculated, 0.1774). This substance has been described by several investigators, notably by Levy and Schultz (*Annalen*, 1881, **210**, 162), who prepared it by the action of bromine on trichlorobenzoquinone.

2 : 3 : 4 : 6-*Tetrachloro-5-bromophenol*.

Hexachlorobromocyclohexenone (1 mol.), dissolved in acetic acid, was treated with potassium acetate (3 mols.) in a manner similar to that employed in the case of the corresponding iodo-compound. It was crystallised from light petroleum, when it separated in white needles, melting at 192° :

0.0531 gave $0.1324 \text{ AgCl} + \text{AgBr}$.

$\text{C}_6\text{HOCl}_4\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.1300$.

The *acetyl* derivative, $\text{C}_6\text{Cl}_4\text{Br}\cdot\text{OAc}$, was obtained by means of acetic anhydride, and when crystallised from ethyl alcohol yielded slender, glistening needles, melting at 144° :

0.0610 gave $0.1334 \text{ AgCl} + \text{AgBr}$.

$\text{C}_8\text{H}_3\text{O}_2\text{Cl}_4\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.1317$.

This substance is only sparingly soluble in ethyl and methyl alcohols, but is readily soluble in acetone.

The *benzoyl* derivative, $\text{C}_6\text{Cl}_4\text{Br}\cdot\text{OBz}$, was prepared in pyridine

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solution, and crystallised from methyl alcohol in small, white prisms, melting at 169° :

0.0505 gave $0.0921 \text{ AgCl} + \text{AgBr}$.

$\text{C}_{13}\text{H}_5\text{O}_2\text{Cl}_4\text{Br}$ requires $\text{AgCl} + \text{AgBr} = 0.0927$.

This substance is sparingly soluble in methyl and ethyl alcohols, but dissolves readily in acetone.

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