

XX.—*p*-Iodophenyltrimethylammonium Perhalides.

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WHEN perhalides of the phenyltrimethylammonium series were under investigation, it seemed of interest to inquire whether perhalides could be obtained in the *p*-iodophenyltrimethylammonium series, or whether the *p*-iodine atom would enter into reaction with chlorine, giving iodochlorides similar in properties to those given by iodobenzene, iodophenols, iodo-acids, etc. It seemed probable that the investigation might lead to the production of either (1) perhalides similar to those of the phenyltrimethylammonium series, (2) *p*-iodochlorides, or (3) substances which were both *p*-iodochlorides and perhalides.* Moreover, there appeared to be a possibility that the residual affinities of the ionic iodine and the *p*-iodine atoms might mutually saturate each other, so that additive compounds with the halogens would not be obtainable.

By passing a very rapid stream of chlorine into a dilute acetic acid solution of the quaternary ammonium iodide, it is possible, on cooling, to isolate yellow crystals which approximate closely to the formula $C_6H_4I \cdot NMe_3Cl_4I$. This product can be degraded with ethyl malonate, yielding the dichloriodide $C_6H_4I \cdot NMe_3Cl_2I$, but this can be isolated in a state of purity only when a solvent of low boiling point, for example, methyl alcohol, is employed as crystallising medium. The pure dichloriodide on treatment with dry acetone yielded the quaternary ammonium chloride.

If the dichloriodide was treated with hot glacial acetic acid, a double perhalide, of a darker shade of yellow, crystallised out, the formula of which approximated to $C_6H_4I \cdot NMe_3Cl_2I + C_6H_4I \cdot NMe_3ClI_2$. This yellowish-brown product, when treated with acetone, yielded the quaternary ammonium iodide, contaminated with 3 per cent. of the chloride. Wright's results are probably to be attributed to changes taking place in the dichloriodide during crystallisation from acetic acid.

This communication also describes a new method of preparation

* An investigation on these lines by Wright and McCombie gave results which may be summarised as follows: Iodo-chlorides were not obtained. Perhalides of the forms $C_6H_4I \cdot NMe_3Cl_2I$ and $C_6H_4I \cdot NMe_3Br_2I$ were isolated. Of these, the latter gave the bromide when treated with acetone, and its behaviour was strictly analogous to that met with in the phenyltrimethylammonium and the *p*-bromophenyltrimethylammonium series. The former, the dichloriodide, gave the iodide, not the chloride, when treated with acetone. It was also found that the tetrachloriodide was not isolated in this series. Inasmuch as the original collaborators discontinued this work, these two points have been re-investigated.

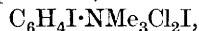
of *p*-iododimethylaniline, the formation of *p*-iodophenyltrimethylammonium tri-iodide, and a rapid and convenient method of estimating the ionisable mixed halogens in perhalides.*

EXPERIMENTAL.

p-Iododimethylaniline, $C_6H_4I \cdot NMe_2$.—To a solution of 30 c.c. of dimethylaniline in 100 c.c. of glacial acetic acid at 18° , 30 grams of iodine and 3 grams of iodic acid were gradually added, with constant shaking and cooling, during thirty minutes. The settled solution was decanted from the small quantity of unchanged iodine, made strongly alkaline with sodium hydroxide, and stirred until the solid product became granular; this was collected after twelve hours and recrystallised from alcohol, 28 grams of white crystals, m. p. 78.5° , identical with those prepared by the usual method of iodination in carbon disulphide, being obtained.

p-Iodophenyltrimethylammonium Iodide, $C_6H_4I \cdot NMe_3I$.—A mixture of 6.5 c.c. of methyl iodide, 20 c.c. of methyl alcohol, and 20.4 grams of *p*-iododimethylaniline was gently heated under reflux for six hours. The white product after recrystallisation from methyl alcohol melted at 190.5° , the yield being 23 grams. Ethyl alcohol may be substituted for methyl alcohol [Found : I (total) = 64.7; I (ionisable) = 32.5. $C_6H_4I \cdot NMe_3I$ requires I (total) = 65.3; I (ionisable) = 32.65 per cent.]. This substance is readily soluble in hot alcohol or methyl alcohol and sparingly soluble in water, ether, or acetone. When treated with chlorine in acetic acid, it yields yellow crystals of $C_6H_4I \cdot NMe_3Cl \cdot ICl_3$, whilst iodine (1 mol.) in alcohol gave the tri-iodide, $C_6H_4I \cdot NMe_3I_3$.

p-Iodophenyltrimethylammonium Chloride Iodotrichloride, $C_6H_4I \cdot NMe_3Cl \cdot ICl_3$.—A rapid stream of chlorine was led into 10 grams of $C_6H_4I \cdot NMe_3I$ in 150 c.c. of glacial acetic acid at 60° , and was continued while the solution was cooled to 20° . Bright yellow needles crystallised out, m. p. 187° with decomposition. Further recrystallisation from acetic acid did not affect the melting point. The crystals lose chlorine somewhat readily when left in a desiccator (Found : $Cl' = 24.4$; $I' = 24.9$. $C_6H_4I \cdot NMe_3Cl_4I$ requires $Cl' = 26.9$; $I' = 24.05$ per cent.). Its constitution was determined by treating the substance with ethyl malonate at $30-40^\circ$, under reduced pressure; the dichloro-iodide,



obtained, on treatment with acetone, gave *p*-iodophenyltrimethylammonium chloride.

* One of the collaborators (S. A. S.) has discontinued this investigation, so the work is submitted for publication in its present state.

p-Iodophenyltrimethylammonium Chloride Iodochloride,

—A solution of 4 grams of the tetrachloroiodide in 35 grams of ethyl malonate was heated to 40° and placed in a desiccator, which was then evacuated, the process being repeated until no more gas was evolved. The golden-yellow, crystalline compound was washed with ether and recrystallised from methyl alcohol. It then melted at 184° with decomposition. The yield was 3 grams (Found: $\text{Cl}' = 15.43$; $\text{I}' = 28.9$. $\text{C}_6\text{H}_4\text{I}\cdot\text{NMe}_3\text{Cl}\cdot\text{ICl}$ requires $\text{Cl}' = 15.42$; $\text{I}' = 27.6$ per cent.). When this compound was shaken with dry acetone, the quaternary ammonium chloride was precipitated (Found: $\text{Cl}' = 11.90$. Calc., $\text{Cl}' = 11.92$ per cent.). Thus the dichloroiodide is the iodine monochloride compound of the quaternary ammonium chloride.

Influence of Heat on the Iodochloride.—Whenever this compound in solution was submitted to a high temperature, for example, in boiling glacial acetic acid, or in ethyl malonate at temperatures above 40° , the product which crystallised on cooling was brown, and contained less chlorine and relatively more iodine than the unchanged dichloroiodide (Found: $\text{Cl} = 11.90$; $\text{I} = 37.8$. Calc. for $\text{C}_6\text{H}_4\text{I}\cdot\text{NMe}_3\text{Cl}\cdot\text{ICl}$, $\text{Cl} = 15.56$; $\text{I} = 27.8$. $\text{C}_6\text{H}_4\text{I}\cdot\text{NMe}_3\text{Cl}\cdot\text{ICl} + \text{C}_6\text{H}_4\text{I}\cdot\text{NMe}_3\text{ClI}_2$ requires $\text{Cl} = 10.60$; $\text{I} = 38.0$ per cent.). Since the di-iodochloride has not yet been isolated, the double perhalide formula is put forward tentatively; but it is supported by the fact that this substance yielded chiefly the quaternary ammonium iodide (97 per cent. with about 3 per cent. of the quaternary ammonium chloride) when treated with acetone (Found: $\text{I}' = 31.0$; $\text{Cl}' = 1.1$. Calc. for $\text{C}_6\text{H}_4\text{I}\cdot\text{NMe}_3\text{I}$, $\text{I}' = 32.8$ per cent.).

p-Iodophenyltrimethylammonium Tri-iodide, $\text{C}_6\text{H}_4\text{I}\cdot\text{NMe}_3\text{I}_3$.—Equimolecular quantities of iodine and *p*-iodophenyltrimethylammonium iodide in alcohol were heated together under reflux. On cooling, brown leaflets of the tri-iodide crystallised out (Found: $\text{I}' = 59.4$. $\text{C}_6\text{H}_4\text{I}\cdot\text{NMe}_3\text{I}_3$ requires $\text{I}' = 59.3$ per cent.). This substance melts with decomposition at 189° and is best recrystallised from alcohol.

Estimation of Ionisable Halogens in Perhalides.

Notwithstanding the fact that perhalides are somewhat unstable substances, no rapid and trustworthy methods of analysis have hitherto been described. Volumetric methods involve in their calculation a knowledge of what halogens are present, whether chlorine, bromine, or iodine, and estimation by Carius's method is slow. The need for a more rapid method than the latter, and especially for one which does not take account of the *p*-halogen

atom in the phenyl group in this series, resulted in the following procedure being adopted.

The accurately weighed perhalide was added to an excess of a hot 4*N*-solution of sodium carbonate, to which had been added a weight of sodium sulphite equal to that of the perhalide. After dissolution, the liquid was faintly acidified with dilute nitric acid, aqueous silver nitrate (containing $\text{AgNO}_3 = 2\frac{1}{2}$ times the weight of the perhalide) added, and the solution boiled to expel sulphur dioxide and diluted (to prevent precipitation of silver sulphate). The precipitate, collected in a Gooch crucible, was dried and weighed. The silver halide was then heated at 200° in a stream of chlorine until entirely converted into silver chloride.

The above method has proved convenient and fairly accurate in the case of *p*-bromo- and *p*-iodo-phenyltrimethylammonium perhalides. The first two estimations may be cited as representative examples of the degree of accuracy obtainable, although many of the later estimations gave more concordant results.

A synthetic specimen of $\text{C}_6\text{H}_4\text{Br}\cdot\text{NMe}_3\text{Cl}\cdot\text{ICl}$ of known purity gave the following figures : 0.1000 and 0.1000 gave 0.1261 and 0.1267, respectively, of mixed AgCl and AgI . Calc., 0.1264.

A series of blank estimations showed that the para-halogen atom was not attacked by this method of estimation.

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