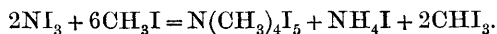


XXIII.—*Studies on Nitrogen Iodide. III. The Action of Methyl and Benzyl Iodides.*

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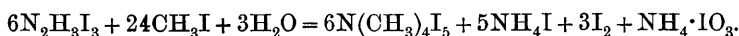
Action of Methyl Iodide.—Previous experiments have been carried out by Stahlschmidt (*Poggendorff's Ann.*, 1863, **119**, 421) on the reaction between nitrogen iodide and methyl iodide under water. He believed that the reaction could be best explained on the assumption of the formula NI_3 for nitrogen iodide. Since Stahlschmidt's experiments, Chattaway has shown the formula to be $\text{N}_2\text{H}_3\text{I}_3$ (*Proc.*, 1899, **17**, 20; *Amer. Chem. J.*, 1900, **23**, 363, &c.), and more recently the constitution $\text{NH}_3:\text{NI}_3$ has been established (Silberrad, *Trans.*, 1905, **89**, 55 and 66), and thus Stahlschmidt's formulation of the reaction becomes inapplicable. It appeared desirable, therefore, to repeat Stahlschmidt's experiments, firstly because this author omitted certain precautions which should obviously be taken, and secondly in order to ascertain quantitatively the molecular proportions of the products formed, and thus to establish the nature of the reaction. In Stahlschmidt's experiments, the nitrogen iodide was prepared by the addition of an alcoholic solution of iodine to concentrated aqueous ammonia. As has been pointed out by Chattaway (*loc. cit.*, p. 363), considerable quantities of iodoform are always produced when alcohol is used in the preparation of nitrogen iodide. Thus the iodoform, which Stahlschmidt believed to be a product of the action of methyl iodide on nitrogen iodide, was simply a by-product in the preparation of the nitrogen iodide, and had no bearing on the reaction. Further, Stahlschmidt evidently did not take sufficient precautions to exclude light, for he found that nitrogen was evolved during the reaction, whereas a repetition of his experiments shows that when the reaction is carried on at a low temperature in the dark no such evolution of nitrogen occurs.

The products isolated by Stahlschmidt, apart from nitrogen and unchanged methyl iodide, were hydriodic acid, ammonium iodide, tetramethylammonium penta-iodide, iodoform, iodine, and a brick-red insoluble compound which was not further investigated. The residual solution evolved ammonia on addition of caustic potash and was then found by him to contain di-iodomethylamine, potassium iodide and iodate, and traces of potassium butyrate. For the formation of iodoform and tetramethylammonium penta-iodide, Stahlschmidt gave the following explanation, assuming the formula of nitrogen iodide to be NI_3 :



This equation is based on the presence of iodoform amongst the products, and as this compound is not due to the methyl iodide, but to the presence of alcohol, Stahlschmidt's deductions as to the constitution of nitrogen iodide are unfounded.

In the present work, nitrogen iodide was allowed to react with a slight excess of methyl iodide under water at a low temperature in the dark. After the removal of the unchanged methyl iodide, the products found were tetramethylammonium penta-iodide, ammonium iodide and iodate, and free iodine; neither iodoform nor di-iodomethylamine could be detected. As is shown quantitatively in the experimental part, the formation of these compounds takes place in accordance with the following equation:



Thus, the action of methyl iodide on nitrogen iodide does not furnish evidence in favour of the formula NI_3 , as supposed by Stahlschmidt, but is completely in accord with the formula $\text{NH}_3\cdot\text{NI}_3$.

Action of Benzyl Iodide.—Similar experiments carried out with benzyl iodide have given rise to two interesting compounds, namely, tribenzylammonium penta-iodide and tribenzylammonium di-iodide. No compound was obtained with benzyl iodide analogous to the tetramethylammonium penta-iodide which resulted from the action of methyl iodide on nitrogen iodide. The two benzyl derivatives both result from the action of benzyl iodide on nitrogen iodide under water, the composition of the resultant compound being dependent on the relative quantities of the reagents.

EXPERIMENTAL.

Action of Methyl Iodide.—The reaction was first carried out under the conditions indicated by Stahlschmidt (*loc. cit.*). A quantity of about 2 grams of nitrogen iodide was prepared by adding a solution of iodine in alcohol to a concentrated aqueous solution of ammonia. After washing well with water, an excess of methyl iodide in alcohol was added, and the mixture left for twenty-four hours in a cold dark room. A brown liquid was obtained, which on evaporation smelt strongly of iodoform and gave a quantity of green crystals, the properties of which agreed precisely with those of the tetramethylammonium penta-iodide described by Stahlschmidt. The crystals were purified by crystallisation from alcohol, in which they are sparingly soluble. Of the five atoms of iodine present in the molecule, four are loosely combined and can be readily estimated by allowing the substance to remain in contact with a slight excess of sodium thiosulphate until it passed completely

into solution, and then titrating back the excess of thiosulphate with decinormal iodine solution.

- (i) 0.2033 required 11.46 c.c. of decinormal sodium thiosulphate.
 (ii) 0.0921 „ 5.19 „ „ „ „
 Found (i) 71.57, (ii) 71.55 per cent. of loosely combined iodine.
 $\text{N}(\text{CH}_3)_4\text{I}_4$ requires 71.63 per cent.

The green crystalline compound can readily be obtained without the use of alcohol; thus, if iodine chloride is allowed to react with aqueous ammonia and the resultant nitrogen iodide treated with methyl iodide under water, a good yield of the compound is obtained.

In order to determine the nature of the reaction between nitrogen iodide and methyl iodide, and to estimate the proportions in which the various products were formed, it was necessary to proceed from a known quantity of nitrogen iodide, and since the drying of the nitrogen iodide in the necessary quantity is impracticable, experiments were first carried out to ascertain the yield of nitrogen iodide from a known quantity of iodine chloride.

Fifty c.c. of a standard solution of iodine chloride (16 per cent. of iodine) were added drop by drop to 1200 c.c. of 10 per cent. aqueous ammonia cooled to 2° . The nitrogen iodide produced was repeatedly washed with water by decantation, the washings being passed through a filter. The whole of the nitrogen iodide, including the small quantity collected on the filter paper, was then decomposed with a measured quantity of a 20 per cent. solution of sodium sulphite and the excess of sulphite titrated with decinormal iodine solution. From the results thus obtained, the quantity of nitrogen iodide present was calculated. As a mean of three experiments, it was found that 50 c.c. of iodine chloride solution gave rise to 8.270 grams of nitrogen iodide. The values obtained in the individual experiments were (i) 8.265, (ii) 8.270, (iii) 8.274.

Having thus ascertained the quantity of nitrogen iodide which results from a known quantity of iodine chloride, the action of methyl iodide was examined with a quantity of nitrogen iodide prepared under precisely similar conditions. The nitrogen iodide was washed, as before, by decantation, the washings being poured through a filter. That which collected on the filter was estimated separately and deducted from the total quantity. When thoroughly washed, the nitrogen iodide was covered with about 250 c.c. of water and treated with 16.47 grams of methyl iodide. The mixture was left for three days at a low temperature in the dark. At the end of this time, crystals of tetramethylammonium penta-iodide had separated, and the liquid in the flask was brown. No evolution of nitrogen occurred at any stage of the operation.

The crystals were ground and allowed to remain in contact with the liquid for another day, after which the flask was heated to about 60° on a water-bath. The distillate which collected consisted of methyl iodide and a small quantity of iodine (distillate A). This distillate was shaken with sodium thiosulphate, and the methyl iodide was separated and weighed. The thiosulphate was titrated back for the estimation of the iodine which had distilled over.

The residue from the distillation was filtered at the pump and washed thoroughly with water (washings B). The crystals were then dried, ground under light petroleum, filtered, and washed (washings C); they were finally dried over sulphuric acid in a vacuum desiccator until their weight was constant.

The aqueous liquid (washings B) was then treated with chloroform for the extraction of the free iodine. When no more free iodine remained in the aqueous solution, the chloroform extract was removed and titrated.

The residual solution (D), which contained ammonium iodide and iodate, was diluted to 500 c.c. with water; a measured portion was treated with sulphurous acid to reduce the iodate to iodide, and the whole of the iodine was liberated with hydrogen peroxide and titrated.

A separate measured portion was treated with excess of potassium iodide and acetic acid in order to estimate the quantity of iodate present, whilst a third portion was taken for the estimation of the ammonia. Thus all the products of the reaction were quantitatively determined. The following data show the quantities found :

Quantity of nitrogen iodide which took part in the reaction.

Total quantity, calculated from iodine chloride.....	= 8.27 grams.
Quantity deposited on filter paper.....	= 0.36 „
Quantity which entered into reaction	= 7.91 „

Quantity of methyl iodide which took part in the reaction.

Quantity taken (moist, free from iodine)...	= 16.47 grams.
Quantity recovered unchanged (distillate A) =	5.32 „
Quantity which entered into reaction	= 11.15 „

Free iodine.

(i) Quantity found in distillate A	= 0.245 gram.
(ii) From washings C by titration with thiosulphate	= 0.221 „

- (iii) From chloroform extract by titration
 with thiosulphate..... = 1.965 grams.
 Total free iodine = 2.431 ,,

Total combined iodine: 25 c.c. of solution D were treated with sulphurous acid and then with hydrogen peroxide in acid solution to liberate the whole of the iodine. The iodine was extracted with chloroform and titrated with thiosulphate.

- Iodine found in 25 c.c. = 0.1234 gram.
 Total combined iodine in solution D = 2.468 grams.

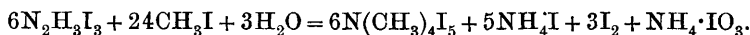
Iodine present as iodate: 25 c.c. of solution D were treated with excess of potassium iodide and acetic acid, and the free iodine was titrated with sodium thiosulphate.

- Iodine found by titration..... = 0.1242 gram.
 Hence iodine present as iodate = 0.0207 ,,
 Total iodine as iodate in solution D..... = 0.414 ,,
 Total iodine as iodide in solution D (by
 difference) = 2.054 grams.

Ammonia: 25 c.c. of solution D were distilled with caustic soda and the ammonia collected in *N*/10 hydrochloric acid and estimated.

- Ammonia obtained from 25 c.c. = 0.0161 gram.
 Total ammonia in solution D..... = 0.322 ,,

The following summary shows the quantities of all the different products which result from nitrogen iodide by the action of methyl iodide. When these are reduced to equivalents, it is seen that they agree closely with the quantities required by the equation :



	Quantity.	Divided by equivalent weight.	Equivalents.	Equivalents required by above equation.
Nitrogen iodide	7.91	1.92	5.89	6
Methyl iodide	11.15	7.85	24.08	24
Free iodine	2.431	1.91	5.85	6
Combined iodine	2.468	1.94	5.95	6
Iodine as iodate	0.414	0.326	1.00	1
Iodine as iodide	2.054	1.62	4.97	5
Ammonia	0.322	1.89	5.80	6
Tetramethylammonium penta- iodide ..	13.96	1.97	6.04	6

Thus the reaction takes place practically quantitatively in accord-

ance with the above equation and also affords a ready method of preparing tetramethylammonium iodide, and is an additional proof of the formula $\text{NH}_3 \cdot \text{NI}_3$ for nitrogen iodide. The equations given by Stahlschmidt, in which iodoform is assumed to be a product of the reaction, are seen to be erroneous, and the formula NI_3 is entirely unsupported by experimental evidence.

Preparation of Tetramethylammonium Penta-iodide direct from the Base.—In order to prepare the periodide direct from the base, 2 grams of the iodide dissolved in the least possible quantity of dilute alcohol were added to an alcoholic solution of 5.2 grams of iodine; on cooling, the characteristic green crystals of the periodide separated (m. p. $126-127^\circ$).

Action of Benzyl Iodide, Formation of Tribenzylammonium Penta-iodide, $\text{N}(\text{C}_7\text{H}_7)_3 \cdot \text{HI}_5$.—Forty-two c.c. of an aqueous solution of iodine chloride containing 0.36 gram of iodine per c.c. were added to a slight excess of ammonia. The nitrogen iodide formed was well washed by decantation, and the supernatant liquid was poured off as completely as possible. Twenty-six grams of benzyl iodide were added and the mixture allowed to stand at $10-15^\circ$ in the dark. Dark green crystals were gradually deposited; after twenty-four hours, these were thoroughly washed with water and then with light petroleum. They still contained a moderate amount of impurity, but were obtained pure by recrystallising rapidly from hot alcohol. It is somewhat difficult to remove the last traces of free iodine from the penta-iodide, since a slight decomposition always occurs during recrystallisation with liberation of iodine, which contaminates the product to some extent. In the pure state, it is sparingly soluble in hot alcohol, but its solubility is considerably increased by the presence of impurities. It melts at $121-122^\circ$. For analysis, the product was recrystallised rapidly from hot alcohol and dried quickly over sulphuric acid in a vacuum desiccator.

0.1033 gave 0.1323 AgI. $\text{I} = 69.23$.

0.1665 „ 0.2122 AgI. $\text{I} = 68.95$.

$\text{N}(\text{C}_7\text{H}_7)_3 \cdot \text{HI}_5$ requires 68.78 per cent.

On liberating the free base with alkali and extracting with ether, an oil was obtained which gradually crystallised when the ether was removed. The base melted at 90.5° , which agrees with the melting point of tribenzylamine (90°).

If the tribenzylamine penta-iodide is left with a slight excess of sodium thiosulphate and a little chloroform, the loosely combined iodine enters into reaction with the thiosulphate, and may be estimated by titration.

0.0842 gave 0.0468 iodine. $I = 55.65$.

0.1538 „ 0.0849 iodine. $I = 55.20$.

$N(C_7H_7)_3HI_5$ requires $4I = 55.02$ per cent.

Tribenzylammonium Di-iodide, $N(C_7H_7)_3HI_2$.—This compound is obtained similarly from nitrogen iodide and benzyl iodide, the only difference being in the ratio in which the reagents are brought together. The di-iodide was obtained by bringing together 50 c.c. of iodine chloride solution (1 c.c. = 0.36 gram) and an excess of ammonia, thoroughly washing the precipitated nitrogen iodide with water by decantation, and adding 42 grams of benzyl iodide. On allowing the mixture to stand, garnet-red crystals were obtained, the yield amounting to 16.5 grams. The crystals dissolved with moderate ease in alcohol and could be readily crystallised from this solvent. This treatment did not, however, effect a complete purification, as the following analyses of the crystallised product show :

0.1523 gave 0.1290 AgI. $I = 45.78$.

0.5661 „ 0.4759 AgI. $I = 45.44$.

$N(C_7H_7)_3HI_2$ requires $I = 46.84$ per cent.

Probably the crystals contained small quantities of tribenzylamine iodide. A much purer product was obtained by grinding the recrystallised compound with water and then drying it in a vacuum desiccator.

0.1204 gave 0.1039 AgI. $I = 46.65$.

0.1573 „ 0.1360 AgI. $I = 46.74$.

$N(C_7H_7)_3HI_2$ requires 46.84 per cent.

The compound melted at $115-116^\circ$ and gave rise to tribenzylamine when treated with caustic potash. If the tribenzylamine di-iodide is left with a slight excess of sodium thiosulphate, the loosely combined iodine enters into reaction with the thiosulphate and may be estimated by titration.

0.2307 required 4.25 c.c. *N*/10-sodium thiosulphate. $I = 23.39$.

$N(C_7H_7)_3HI_2$ requires $I = 23.42$ per cent.

Interconversion of the Penta-iodide and Di-iodide.—The formula of the red compound is further proved by its formation from the green penta-iodide by the partial abstraction of the iodine by potassium iodide. One gram of the penta-iodide was boiled with 3 grams of potassium iodide in 25 c.c. of water for half an hour. On filtering the red liquid, garnet-red crystals melting at $115-116^\circ$ were obtained. Conversely, the green compound may be regenerated from

the red crystals by warming with the theoretical quantity of iodine in a little alcohol, and both compounds may be prepared directly from the base by the addition of the requisite quantity of iodine dissolved in hot chloroform to the hydriodide of the base also dissolved in the same solvent. For the preparation of the di-iodide, the best results are obtained by the addition of 16.8 grams of iodine dissolved in 170 c.c. of hot chloroform to 56 grams of tribenzylamine hydriodide in 120 c.c. of chloroform, and for the preparation of the penta-iodide by the addition of 35 grams of tribenzylamine hydriodide dissolved in 200 c.c. of chloroform to a hot solution of 43 grams of iodine in 550 c.c. of chloroform. In both cases, the compounds crystallise out on cooling, and are identical with those prepared by the action of benzyl iodide on nitrogen iodide.

In conclusion we wish to express our thanks to the Explosives Committee for permission to publish these results.

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