LXXII.—*Nitrites of the Mercurialkyl- and Mercurialkylaryl-ammonium Series.*

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IT has already been mentioned that the investigation of the interaction of mercuric nitrite and the alkylamines was primarily undertaken with a view to ascertain if the nitrite analogues of the haloid mercury derivatives of the substituted ammonias could be obtained (Trans., 1911, **99**, 1972). The preparation of the first member of the series, trimercuridiethylammonium nitrite, suggested further work on other alkyl substituted compounds, and incidentally this study has afforded an opportunity of gaining an insight into the constitution of mercuriammonium bases.

At the outset it may be laid down as a rule of general application that any amine which with mercuric nitrite gives a substituted compound also necessarily yields in the filtrate a corresponding amine nitrite, including those of the weakest bases, like aniline and toluidine, although the latter undergo decomposition during concentration. The converse, however, does not always hold good; for instance, secondary amines of the purely aliphatic series, for example, dimethyl-, diethyl-, and dipropyl-amines, have not been found to give the corresponding substituted mercury nitrites; but secondary mixed amines with alkylaryl radicles have yielded the expected result (compare Nos. VII and VIII).

The question of the constitution of the so-called infusible white precipitate has given rise to much controversy. One of us has supported the view (*Zeitsch. anorg. Chem.*, 1902, **33**, 193) that this compound may be regarded, not as a double salt as formulated by Rammelsberg (NHg_2Cl,NH_4Cl), but simply with half the molecular weight as mercuriammonium chloride, $NHg^{II}H_2Cl$; and the fact that an analogous compound derived from ethylamine has the simple formula NHEtHgCl has also been adduced in favour of the latter view. The nitrite and its several haloid derivatives have also been referred to the type of dimercuriammonium compounds (NHg_2^{II}) (Trans., 1902, **81**, 645). Of the eleven nitrites which form the subject matter of the present communication, only Nos. I and II can, however, be placed under this category. The remaining nine may be classed as additive compounds of mercuric nitrite with substituted ammonias, including alicyclic bases. It will also be noticed that mercuric nitrite sometimes combines with one molecule of the base and sometimes with two; in fact, a striking analogy is found to exist between this series and the corresponding compounds with mercuric chloride, as described by Pesci (*Zeitsch. anorg. Chem.*, 1897, **15**, 225), the latter being termed by Franklin as mercuric chloride "with amine, pyridine, and quinoline of crystallisation" (*J. Amer. Chem. Soc.*, 1907, **29**, 35). Mercuric nitrite has been found to be the exact analogue of the chloride in this respect.

It is noteworthy that whilst butylamine gives a salt of the type $N_2Hg_3(C_4H_9)_2(NO_2)_2$, its isomeride simply gives an additive compound (No. III). We have not been successful in preparing any substituted compound with propylamine, dimercuriammonium nitrite being invariably obtained. In view of the remarkable family likeness which obtains throughout the haloid and nitrite series of the mercuriammonium bases, it may be pointed out that the hydrated salts, for example, $NHg_2NO_2,\frac{1}{2}H_2O$; $NHg_2Cl,\frac{1}{2}H_2O$; and $NHg_2Br,\frac{1}{2}H_2O$ (Rây, Trans., 1902, **81**, 647), as also Nos. II and III, are not to be looked on as hydroxy-compounds, as Franklin is inclined to do (*loc. cit.*, p. 63). Both mercuric chloride and nitrite,* unlike mercuric nitrate, are very feebly ionised in solution, and hence none of them yields with sodium sulphate the basic sulphate known as "turpeth mineral." In fact, the halide and nitrite derivatives have to be sharply differentiated from the salts of Millon's base.

EXPERIMENTAL.

For convenience of reference the salts described below have been numbered *seriatim*, the first member of the series, trimercuridiethylammonium nitrite, being named No. I.

II. *Trimercuridibutylammonium Nitrite*, $NHg_3(C_4H_9)_2(NO_2)_2,H_2O$.

Trimercuridibutylammonium nitrite was prepared by the same method as used in preparing its lower homologue (Rây and

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* A paper on the ionisation of mercuric nitrite, as based on conductivity, will shortly be communicated.

Rakshit, Trans., 1911, **99**, 1972). It is a white powder, and can be dried at 100° without decomposition.

Found: Hg=69·21; C=11·15; N=6·99.

$C_8H_{18}NHg_3(NO_2)_2,H_2O$ requires Hg=70·42; C=11·26; N=6·57 per cent.

III. *Mercuriisobutylammonium Nitrite*, $C_4H_9{\cdot}NH_2,Hg(NO_2)_2,H_2O$.

This compound is obtained as a dirty white powder. It is appreciably soluble in water; during washing nearly one-third of it passed into solution. It was dried at 100°.

Found: Hg=52·57; C=11·88; N=11·18.

$C_4H_{11}N,Hg(NO_2)_2,H_2O$ requires Hg=52·22; C=12·28; N=10·97 per cent.

IV. *Mercuribenzylammonium Nitrite*, $C_6H_5{\cdot}CH_2{\cdot}NH_2,Hg(NO_2)_2,H_2O$.

This is obtained as a white precipitate by adding excess of benzylamine to the nitrite solution. The precipitate was washed carefully to free it from adhering sodium nitrite, and finally dried in the steam-oven.

Found: Hg=48·65; C=20·76; N=9·46.

$C_7H_9N,Hg(NO_2)_2,H_2O$ requires Hg=48·00; C=20·14; N=10·07 per cent.

The substance decomposes at 150—160°, giving mercury, mercuric oxide, benzaldehyde, a nitroso-compound, nitric oxide, and nitrogen.

V. *Mercuridiphenylammonium Nitrite*, $2C_6H_5{\cdot}NH_2,Hg(NO_2)_2,H_2O$.

Mercuridiphenylammonium nitrite is obtained as a pale yellow, crystalline precipitate when a saturated solution of aniline is added to sodium mercuric nitrite. The colour of the substance slightly deepens on drying. It decomposes below 100°; consequently it was dried in a vacuum over sulphuric acid. The crystals are unctuous to the touch.

Found: Hg=41·05; C=29·02; N=11·07.

$C_{12}H_{14}N_2,Hg(NO_2)_2,H_2O$ requires Hg=40·32; C=29·03; N=11·29 per cent.

VI. *Mercuridi*-p-*tolylammonium Nitrite*, $2C_6H_4Me\cdot NH_2,Hg(NO_2)_2,H_2O$.

Mercuridi-p-*tolylammonium nitrite* was prepared similarly to the above, only the solution of *p*-toluidine had to be effected with warm water. It resembles in property the preceding compound.

Found: Hg=39·57; C=32·18; N=10·16.

$C_{14}H_{16}N_2,Hg(NO_2)_2,H_2O$ requires Hg=38·16; C=32·06; N=10·68 per cent.

VII. *Mercuridibenzylmethylammonium Nitrite*, $2C_6H_5\cdot CH_2\cdot NHMe,Hg(NO_2)_2$.

When a solution of benzylmethylamine is added to sodium mercuric nitrite, a white cloudiness immediately appears. After some time a viscous oil collects, which soon solidifies to a mass of crystals.

Found: Hg=37·42; C=35·12; N=10·91.

$C_{16}H_{22}N_2,Hg(NO_2)_2$ requires Hg=38·02; C=36·05; N=10·64 per cent.

VIII. *Mercuridibenzylethylammonium Nitrite*, $2C_6H_5\cdot CH_2\cdot NHEt,Hg(NO_2)_2$.

This was obtained as usual by adding a solution or rather an aqueous emulsion of benzylethylamine to sodium mercuric nitrite. Like the preceding member, it passed through the intermediate stage of an oil. It was obtained as a white mass, which was dried at 100°.

Found: Hg=35·06; C=36·61; N=10·42.

$C_{18}H_{26}N_2,Hg(NO_2)_2$ requires Hg=35·59; C=38·43; N=9·96 per cent.

The value found for nitrogen is a little high, whereas that for the carbon is a little too low; this is accounted for by the oily liquid entangling the mother liquor, rich in sodium nitrite, and crystallising out along with the latter.

IX. *Mercuridipyridinium Nitrite*, $2C_5H_5N,Hg(NO_2)_2$.

To a concentrated solution of mercuric nitrite a concentrated solution of pyridine was added in excess, when a yellow oil immediately separated. The substance crystallises with difficulty, and on being dried loses pyridine; hence it could not be obtained in the pure condition.

Found: Hg=45·99; C=23·84; N=11·79.

$C_{10}H_{10}N_2,Hg(NO_2)_2$ requires Hg=44·44; C=26·66; N=12·44 per cent.

X. *Mercuriquinolinium Nitrite*, $2C_9H_7NH,Hg(NO_2)_2$.

As quinoline is sparingly soluble in water, an aqueous emulsion of it was added to sodium mercuric nitrite as usual, when a yellow oil separated, which, unlike the corresponding pyridine salt, solidified almost immediately. This was collected, washed, and dried in a vacuum over sulphuric acid.

Found: Hg=34·66; C=41·21; N=9·51.

$C_{18}H_{16}N,Hg(NO_2)_2$ requires Hg=36·1; C=39·3; N=10·2 per cent.

The excess in the percentage of carbon is due to a little free quinoline being carried down with the salt, which was precipitated in the oily condition. The percentage of mercury is necessarily low.

XI. *Mercuripiperazinium Nitrite*, $C_4H_{10}N,Hg(NO_2)_2$.

This compound is a white powder, sparingly soluble in water. It was dried at 100°.

Found: Hg=52·91; C=12·43; N=14·50.

$C_4H_{10}N_2,Hg(NO_2)_2$ requires Hg=52·60; C=12·69; N=14·81 per cent.

Attempts to obtain the α-naphthylamine derivative were unsuccessful.

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