

XLV.—*Alkaloidal Derivatives of Mercuric Nitrite.*

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It has been shown in previous communications that not only aliphatic and aromatic amines, but also heterocyclic carbon-nitrogen ring compounds, such as pyridine, quinoline, piperazine, etc., yield definite salts with mercuric nitrite (T., 1912, **101**, 616). The action of mercuric nitrite on some alkaloids has now been studied, and in most cases definite compounds have been obtained.

EXPERIMENTAL.

General Method of Preparation.—The alkaloids were dissolved in suitable solvents, such as alcohol, ether, chloroform, etc., but rarely in water. The solution was added in a thin stream to a solution of sodium mercuric nitrite with constant stirring, care being taken that the latter reagent was always in excess. As a rule, precipitates were obtained at once, but in some cases there was a considerable interval before they were formed. They were then dried in a vacuum over sulphuric acid.

Nicotine and Mercuric Nitrite.—The compound had the composition $C_{10}H_{14}N_2, Hg(NO_2)_2$.

Found: Hg=43·42. N=11·69.

$C_{10}H_{14}N_2, Hg(NO_2)_2$ requires Hg=44·05; N=12·31 per cent.

Coniine and Mercuric Nitrite.—A pasty mass was obtained which gradually hardened.

Found: Hg=47·81; N=9·06.

$C_8H_{17}N, Hg(NO_2)_2$ requires Hg=47·73; N=10·02 per cent.

Quinine and Mercuric Nitrite.—The compound was an amorphous, granular, white powder:

0·1027 gave 0·0395 HgS. Hg=33·15.

0·0748 „ 5·2 c.c. N_2 at 30° and 760 mm. N=8·41.

$C_{20}H_{24}O_2N_2, Hg(NO_2)_2$ requires Hg=32·46; N=9·09 per cent.

Quinidine and Mercuric Nitrite.—An amorphous, white powder:

0·0936 gave 0·1108 CO_2 and 0·0334 H_2O . C=32·28; H=3·97.

0·0682 „ 5·1 c.c. N_2 at 28° and 760 mm. N=10·20.

0·1086 „ 0·0470 HgS. Hg=37·31.

$2C_{20}H_{24}O_2N_2, 3Hg(NO_2)_2$ requires C=31·49; H=3·67; N=9·19;
Hg=39·36 per cent.

The filtrate from the above when further treated with the alkaloid yielded a compound of different constitution:

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0.1110 gave 0.0422 HgS; Hg=33.07.

$C_{20}H_{24}O_2N_2, Hg(NO_2)_2$ requires Hg=32.40 per cent.

Cinchonidine and Mercuric Nitrite.—On adding an alcoholic solution of the base to mercuric nitrite solution, a small quantity of precipitate was obtained; but on diluting with water a white, voluminous mass was produced. It was washed first with water and then with alcohol and dried in a vacuum over sulphuric acid.

Found: Hg=35.85; N=9.18.

$C_{19}H_{22}ON_2, Hg(NO_2)_2$ requires Hg=34.25; N=9.60 per cent.

A second preparation gave the ratio of the alkaloid to mercuric nitrite as 2:3:

0.1266 gave 0.1358 CO_2 and 0.0472 H_2O . C=29.26; H=4.14.

0.1020 „ 7.5 c.c. N_2 at 30° and 760 mm. N=8.12.

0.1598 „ 0.0732 HgS. Hg=39.48.

$2C_{19}H_{22}ON_2, 3Hg(NO_2)_2$ requires C=31.14; H=3.00; N=9.56;
Hg=40.97 per cent.

Codeine and Mercuric Nitrite.—On using a chloroform solution of the alkaloid a viscid mass was obtained which hardened on keeping:

0.1214 gave 0.0345 HgS. Hg=24.50.

0.0702 „ 4.0 c.c. N_2 at 31° and 760 mm. N=6.28.

$2C_{18}H_{21}O_3N, Hg(NO_2)_2$ requires Hg=22.42; N=6.28 per cent.

On using an alcoholic solution of the alkaloid, a pale yellow, granular precipitate was obtained.

Found: Hg=41.70.

$2C_{18}H_{21}O_3N, 3Hg(NO_2)_2$ requires Hg=40.70 per cent.

Slight reduction of mercuric nitrite took place.

Narcotine and Mercuric Nitrite.—A chloroform solution of the alkaloid was used:

0.0652 gave 0.1408 CO_2 and 0.0428 H_2O . C=58.88; H=7.29.*

0.1116 „ 2.6 c.c. N_2 at 29° and 760 mm. N=2.59.

0.2562 „ 0.0162 Hg. Hg=6.32.

$6C_{22}H_{23}O_7N, Hg(NO_2)_2$ requires C=57.19; H=4.98; N=4.04;
Hg=7.22 per cent.

A slight reduction of mercuric nitrite was noticed.

Strychnine and Mercuric Nitrite.—On adding a chloroform solution of the alkaloid to mercuric nitrite solution and stirring for ten to fifteen minutes the liquid began to turn cloudy and ultimately a precipitate was obtained:

* In the case of mercury compounds the estimation of hydrogen is often untrustworthy, as traces of mercury vapour are apt to be carried into the calcium chloride tube.

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0.0906 gave 0.1574 CO₂ and 0.0470 H₂O. C=47.38; H=5.77.*
 0.1280 „ 8.8 c.c. N₂ at 31° and 760 mm. N=7.57.
 0.2315 „ 0.0596 Hg. Hg=25.77.
 3C₂₁H₂₂O₂N₂, 2Hg(NO₂)₂ requires C=47.66; H=4.16; N=8.82;
 Hg=25.21 per cent.

Brucine and Mercuric Nitrite.—The compound was a pale pink, amorphous powder:

0.0754 gave 0.1342 CO₂ and 0.0436 H₂O. C=48.54; H=6.43.
 0.0780 „ 4.4 c.c. N₂ at 29° and 760 mm. N=6.26.
 0.1125 „ 0.2350 HgS. Hg=18.01.
 2C₂₃H₂₆O₄N₂, Hg(NO₂)₂ requires C=51.11; H=4.82; N=5.19;
 Hg=18.52 per cent.

A second preparation gave the percentage of mercury as 18.61. On repeating the preparation a third time the compound obtained had a pale yellow colour instead of pink, as in the preceding instances:

0.0925 gave 0.0158 HgS. Hg=14.73.
 0.0662 „ 4.8 c.c. N₂ at 25° and 760 mm. N=8.18.
 3C₂₃H₂₆O₄N₂, Hg(NO₂)₂ requires Hg=13.57; N=7.60 per cent.

Cocaine and Mercuric Nitrite.—The alcoholic solution of cocaine gave no immediate precipitate, but after twenty-four hours clusters of fine, white, silky needles were deposited:

0.0385 gave 0.0468 CO₂ and 0.0205 H₂O. C=33.15; H=5.92.
 0.0902 „ 5.4 c.c. N₂ at 26° and 760 mm. N=6.72.
 0.1308 „ 0.0512 HgS. Hg=33.74.
 C₁₇H₂₁O₄N, Hg(NO₂)₂ requires C=34.28; H=3.53; N=7.06;
 Hg=33.61 per cent.

Conductivity Experiments.

The cinchonidine and cocaine compounds were appreciably soluble in water, and thus they lent themselves to conductivity experiments.

Cinchonidine Mercuric Nitrite.

S.	μ.
1,750	198
3,500	225
7,000	241

* See footnote, p. 508.

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λ .	μ .
6,000	187
12,000	252

Evidently in both cases the salts dissociate into three ions.

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