549. *Derivatives of Some Tertiary Amides with Mercuric Chloride*

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MERCURIC CHLORIDE forms a derivative with *N*-formylpiperidine.[1] During certain synthetic studies [2] it became desirable to characterise *N*-formyl-1,2,3,4-tetrahydroisoquinoline, and because of its structural relationship with *N*-formylpiperidine the mercuric chloride derivative was chosen. Elemental analysis of this crystalline derivative suggested the formula $2C_{10}H_{11}NO,3HgCl_2$, in contrast to $C_6H_{11}NO,HgCl_2$, for the *N*-formylpiperidine derivative. A number of mercuric chloride derivatives of other tertiary *N*-formyl compounds were examined, and in all cases the amide : mercuric chloride ratio was either 1 : 1 or 2 : 3.

The mercuric chloride derivatives of the cyclic tertiary amides 1,3-dimethyl- and 1,3,3-trimethyl-oxindole [3] and *N*-methyl-2-piperidone [4] have been reported. We have now prepared the corresponding derivatives of *N*-methyl-2-pyridone and *N*-methylpyrrolidone and found that the amide : mercuric chloride ratio was 1 : 1 in both cases. We failed to obtain a derivative from pyrrolidone.

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[1] M. W. Farlow and H. Adkins, *J. Amer. Chem. Soc.*, 1935, **57**, 2222.
[2] I. Baxter, L. T. Allan, and G. A. Swan, *J.*, 1965, in the press.
[3] P. L. Julian, J. Pikl, and D. Boggess, *J. Amer. Chem. Soc.*, 1934, **56**, 1797.
[4] J. Renault, *Ann. Chim.* (*France*), 1955, **10**, 135.

Amide	Yield of amide (%)	M. p. of $HgCl_2$ derivative	Found (%)			Reqd. (%)		
			C	H	N	C	H	N
N-Formylpiperidine	34	148°	19·15	2·6	3·65	18·75	2·9	3·65
NN-Dimethylformamide *	—	116	7·4	1·3	2·7	7·5	1·5	2·9
N-Methylformanilide	73	81	23·7	2·3	3·9	23·7	2·25	3·45
N-Formylmorpholine *	15	130	11·65	1·55	2·6	11·5	1·75	2·7
N-Formyl-2,6-dimethylpiperidine	53	106	—	—	3·45	—	—	3·4
N-Formyl-1,2,3,4-tetrahydroisoquinoline †	56	141	—	—	—	—	—	—
N-Methylpyrrolidone	—	126	16·0	2·3	3·65	16·3	2·45	3·8
N-Methyl-2-pyridone	—	126	19·05	1·95	3·6	18·9	1·85	3·7

* The analyses are calculated for an amide : mercuric chloride ratio of 1 : 1 except when marked with an asterisk; then the ratio is 2 : 3. † For the analysis see ref. 2.

The infrared spectra of the derivatives prepared were very similar to those of the corresponding parent amides, except that the carbonyl stretching frequency was lowered by 15—30 cm.$^{-1}$. Further, two peaks of low intensity appeared in the region 3520—3575 cm.$^{-1}$. A similar lowering of the carbonyl stretching frequency of dimethylacetamide in complex-formation with a number of inorganic salts has been attributed to co-ordination occurring through the oxygen atom of the amide.[5] The mercuric chloride derivatives were readily decomposed in hot aqueous solution by the action of hydrogen sulphide, with the formation of mercuric sulphide and the liberation of the parent amide. Thus the mercuric chloride derivatives provide a convenient method for the purification of simple *N*-formyl compounds.

Experimental.—N-*Formyl compounds.* All these compounds, with the exception of dimethylformamide which was a commercial sample, were prepared from the corresponding secondary amine by the following general procedure. To a cooled solution of the secondary amine (2·7 g.) in dry ether (20 ml.) was added, with caution, a cold mixture of 98—100% formic acid (3·4 ml.) and acetic anhydride (8·2 ml.) which had been previously heated at 60° for 2 hr. The mixture was kept at room temperature for 24 hr. and fractionally distilled.

Mercuric chloride derivatives. The tertiary amide was added, with stirring, to an excess of a 5% aqueous solution of mercuric chloride. The crystalline solid which was deposited was filtered off, dried, and recrystallised from ethyl acetate–light petroleum (b. p. 60—80°).

Decomposition of the mercuric chloride derivatives. The mercuric chloride derivative (1 g.) was suspended in water (20 ml.) and boiled gently until dissolved. Hydrogen sulphide was passed through the hot solution for 15 min., and the mixture cooled and filtered. The collected solid was washed with a large volume of water and the combined washings and filtrate were extracted with either ether or chloroform. The dried extract (K_2CO_3) was evaporated to dryness under reduced pressure on a water-bath, and the residue distilled. The recovery of the amide was *ca.* 90%.

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[5] W. E. Bull, S. K. Madan, and J. E. Willis, *Inorg. Chem.*, 1963, **2**, 303.