Tetrahedron Vol 32. pp. 1909 to 1910 Pergamon Press 1976 Printed in Great Britain

MERCURY(II) DERIVATIVES OF AZOLES

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(*Received in the UK* 10 *November* 1975. *Accepted for publication* 2 *January* 1976)

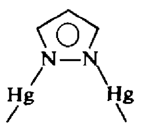
Abstract—The reaction between mercury(II) chloride and azoles(pyrazole, 3,5-dimethylpyrazole, benzotriazole, 1,2,4-triazole) afforded mainly N-chloro mercury derivatives, although other reactions, such as the well known ring mercuration or the formation of a complex, were observed simultaneously. Therefore, no simple generalization explains the observed reactivity of azoles towards mercury(II) chloride, each reaction investigated being a different case.

In continuing our studies in the field of heterocyclic derivatives of metals[1,2] we have investigated the reaction between certain azoles, having no substituent on the 1-nitrogen atom, and mercury(II) chloride. In principle, mercuration of azoles[3,4] can yield N-mercury and C-mercury derivatives, or the nitrogen atom of the azole may give an adduct with $HgCl_2$, or the hydrogen halide, set free during the formation of N- and C-derivatives, may give derivatives of $HgCl_3^-$. Granberg *et al.*[5] were concerned with the ring mercuration of many pyrazoles, only one of which was a N-unsubstituted molecule. The compound used, 4-methyl-3,5-dipropylpyrazole, gave the nitrogen bonded chloro mercury(II) derivative after 5 hr treatment with mercury(II) acetate and then with potassium chloride in refluxing methanol, obviously, no ring mercuration being possible. It was therefore decided to carry out an investigation on the reaction of mercury(II) chloride with selected azoles, with a view to shedding light on the reactivity of these heterocyclic compounds.

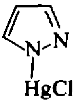
RESULTS AND DISCUSSION

We observed that the reaction between mercury(II) chloride and azoles (pyrazole, 3,5-dimethylpyrazole, benzotriazole, 1,2,4-triazole) carried out in aqueous solution afforded insoluble products immediately upon mixing. This reaction cannot be extended to other mercury(II) halides, e.g. $HgBr_2$, $Hg(CN)_2$, in agreement with the known singular reactivity of the chloride.[6]

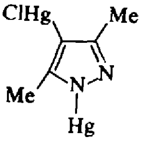
Reaction was also attempted with other azoles, such as indazole, but the products obtained were not pure, according to analytical data, and could not be purified due to insolubility. The products were white solids which gradually decomposed on heating, their insolubility may be understood if it is remembered that pyrazoles act as bridged bidentate ligands[4] i.e.



Such bridging was observed in the gold(I) derivatives of pyrazole and related molecules[7] and in other metal derivatives,[4] here it could afford an insoluble coordination polymer. According to elemental analyses (Table 1), the simplest formulae (monomer) of the compounds obtained, are:



1



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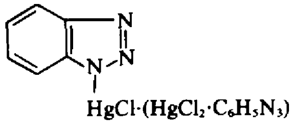

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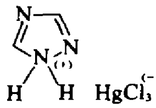

4

These do not belong to the same class of compounds, but are different in each case. No molecular weight determination could be carried out. Formulae **1**–**4** are supported by IR spectra. In compounds **1** and **2** no N–H stretching or bending vibrations were observed, which were found in **3** and **4**. The only bands above 3000 cm^{-1} (3123, 3105) observed in **1** are due to the ν(C–H) of the pseudoaromatic ring. These bands are very sharp and lie in the same position as in metal bis-(1-pyrazolyl)borates and pyrazolyl-gold(I) compounds but are absent in **2**, as anticipated. In the case of **4**, the observed ν(Hg–Cl) cannot be compared with the values found[8] in simple $(HgCl_3)_n^{n-}$ (453, 291, 261, 103 cm^{-1}) derivatives, because in our compound there is at least another nitrogen donor atom which allows formation of a coordination polymer. The consequence of the intermolecular dative bonds cannot be evaluated. In all the compounds the Hg–Cl streching vibrations were observed between 300 and 350 cm^{-1}, as expected.

In order to establish that the organic ligand was not altered upon reaction, the aqueous suspension of the complex was decomposed with hydrogen sulphide. The resulting organic species was identified through the picrate, as the corresponding azole.

It is evident that N-mercuration took place in **1**, **2**, and **3**, but not in **4**; in addition, C-mercuration was observed in **2**, but not on the parent pyrazole nor on the aromatic ring of the triazole. In **1** the strong and broad band (IR) at 3400–2500 cm^{-1} assigned to the hydrogen bond of pyrazole was absent. Furthermore compound **3** is a 1:1 adduct of the N-chloro-mercury(II) derivative and a 1:1 benzotriazole complex of mercury chloride.

Clearly, no simple generalization can explain the observed reactivity of azoles towards mercury(II)

Table 1. Analytical data

	%C		%H		%N		%Cl		%Hg	
Comp.	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1	11.89	12.05	0.99	0.90	9.24	9.55	11.70	11.95	66.18	67.32
2	10.61	10.75	1.07	1.39	4.95	4.94	12.52	12.40	70.66	70.26
3	19.34	19.26	1.21	1.15	11.27	11.29	14.28	14.08	53.85	53.22
4	6.40	6.63	1.06	0.64	11.21	11.02				

Table 2. IR data†

Comp.	
1	3123w, 3105m, 1377s, 1301s, 1190s, 1068s, 759vs, 620s, 309m.
2	1570w, 1532m, 1322m, 1195w, 1162m, 1050s, 805s, 798s, 768w, 650w, 470w, 375s, 341s.
3	3280s, 1620w, 1592m, 1265s, 1225s, 1220sh, 1150m, 1090vs, 1021s, 905m, 777s, 760s, 747sh, 742vs, 645w, 433m, 423m, 330sh, 327s.
4	3120m(broad), 1641w(broad), 1312m, 1294s, 1279m, 1270m sh, 1200w, 1180w sh, 1162s, 1149s, 1082s, 1060m sh, 1000m sh, 992m 960w, 870m(broad), 720m(broad), 666m, 641s, 332m sh, 325m.

1 = $C_3H_2ClHgN_2$; **2** = $C_5H_6Cl_2hG_2n_2$;
3 = $C_{12}H_9Cl_3Hg_2N_6$; **4** = $C_2H_4Cl_3HgN_3$

†In Nujol mull.

chloride, each reaction investigated being a special case. Substitution of the nitrogen bonded hydrogen atom seems to be the easiest step, although other reactions, such as the well known ring mercuration in the formation of a complex, are sometimes likely to be observed.

EXPERIMENTAL

IR spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer as Nujol mulls, in the range 4000–250 cm^{-1}. Calibration was performed against either polystyrene film or *cis*-$Pt(PEt_3)_2$–Cl_2 and frequencies were considered accurate to ±2 cm^{-1}. Analytical and IR data are collected in Tables 1 and 2 respectively.

Synthesis of the mercury–azole complexes

All compounds were synthesized by mixing equimolar amounts of $HgCl_2$ and an azole (pyrazole, 3,5-dimethylpyrazole, benzotriazole, 1,2,4-triazole) in water solution, yielding complexes **1**, **2**, **3** and **4**, respectively. Thus, for example, a water solution of pyrazole (0.01 mole, 5 ml H_2O) was added, dropwise, whilst stirring to an equimolar solution of $HgCl_2$ at room temperature. A white precipitate promptly formed which was successively washed with water, ethanol, and ethyl ether, and dried *in vacuo* (quantitative yield). All compounds were insoluble in most common solvents.

Decomposition of the mercury–azole complexes with H_2S

All of the decompositions were performed by suspending the complex in a saturated water solution of H_2S. Mercury(II)sulphide precipitated after a few minutes. To the solution, an approximately equimolar quantity of picric acid (saturated water solution) was added. Concentration of the solution gave yellow crystals, which were identified as the corresponding azole-picrates, by comparision with authentic samples (m.p. IR spectra). The yield was nearly quantitative.

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