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STUDIES OF HETEROCYCLIC COMPOUNDS

III*. SYNTHESIS AND THERMAL DECOMPOSITIONS OF SOME 2-THIOPHENEMERCURIC DERIVATIVES

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Summary

2-Thiophenemercuric chloride(I), on reaction with sodium or silver thiocyanate, silver azide, silver acetate, and silver trifluoromethanesulfonate gave the 2-thiocyanate (2), 2-azide (4), 2-acetate (5) and 2-trifluoromethanesulfonate (6), respectively. The thermal decompositions of these compounds, together with that of 2,2′-dithienyl mercury, have been studied. The 2-thiophenemercuric triflate (6) decomposes at room temperature to give 2,2′-dithienylmercury. The 2-azide (4), when treated with either cyclohexene or triphenylphosphine, gave only the 2,2′-dithienylmercury. All the 2-thiophenemercuric salts decompose at about 300°C to give only a black insoluble residue. With the aid of some control experiments and comparison with previous work on phenyl- and *p*-tolylmercuric salts, a mechanism is proposed to account for the results.

Introduction

Many studies have been reported on the demercuration reactions of organomercurials. These include photolytic demercuration of organomercuric salts [1—3], the peroxide-induced decomposition of organomercuric compounds [4—5] and some thermal demercuration reactions [6—8].

Further studies into the demercuration reactions of organomercurials include the interesting work of Kretchmer and Glowinski [9], which involves the conversion of arylmercuric salts to biaryls in high yield by the treatment of the appropriate arylmercuric salt with copper and a catalytic amount of $PdCl_2$ in

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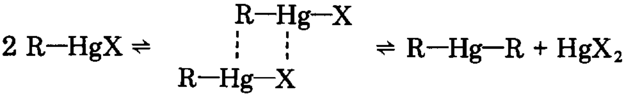
pyridine solvent:

$$2\,ArHgX + Cu \xrightarrow[PdCl_2,\ 115^\circ C]{Pyridine} Ar{-}Ar + 2\,Hg + CuX_2$$

In the work of Inamoto and Toshifuji [8], which involved the thermal demercuration of some alkylmercuric salts and phenyl and *p*-tolylmercuric derivatives in the presence or absence of mercuric salts, three possible mechanisms were proposed for the thermal demercurations. For the phenyl- and *p*-tolylmercuric salts, it was found that benzene and toluene, respectively, were the main products and they concluded that their decompositions follow the following mechanism:



$$2\,R{-}HgX \rightleftharpoons \begin{array}{l} \quad\ \ R{-}Hg{-}X \\ \quad\ \ \vdots \quad\ \ \vdots \\ R{-}Hg{-}X \end{array} \rightleftharpoons R{-}Hg{-}R + HgX_2 \qquad (i)$$

$$R{-}Hg{-}R \rightarrow Hg + 2\,R^{\bullet} \qquad (ii)$$

$$Hg + HgX_2 \rightarrow Hg_2X_2 \qquad (iii)$$

$$2\,R^{\bullet} \rightarrow 2\,RH \qquad (iv)$$

In continuation of our studies on thiophene derivatives [10,11], some 2-thiophenemercuric derivatives were synthesized and their thermal decomposition behaviour studied. The results were compared with those of phenyl and *p*-tolylmercuric salts.

Experimental

IR spectra were recorded as potassium bromide discs on a Perkin-Elmer 727B spectrometer. NMR spectra were measured with a Varian T60 spectrometer in deuterated acetone or deuterated DMSO as appropriate using tetramethylsilane as internal standard. Elemental analysis were by the Analytical Division of the Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Canada. Mass spectra were determined with an AEL MS12 spectrometer.

2-Thiophenemercuric chloride (1). The reaction of thiophene with mercuric chloride in the presence of sodium acetate by the method of Volhard [12] gave the mercuric chloride **1** (extracted with hot ethanol), m.p. 183°C (lit. [12] 182—183°C).

2-Thiophenemercuric thiocyante (2). This was prepared from 2-thiophenemercuric chloride **1** and sodium thiocyanate (1 equiv.) [12] or silver thiocyanate in acetone. M.p. 197—198°C (lit. [12] 196—197°C). IR 2145 cm^{-1} ($-S-C{\equiv}N$). The mass spectrum shows the molecular ion, M^+, at *m/e* 343.

2-Thiophenemercuric azide (4). A mixture of 2-thiophenemercuric chloride (5 g, 15.6 mmol) and silver azide (2.3 g, 1 equiv.) in 1/1 methylene chloride/benzene mixture (100 ml) was stirred at room temperature for 12 h. The silver chloride was filtered off; removal of the solvent gave the mercuric azide **4** (4.5 g, 89%) as beige needles, m.p. 134—136°C (dec.) (Found: C, 14.7; H, 1.0; N, 12.9. $C_4H_3HgN_3S$ calcd.: C, 14.7; H, 0.9; N, 12.8%) IR 2050 cm^{-1} (N_3). This is in the range (2020—2080 cm^{-1}) [16] recorded in the literature for some organomercuric azides.

Reactions of 2-thiophenemercuric azide

(i) With cyclohexene. The azide (1 g) in THF (10 ml) was heated with cyclohexene (0.26 g, 1 equiv.) for 3 days. Removal of solvent gave a product shown to be 2,2′-dithienylmercury (IR, analysis, mass spectrum), m.p. 199—200°C), in quantitative yield.

(ii) With triphenylphosphine. As above, equimolar quantities of the azide and triphenylphosphine were heated in THF (10 ml) at reflux to afford mainly 2,2′-dithienylmercury with some mercury metal (5%) (formed by thermal decomposition of the 2,2′-dithienylmercury).

2-Thiophenemercuric acetate (5). 2-Thiophenemercuric chloride (1 g, 3.1 mmol) and silver acetate (0.52 g, 1 equiv.) were heated in refluxing methylene chloride/benzene mixture (25 ml) for 10 min and the silver chloride was filtered off. Removal of the solvent afforded the mercuric acetate **5** (1 g, 95%), m.p. 118—120°C (found: C, 21.0; H, 1.8. $C_6H_6HgO_2S$ calcd.: C, 20.9; H, 1.7%). IR 1585 (C=O of mercuric acetate group), 1295 cm^{-1} ($-O-COCH_3$ ester group). NMR ($CDCl_3$), δ 2.0 ppm (s, 3 H, $Hg-O-COCH_3$).

2-Thiophenemercuric triflate (6). 2-Thiophenemercuric chloride (1.5 g, 4.7 mmol) and silver trifluoromethanesulfonate (1.2 g, 1 equiv.) in a methylene chloride/benzene mixture (1/1) (20 ml) was stirred in a flask protected from light for 12 h. Removal of the solvent at 15°C under reduced pressure gave the mercuric triflate **6** which is unstable at room temperature. The same reaction was repeated in dimethyl sulfoxide, a solvent in which the 2-thiophenemercuric triflate is stable.

IR: 1150, 1340 (SO_2), 1105, 1015 (SO), 1240(br) (CF_3) cm^{-1}. The mass spectrum showed the molecular ion at *m/e* 434 (3.6%).

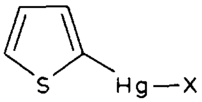
Results and discussion

Reaction of thiophene with mercuric chloride in the presence of sodium acetate gave the 2-mercuric chloride **1** [12]. This product was treated with sodium thiocyanate, and silver azide, acetate and trifluoromethanesulfonate to give the 2-thiocyanate (**2**) and 2,2′-dithienylmercury (**3**) [12], 2-azide (**4**), 2-acetate (**5**), and 2-trifluoromethanesulfonate (**6**), respectively (Fig. 1), all of which were characterized by melting point, elemental analysis, IR, NMR (for the acetate) and mass spectrometry.

The results on the thermal reactions of the 2-thiophenemercuric derivatives are shown in Table 1, together with the result observed with phenylmercuric chloride.

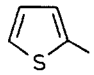
It is interesting to note that in the decomposition of phenyl- or tolylmercuric derivatives, the major product, apart from mercury (0.4—6%), is benzene (25—50%) or toluene (47%), respectively, whereas the thiophenemercuric compounds gave, apart from mercury, only an insoluble residue.

The demercuration reaction of 2-thiophenemercuric chloride, at 300°C, gave only a grey residue with no mercury metal. Neither thiophene nor 2-chlorothiophene was formed. The residue was insoluble in all organic solvents but elemen-



(1 , X = Cl ;

2 , X = SCN ;

3 , X =  (Th) ;

4 , X = N_3 ;

5 , X = $OCOCH_3$;

6 , X = OSO_2CF_3)

Fig. 1. Compounds synthesized and studied.

tal analysis gave C (8.6%) and H (0.5%). In the mass spectrum, the major peaks were that of Hg at *m/e* 202 together with less intense peaks at *m/e* 474, 426 and 378, together with the surrounding peaks characteristic of mercury. Other peaks are due mainly to the thiophene nucleus at *m/e* 83, 57, 45 and 39. The nature of the residue is not yet understood but from the mass spectrum, it appears to be a mixture of mercurous chloride (Hg_2Cl_2, *m/e* 474) and some other compounds. However, increasing the temperature to 500°C gave 15% mercury and an insoluble black residue. The reaction of the thiophenemercuric thiocyanate at about 300°C gave about 30% mercury. Neither thiophene cyanide nor thiophene thiocyante could be detected from the infrared spectrum of the insoluble black residue.

With the 2-thiophenemercuric azide. In general, organic azides are known to be unstable thermally with respect to the loss of a nitrogen molecule. Alkyl azides [13], aryl azides [14], organic sulfonyl azides [15] and organometallic azides of B, Si, Ge, P and As [16] all are believed to decompose thermally via an intermediate nitrene (group I), while other organometallic azides of Sn, Al, Tl, Sb, Ti, Zr, Pb, Hg, etc. lose all their nitrogen during thermal decomposition in a manner similar to ionic azides [16], without going through an intermediate nitrene (group II). The thermodynamic driving force is the liberation of heat [17] as shown in equation 1.

$$2\,N_3^{\bullet} \xrightarrow[\Delta]{} 3\,N_2 \qquad \Delta H = -210 \text{ kcal/mole} \tag{1}$$

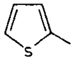
Heating of 2-thiophenemercuric azide at 200°C for 6 h left it unchanged. Increasing the heating temperature to 300°C for 2 h gave 57% mercury and a black insoluble residue whose IR spectrum showed no azide absorption and whose mass spectrum showed only the peak corresponding to mercury ion at *m/e* 202 and 101. Further reaction of 2-thiophenemercuric azide (4) was carried out in tetrahydrofuran. With cyclohexene (experiment 12), at 128°C for 2 days, the main products were the 2,2′-dithienylmercury, together with unreacted $ThHgN_3$. The reaction went to completion upon increasing the temperature and using a longer reaction time.

TABLE 1

THERMAL REACTIONS OF 2-THIOPHENEMERCURIC DERIVATIVES [a]

ThHg—X X	Temp. (°C)	Products (%)			"Other Products" (%)	Recovered Reactant (%)
		Th—X	Th—H	Hg		
1. Cl	290—300	—	—	—	100 [b] (0.73 g)	—
	500					
2. SCN	290—300	—	—	30(0.18 g)		—
3. N_3	290—300	—	—	57(0.35 g)	(0.37 g)	—
4. $OCOCH_3$	300—310	—	—	64 [c](0.38 g)	(0.4 g) [c]	—
5. Th + $HgCl_2$	290—300	—	—	60	Black residue	
6. OSO_2CF_3	Room temp.	—	—	—	ThHgTh + $(CF_3SO_3)_2Hg$	
7. PhHgCl	300—400	0.4	33	0.4		5 ref. 8
		PhCl	PhH			
8. ThH	300	—	Main	—		100
9. ThH + Hg_2Cl_2	300	—	Main	—	Hg_2Cl_2	100
10. ThH + H + $HgCl_2$	300				Black residue	
11. ThH + $Hg(OAc)_2$	500	—		99	ACOH, CS_2, black residue	—
12. N_3(+ 	(i)128 (2 days)				ThHgTh(+unreacted $ThHgN_3$)	
	(ii)165 (3 days)				(ThHgTh)100	
13. N_3 + Ph_3P	140			5	ThHgTh	

[a] Reactions were run in sealed ampoules placed in steel bombs (1.0 g each of reactant). [b] only a grey insoluble material was formed. [c] AcOH was also formed although in low yield (20%).

Th = 

Moreover, treatment of the azide 4 with triphenylphosphine did not give any iminophosphorus compound typical of azides assigned as group II above (since these types of azides decompose losing all their nitrogen as stated above) but gave mainly the 2,2′-dithienylmercury together with about 5% mercury, probably formed by thermal decomposition of the 2,2′-dithienylmercury.

Thermolysis of 2-thiophenemercuric acetate (expt. 4) gave mainly mercury, and the black residue as obtained for others above. The other product was acetic acid, although in low yield (20%). Under the reaction conditions, the acetic acid (or acetoxy radical) has probably decomposed further to carbon dioxide and methyl radical. No thiophene acetate was formed.

From these results, it is difficult to determine the mechanism by which these decompositions occur. If one uses the results from thermal demercuration reactions of phenylmercuric derivatives or tolylmercuric salts, which gave mainly benzene or toluene, respectively [8], then it can be assumed that the thermal decompositions of 2-thiophenemercuric derivatives occur via thiophene or thiophene radicals. In order to test this assumption, experiments 8—11 were carried out which involved the thermal reactions of thiophene either alone or with a mercury salt. Heating of thiophene alone at 300°C (expt. 8) gave back mainly thiophene (from the mass spectrum) and no black residue.

Thiophene with mercurous chloride (expt. 9) gave back the mercurous chloride, neither mercury nor black residue was formed.

The reaction between thiophene and mercuric chloride (expt. 10), however, gave the same black residue as observed for other thiophenemercuric salts but with small amounts of mercury. When the reaction was repeated, but with mercuric acetate as salt, a considerable amount of mercury (90%) was obtained, along with volatile CO_2, CS_2, ACOH and the 'usual' black residue.

These results show that once thiophene is formed, the presence of a mercury(II) salt leads to the destruction of the thiophene nucleus, leading to the black residue.

Hence, the decomposition of 2-thiophenemercuric derivatives may be proposed to follow the following scheme:

$$2\ \mathrm{Th{-}HgX} \rightleftharpoons \mathrm{Th{-}Hg{-}Th} + \mathrm{HgX_2} \qquad \text{(i)}$$

$$\mathrm{Th{-}Hg{-}Th} \rightarrow 2\ \mathrm{Th^{\bullet}} + \mathrm{Hg} \qquad \text{(ii)}$$

$$2\ \mathrm{Th^{\bullet}} \rightarrow 2\ \mathrm{Th{-}H} \qquad \text{(iii)}$$

$$2\ \mathrm{Th^{\bullet}} \rightarrow \mathrm{Th{-}Th} \qquad \text{(iv)}$$

$$2\ \mathrm{Th{-}H} + \mathrm{HgX_2} \rightarrow \mathrm{Hg} + 2\ \mathrm{HX} + \text{“black residue”} \qquad \text{(v)}$$

$$\mathrm{Th{-}Th} + \mathrm{HgX_2} \rightarrow \mathrm{Hg} + 2\ \mathrm{HX} + \text{“black residue”} \qquad \text{(vi)}$$

$$\mathrm{Hg} + \mathrm{HgX_2} \rightarrow \mathrm{Hg_2X_2} \qquad \text{(vii)}$$

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