Mercury and Organomercury Derivatives of Cyclodiazahexathiane and Cycloazaheptathiane: Preparation and Decomposition

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New mercury derivatives of cycloazathianes have been prepared: *viz.* inorganic mercury derivatives of 1,4- and 1,5-$(HN)_2S_6$; $(PhHgN)S_7$ and 1,3-, 1,4-, and 1,5-$(PhHgN)_2S_6$; and $(MeHgN)S_7$ and 1,4-$(MeHgN)_2S_6$. The compounds are readily isolated but decompose at room temperature at varying rates, giving rise to mixtures of known sulphur nitrides. The decomposition products were unsuccessfully examined for new sulphur nitrides such as the cyclic ' aromatic ' compounds predicted by Banister.

THE cycloazathianes $(HN)_xS_{8-x}$ ($x = 1$—4) are weak Brönsted acids. With strong bases (*e.g.* LiEt, LiOH, or KOH) in tetrahydrofuran they afford ionic salts,[1,2] and several covalent derivatives with post-transition metals have been described.[3] These metal derivatives could be as useful for the synthesis of new sulphur–nitrogen compounds as organo-lithium and -mercury compounds have been in organic synthesis, but they have been little exploited. One possible application is to fairly predictable syntheses in which the sulphur–nitrogen ring is preserved, for example as in equations (1) and (2).[2] A

$$(\text{HN})\text{S}_7 + \text{LiOH} \xrightarrow[0\ °\text{C}]{\text{thf}} \text{NS}_7^- + \text{Li}^+ + \text{H}_2\text{O} \qquad (1)$$

$$\text{NS}_7^- + \text{MeI} \xrightarrow[0\ °\text{C}]{\text{thf}} (\text{MeN})\text{S}_7 + \text{I}^- \qquad (2)$$

second type of synthesis involves breakdown of the original sulphur–nitrogen rings, as equations (3) and (4) for the preparation of tetrasulphur nitride.[4] We

$$5(\text{HN})_4\text{S}_4 + 10\text{Hg}(\text{O}_2\text{CMe})_2 \xrightarrow[20\ °\text{C}]{\text{C}_5\text{H}_5\text{N}} 2\text{Hg}_5(\text{NS})_8\!\downarrow + \text{S}_4\text{N}_4 + 20\,\text{MeCO}_2\text{H} \qquad (3)$$

$$\text{Hg}_5(\text{NS})_8 + \text{S}_2\text{Cl}_2 \xrightarrow[20\ °\text{C}]{\text{CS}_2} \text{S}_4\text{N}_2 \qquad (4)$$

recently reported an even better synthesis of S_4N_2 by decomposition of $Hg(NS_7)_2$.[5] Reactions of this second kind, the course of which cannot yet be predicted, deserve further investigation because they may yield new ' electron-rich ' sulphur nitrides and to help to test current theories of inorganic aromaticity.

In order to develop these ideas most effectively, it seemed desirable to find out more about the metal derivatives themselves, which have been only incompletely studied. We therefore report the preparation and properties of some new mercury and organomercury derivatives. Previous to our work only $Hg(NS_7)_2$ and $Hg_2(NS_7)_2$ [derived from $(HN)S_7$], and $Hg_5(NS)_8$, $[Hg(NS)_2]_n$, and $[Hg(NS)]_n$ [derived from $(HN)_4S_4$] had been described.[3] We have given particular attention to phenylmercury compounds, which we find to be somewhat more stable than inorganic mercury derivatives, and to the three isomeric diazahexathianes, of which no mercury derivatives were previously known. We also report on the decomposition products of $Hg(NS_7)_2$ and three of the new mercury derivatives.

RESULTS AND DISCUSSION

Preparation of Inorganic Mercury(II) *Derivatives.*—Addition of a methanol solution of mercury(II) acetate to $(HN)S_7$ in methanol at −15 °C gave a nearly white precipitate of $Hg(NS_7)_2$, as reported by Meuwsen and Schlossnagel.[6] The same procedure with 1 mol of any of the three isomers of $(HN)_2S_6$ and 2 mol $Hg(O_2CMe)_2$, afforded buff-yellow precipitates which in two cases gave fair but not perfect analyses for ' HgN_2S_6 ' (Table 1). The 1,3-diaza-derivative was too unstable to be analysed. Only polymeric structures are likely for these derivatives, and the i.r. spectra of saturated CS_2 solutions of the 1,4- and 1,5-diazahexathiane mercury compounds showed weak bands at 3 400 cm^{-1} which we attribute to the NH end-groups of linear oligomers. The analyses fit the formula $(HN)S_6N(HgNS_6N)_xH$, with $x \approx 10$ in the 1,4 case and ≈ 7 in the 1,5 case.

As previously reported, $Hg(NS_7)_2$ darkens over a period of hours at 20 °C. The 1,4 and 1,5 mercury compounds are rather less stable and the 1,3 compound much less stable than this (Table 1).

Preparation of Organomercury Derivatives.—We reported the compound $(PhHgN)S_7$ in a note.[7] Addition of a stoicheiometric amount of solid phenylmercury acetate to a stirred methanol solution of $(HN)S_7$ at 20 °C, or to any of the three isomers of $(HN)_2S_6$ at 0 °C, gave a buff precipitate of $(PhHgN)S_7$ or 1,3-, 1,4-, or 1,5-$(PhHgN)_2S_6$ respectively. These compounds gave excellent analyses (Table 1). At room temperature $(PhHgN)S_7$ does not change colour when kept in darkness for a week, but becomes orange on exposure to light. The $(PhHgN)_2S_6$ derivatives rapidly turn black at room temperature in dull daylight. All four compounds are sparingly soluble in CS_2 (Table 1). In their i.r. spectra in the NaCl region, the strong bands can be assigned with confidence to phenyl vibrations and S–N stretching

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[1] M. H. Mendelsohn and W. L. Jolly, *J. Inorg. Nuclear Chem.*, 1973, **35**, 95.

[2] B. A. Olsen and F. P. Olsen, *Inorg. Chem.*, 1969, **8**, 1736.

[3] J. Weiss, *Fortschr. Chem. Forsch.*, 1966, **5**, 635.

[4] A. Meuwsen, *Z. anorg. Chem.*, 1951, **266**, 250.

[5] H. G. Heal and R. J. Ramsay, *J. Inorg. Nuclear Chem.*, 1975, **37**, 286.

[6] A. Meuwsen and F. Schlossnagel, *Z. anorg. Chem.*, 1953, **271**, 226.

[7] H. G. Heal and R. J. Ramsay, *J. Inorg. Nuclear Chem.*, 1974, **36**, 950.

vibrations (Table 1 and footnotes). The ^1H n.m.r. spectrum of $(PhHgN)S_7$ in CS_2 was a multiplet centred at τ 2.76 with J(Hg-C-C-H) 174 Hz.

Attempts to prepare a monophenylmercury derivative of 1,4-$(HN)_2S_6$ in methanol failed, even when a solution of $HgPh(O_2CMe)$ was added very slowly to a well stirred solution of a large excess (2 : 1 mol) of the thiane. A precipitate of the bis(phenylmercury) derivative always formed, and addition of water to the filtrate precipitated more of the same compound. The explanation is probably a rapidly established redistribution equilibrium [equation (5)] which is driven to the right by

$$2(HN)(PhHgN)S_6 \rightleftharpoons (HN)_2S_6 + (PhHgN)_2S_6 \quad (5)$$

the low solubility of $(PhHgN)_2S_6$ in methanol. Gradual addition of a methanol solution of $(HN)_4S_4$ to an excess (1 : 5 mol) of $HgPh(O_2CMe)$ in methanol at 0 °C gave a beige precipitate analysing approximately for $[(PhHgN)S]_4$ (Table 1). A similar precipitate with a somewhat better analysis resulted from mixing the reagents in *NN*-dimethylformamide at 0 °C and adding acetone. The i.r. spectrum of the first product (KBr disc) lacked any detectable ν(N-H) band.

The methylmercury derivatives $(MeHgN)S_7$ and 1,4-$(MeHgN)_2S_6$ were precipitated as buff powders on addition of a stoicheiometric amount of solid methylmercury acetate to stirred methanol solutions of the corresponding thianes at 0 or −15 °C respectively. These derivatives gave good analyses and in thermal stability resembled their phenyl analogues (Table 1).

Silver(I) *and Thallium*(I) *Derivatives*.—Exploratory experiments confirmed an earlier report[8] that a red-brown silver derivative of $(HN)S_7$ is precipitated on mixing alcohol (in our experiment methanol) solutions of $(HN)S_7$ and silver(I) nitrate, which rapidly turns black at room temperature. A similar experiment with 1,3-$(HN)_2S_6$ gave a red-brown precipitate which turned black even at −15 °C. After separation of the decomposed material it contained 35.4% S and 3.0% N, intermediate between $(AgN)_2S_6$ and Ag_2S. A red-brown precipitate which turned black on standing at room temperature was also obtained on mixing benzene solutions of thallium(I) ethoxide and $(HN)S_7$ at 20 °C, and similarly gave an analysis (19.9% S, 0.7% N) intermediate between $(TlN)S_7$ and Tl_2S. Thallium(I) acetate and $(HN)S_7$ gave no precipitate in methanol, confirming an earlier report.[6]

Choice of Metal Derivatives for Use in Syntheses.—Of the various metal derivatives of the azathianes examined, the phenylmercury compounds are easier to make in a pure state and more thermally stable than the inorganic mercury, silver, or thallium derivatives, and safer to

TABLE 1

New mercury and organomercury derivatives of cycloazathianes

Compound	Analysis[a] (%)					Decomposition temperature[b] (θ_c/°C)	Solubility at 20° C	I.r. spectrum[c] (cm^{-1})	
	S	N	Hg	C	H			S–N	organic
Hg^{II} derivatives of $(HN)_2S_6$:									
1,3		[d]	[d]			0	[d]	[d]	
1,4	47.6	7.1	45.1			0—20	sparingly soluble in CS_2	800br	
1,5	48.3	7.2	44.2			0—20			
	(45.7)[e]	(6.7)[e]	(47.6)[e]						
$(PhHgN)S_7$	43.7	2.4	38.0	14.0	1.0	*ca.* 80	1.1 g per 100g CS_2, 1.1 g per 100 g thf	790br, 775 and 790 in KBr disc	690, 730
	(43.4)	(2.7)	(38.9)	(14.0)	(1.0)				
Isomers of $(PhHgN)_2S_6$									
1,3	24.5	3.6	51.8	18.3	1.3	*ca.* 68	slightly sol. CS_2	790	695, 725
1,4	24.8	3.7	51.6	18.4	1.3	*ca.* 45	0.33 g per 100 g CS_2		690, 725
1,5	25.1	3.5	51.7	18.6	1.3	*ca.* 41	slightly sol. CS_2		690, 725
	(24.8)	(3.6)	(51.7)	(18.6)	(1.3)				
Phenylmercury derivatives of $(HN)_4S_4$:[f]									
(*i*)	10.2	4.9		20.2	1.5			1 070, 1 080 (KBr disc)	690, 720 (KBr disc)
(*ii*)		4.8		20.9	1.3				
(*iii*)		4.3		21.3	1.6				
	(9.9)[g]	(4.3)[g]		(22.3)[g]	(1.6)[g]				
$(MeHgN)S_7$	49.4	3.3	44.2	2.9	0.7	*ca.* 80	slightly soluble in CS_2, MeOH, and Et_2O	790	
	(49.4)	(3.1)	(44.2)	(2.6)	(0.7)				
1,4-$(MeHgN)_2S_6$	61.5	4.3	29.5	3.8	0.9	*ca.* 30	slightly soluble in CS_2	800br	
	(61.6)	(4.3)	(29.5)	(3.7)	(0.9)				

[a] Calculated values are given in parentheses. [b] On rapid heating of the freshly prepared sample. [c] For saturated solutions in CS_2 unless otherwise stated, NaCl region only. All the solution spectra were rather weak due to the low solubility of the compounds; phenyl vibrations, where present, were the strongest. Bands other than those listed were present but were too weak and ill defined to be listed. [d] Not determined. [e] Calc. for HgN_2S_6. [f] (*i*), Precipitated at 0 °C from AnalaR methanol; (*ii*), as (*i*) but using anhydrous deoxygenated methanol; (*iii*), reaction at 0 °C in *NN*-dimethylformamide, product precipitated at 0 °C from acetone. [g] Calc. for $[(PhHgN)S]_4$.

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[8] M. Goehring, 'Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen,' Akademie-Verlag, Berlin, 1957.

work with than the methylmercury compounds. They are therefore recommended as intermediates for the synthesis of new azathiane derivatives, an application on which we report fully in the following paper.

Decomposition of Mercury and Phenylmercury Derivatives.—We examined in detail the decomposition products of $Hg(NS_7)_2$, the inorganic mercury derivative of 1,4-$(HN)_2S_6$, and the phenylmercury compounds $(PhHgN)S_7$ and 1,4-$(PhHgN)_2S_6$. Meuwsen and Schlossnagel[6] reported the rapid decomposition of $Hg(NS_7)_2$ at room temperature, but did not investigate the products. These were of special interest to us because of the possibility that they might include new sulphur–nitrogen compounds, such as S_3N_4, S_4N_6, S_5N_4, and S_6N_6 which Banister[9] has postulated as aromatic species under Hückel's '$4n + 2$' rule. The decomposition of $Hg(NS_7)_2$ and other mercury derivatives of the azathianes seemed to offer particular hope of obtaining these compounds, because sulphur–nitrogen and polysulphur radicals capable of combining together in a variety of ways would probably be formed and the decomposition and work-up might be performed at low enough temperatures to give even unstable products a chance of survival. In the event, at room temperature, $Hg(NS_7)_2$ and 1,4-$(PhHgN)_2S_6$ decomposed in *ca.* 3 d without noticeable heating. The inorganic mercury derivative of 1,4-$(HN)_2S_6$ decomposed within hours; one of our two samples spontaneously reached *ca.* 70 °C, but the other stayed relatively cool. The compound $(PhHgN)S_7$ decomposed so slowly that it was necessary to accelerate the process by heating the compound under reflux in CS_2 under nitrogen (45 °C).

TABLE 2

Decomposition products of mercury and phenylmercury derivatives of cycloazathianes

Compound	Conditions of decomposition	Products recovered (g per g of decomposed starting material)							
		HgS	$HgPh_2$	S_8	$(S_7N)_2S_x$ [a]	S_4N_2	S_4N_4	1,4-$(HN)_2S_6$	Total
$2Hg(NS_7)_2$	Solid left for 3 d at 20 °C [b]	0.343		0.245	0.182	0.151	0.038		0.959
Hg derivative of 1,4-$(HN)_2S_6$	Solid left for 1 d at 20 °C [b,c]	0.521		0.231	0	0.043	0.140	0.029	0.964
$(PhHgN)S_7$	Heated under reflux for 3 h in CS_2 under nitrogen (46 °C) [b]	0.257	0.359	0.091	0.189	0.062	0.003		0.961
1,4-$(PhHgN)_2S_6$	Solid left for 3 d at 20 °C [d]	0.368	0.411	0.089	0	0.021	0.108	0.011	1.008

[a] In the decomposition products of $Hg(NS_7)_2$, x (an average value) was *ca.* 5 but the i.r. spectrum showed a little $S_{15}N_2$ ($x = 1$) to be present. In the products from $(PhHgN)S_7$, the average value of x was between 1 and 4, and no $S_{15}N_2$ was found. Compounds of this series with x between 2 and 5 are difficult to differentiate by i.r. spectroscopy, gel-permeation chromatography elution volume, or elemental analysis. [b] Decomposition essentially complete. [c] This sample did not heat up noticeably during decomposition. Another sample became hot (*ca.* 70 °C) but gave the same decomposition products in similar proportions. [d] One percent of the starting material was recovered unchanged in the work-up.

With our method of separation, molecular-exclusion chromatography on a non-catalytic polystyrene gel, we recovered all CS_2-soluble products almost quantitatively, and the elution volumes of Banister's postulated species could be predicted. However, the only sulphur–nitrogen compounds found were known ones (Table 2). Mercury(II) sulphide was the only CS_2-insoluble product, showing that salts of sulphur–nitrogen ions were absent. The sulphur-rich compounds $(S_7N)_2S_x$ (x *ca.* 1—5) and S_4N_2 predominated in the products from $Hg(NS_7)_2$ and $(PhHgN)S_7$, while the N_2S_6 derivatives gave no $(S_7N)_2S_x$ and relatively large amounts of S_4N_4. These results do not, of course, disprove the existence or stability of Banister's compounds, a conclusion reinforced by the fact that the most stable of all nitrogen sulphides, $S_{11}N_2$,[10] was not found in the decomposition products. Also, we could have missed substances formed in very small yield, say <1%. It does now appear, however, that structurally planned syntheses are more likely than random radical processes to produce Banister's compounds.

Regarding decomposition mechanisms the products from $Hg(NS_7)_2$ and $(PhHgN)S_7$ contain intact S_7N rings, together with compounds and fragments (S_4N_4, S_4N_2, and $-S_x-$) which imply ring breakdown. One plausible suggestion is that NS_7 radicals are produced, and that a proportion of these break down to give NS radicals, fragments of sulphur chain, *etc.* which combine with each other and with the surviving NS_7 radicals. The two compounds with N_2S_6 rings did not yield any products containing these rings [except a little 1,4-$(HN)_2S_6$ of unknown origin], suggesting that this ring is relatively short lived as a radical or part of a radical. The decomposition of the phenylmercury compounds gave diphenylmercury in nearly the yield corresponding to the equations (6) and (7), suggesting that decomposition may begin in this way with disproportionation.

$$(PhHgN)S_7 \longrightarrow HgPh_2 + Hg(NS_7)_2 \qquad (6)$$

$$1,4\text{-}(PhHgN)_2S_6 \longrightarrow HgPh_2 + \text{`}HgN_2S_6\text{'} \qquad (7)$$

The material balance based on identified products was satisfactory except in the case of the inorganic mercury derivative of 1,4-$(HN)_2S_6$, from which *ca.* 24% of the nitrogen was lost, perhaps because elemental nitrogen had been formed at points of local high temperature in the decomposing mass.

EXPERIMENTAL

Materials.—Azathianes of >99% purity were prepared by published methods.[8,11] Mercury(II) acetate (B.D.H.),

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[9] A. J. Banister, *Nature (Phys. Sci)*, 1972, **237**, 92.

[10] H. G. Heal, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 375.

[11] H. G. Heal and J. Kane, *Inorg. Synth.*, 1968, **11**, 184.

methylmercury acetate (Alfa Inorganics), and phenylmercury acetate (B.D.H.) were used. Methanol was of AnalaR grade, not specially dried. Carbon disulphide was distilled under nitrogen from P_2O_5 immediately before use. Diethyl ether was distilled under nitrogen from lithium tetrahydridoaluminate immediately before use.

Preparation of Mercury and Organomercury Derivatives.—All preparations involved between 0.5 and 10 mmol of reagents. The azathianes were used as 0.3—0.7% solutions in methanol, and the mercury compounds added either as solids or as 2% solutions in methanol, under dried White Spot nitrogen and with magnetic stirring. Separation of precipitates at low temperatures was made under nitrogen, sometimes with a cold-jacketed sintered-glass funnel (porosity 3) and sometimes with a M.S.E. 18 refrigerated centrifuge.

Decomposition Reactions.—The compound (*ca.* 1 g) to be decomposed was freshly prepared as described above, washed with methanol and diethyl ether at 0 °C, and pumped dry at 0 °C in a diffusion-pump vacuum. It was then allowed to stand in dull daylight at room temperature in a closed glass bulb under dry nitrogen [except for $(PhHgN)S_7$, see Table 2]. The decomposed sample was Soxhlet extracted with CS_2 (20 cm^3) until the refluxing liquid became colourless. The black solid left in the Soxhlet thimble was identified in all cases as HgS by elemental analysis. The i.r. spectrum of the CS_2 extract did not, in any of the four cases, contain any bands which could be attributed to known sulphur nitrides or diphenylmercury. The CS_2 extract was concentrated *in vacuo* to 4 cm^3. In three cases some solid separated, identified as S_4N_4 [from the $(HN)_2S_6$ derivatives] or $(S_7N)_2S_x$ [from $(PhHgN)S_7$]. The solution was subjected to molecular-exclusion chromatography on polystyrene beads (Bio Beads S-X8, from Bio-Rad Laboratories, Richmond, California), eluting with CS_2. A Whatman precision column 1 m × 15 mm was employed which had been calibrated with S_8, $S_{16}N_2$, and polystyrene standards. It had *ca.* 1 400 theoretical plates. Fractions (2 cm^3) were collected and their contents determined by evaporation and weighing, followed by i.r. and elemental analysis.

A Varian HR 100 instrument was used for the n.m.r. spectrum, with tetramethylsilane as internal standard.

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