J. inorg. nucl. Chem., 1974, Vol. 36, pp. 950–951. Pergamon Press. Printed in Great Britain.

Sulphur (N-phenylmercury) imides as reagents for synthesis

(*Received* 20 *April* 1973)

THE HYDROGEN atoms of the cyclic sulphur imides $S_{8-x}(NH)_x$ can be replaced by various metals[1–4]. Some of the resulting metal derivatives have possibilities as reagents for the synthesis of compounds containing sulphur–nitrogen rings. Such reactions have been little studied, though a few are known. For example, $S_7N^-Li^+$ gives S_7NCH_3 with methyl iodide[2], while $Hg_5(NS)_8$ (obtained from $S_4(NH)_4$ and mercury (II)) reacts with S_2Cl_2 to give S_4N_2[4]. The mercury derivatives should be particularly useful reagents, because the "*b*" or "soft acid" character of mercury ought to favour substitutions of the type

$$-MX + -HgNS_7 \rightarrow -MNS_7 + -HgX$$
$$(X = Cl, Br, I).$$

Unfortunately, however, $Hg(S_7N)_2$[5] and $Hg_2(S_7N)_2$[6], also corresponding mercury derivatives of the hexasulphur diimides[7], decompose rapidly at room temperature. We now report that the previously undescribed phenylmercury derivatives are relatively stable, reactive, and convenient for use in many syntheses.

Heptasulphur (N-phenylmercury) imide, $S_7NHgC_6H_5$, (I), precipitates quantitatively as a buff powder when phenylmercury acetate is added to a solution of heptasulphur imide in methanol. It is stable for hours at room temperature. In carbon disulphide (in which it is moderately soluble) it reacts quickly at room temperature with various covalent halides MX_n, precipitating C_6H_5HgX and leaving in solution compounds with S_7N ligands attached to M. For example, SCl_2 and S_2Cl_2 gave the known[8, 9] compounds $(S_7N)_2S$ and $(S_7N)_2S_2$ respectively. With $(CH_3)_3SnCl$, the new compound $S_7NSn(CH_3)_3$ was formed. With BCl_3 in appropriate mole ratios, (I) gave the known[10] S_7NBCl_2 and the new compounds $(S_7N)_2BCl$ and $(S_7N)_3B$. Reaction has also been noted with HCl, $SiCl_4$, $GeCl_4$, $SnCl_4$, $(C_2H_5)_3PbCl$, $(C_6H_5)_2PCl$, CH_3COCl and C_6H_5COCl.

With BBr_3, steric hindrance in the transition state seemed to prevent total replacement of halogen. Only two Br atoms could be replaced, though $(S_7N)_3B$ does exist and the "*b*" character of mercury would lead one to expect a more favourable ΔG for the replacement of the third Br than for Cl. Probably again for steric reasons, (I) did not react with $(C_6H_5)_3SnCl$. With two of the halides tested, CH_3I and CCl_3SCl, (I) failed to react although there is no obvious steric hindrance.

(I) is easier to make and handle than other known metal derivatives of heptasulphur imide. Since it is obtained in pure, weighable form, and is soluble in CS_2, the stiochiometry of its reactions is more easily controlled than with, for example, $S_7N^-Li^+$ or S_7NMgI[1]. Subject to the limitations on reactivity just mentioned, it should form a convenient starting point for the preparation of many new compounds containing S_7N rings.

In preliminary experiments, we have found that the bis(N-phenylmercury) derivatives of the hexasulphur diimides[11] resemble (I) in properties and stability. These compounds promise to be useful in the synthesis of new fused-ring and cage sulphur nitrides[9].

EXPERIMENTAL

Heptasulphur (N-phenylmercury)imide, $S_7NHgC_6H_5$, (I)

To a solution of 5 m-mole of >98 per cent heptasulphur imide[11] in 200 ml AnalaR methanol (not specially dried) 5 m-mol of solid phenylmercury acetate were added with stirring. The resulting buff precipitate was filtered, washed with methanol and then hexane, and freed from solvent *in vacuo*. Found: S 43·7; N 2·4; C 14·0; H 1·0; Hg 38·0 per cent; molecular weight (Mechrolab vapour-pressure osmometer, CS_2 solution) 512. $S_7NHgC_6H_5$ requires S 43·4; N 2·7; C14·0; H 1·0; Hg 38·9 per cent; mol.wt. 516. Yield almost quantitative.

The compound developed an orange colour after a few hours at room temperature, but could be stored indefinitely at −78°C without change. On heating it sintered and decomposed at about 80°C.

Its solubility in CS_2 at 17°C was approximately 1·1 g per 100 g solvent.

The i.r. spectrum in CS_2 showed a broad S–N stretch [12] at 790 cm^{-1} (resolved in a KBr disk into bands at 775 and 790 cm^{-1}), and also phenyl vibrations at 730 and 690 cm^{-1}.

Reactions of (I) with halides

Liquid halides were freed from dissolved hydrogen halide by distillation.

Typically, a solution of *ca.* 2 m-mol of (I) in 100 ml CS_2 (freshly distilled from phosphorus (V) oxide) was added gradually to a vigorously-stirred solution of the stiochiometric amount of the halide in the same solvent. Reaction was shown by the formation of a silky precipitate of the phenylmercury halide, identified by i.r., m.p. and elemental analysis. After filtration under nitrogen, the filtrate was evaporated to dryness *in vacuo*, and the product extracted into a few ml of CS_2, which left undissolved a little more phenylmercury halide. Yields of phenylmercury halide were nearly quantitative. (Solubilities of C_6H_5HgX in CS_2 at 17°C were found to be 0·14, 0·05 and 0·12 g per 100 g CS_2 for X = Cl, Br, I respectively.)

In the product solutions $(S_7N)_2S$ and $(S_7N)_2S_2$ were identified by i.r.[9]. $(S_7N)_2BCl$, $(S_7N)_3B$, S_7NBBr_2 and $(S_7N)_2BBr$ were identified by i.r. and by quantitative hydrolysis to S_7NH, H_3BO_3 and HCl or HBr, as described in an earlier publication[10]. Crystalline monopyridine adducts of all these boron compounds were isolated[10] and gave satisfactory elemental analyses.

$S_7NSn(CH_3)_3$ was obtained as small orange crystals (dec. at 50°C) by evaporation of the product solution from (I) and $(CH_3)_3SnCl$. Found: S 55·8; N 3·3; C 9·1; H 2·0. $S_7NSn(CH_3)_3$ requires S 55·8; N 3·5; C 9·0; H 2·3.

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J. inorg. nucl. Chem., 1974, Vol. 36, p. 951. Pergamon Press. Printed in Great Britain.

ERRATUM

J. C. BARNES: Studies of some complexes of copper(II) halides with organic donors. *J. inorg. nucl. Chem.* **31**, 95 (1969).

FURTHER work has shown that the enthalpies of decomposition for three of the compounds are incorrect. The error was introduced by a temporary instrumental malfunction. The correct data are as follows.

Compound	Temperature range T(K)	ΔH(kcal mol^{-1})
$(CuCl_2)_3 . 2DX$	453–512	$34{\cdot}3 \pm 0{\cdot}6$
$(CuBr_2)_3 . 2DX$	368–460	$30{\cdot}1 \pm 0{\cdot}5$
$CuBr_2$	470–535	$10{\cdot}3 \pm 0{\cdot}6$

This revision removes two anomalies in the data. The enthalpy for the decomposition of $CuBr_2$ into CuBr now agrees with the literature value[1] and the enthalpy of removal of one mole of dioxan is now within the range found for dioxan complexes of other metal ions[2, 3].

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