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REACTIONS OF SILYLPHOSPHINE WITH AMINES AND IMINES

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Three methods have been commonly used for the preparation of silyl compounds containing silicon-nitrogen bonds: reaction of a silyl halide with an amine (1), cleavage of trisilylamine by a protonic acid (2), and reaction of a silyl halide with a silver salt (3), according to equations 1-3 respectively.

$$SiH_3X + 2HNRR' \longrightarrow SiH_3NRR' + RR'N\overset{+}{H}_2\overset{-}{X} \qquad 1.$$

$$(SiH_3)_3N + 4HY \longrightarrow 3SiH_3Y + N\overset{+}{H}_4\overset{-}{Y} \qquad 2.$$

$$SiH_3X + AgY \longrightarrow SiH_3Y + AgX \qquad 3.$$

Reaction 1 requires the salt $RR'N\overset{+}{H}_2\overset{-}{X}$ to have a low dissociation pressure, so that RR'NH must be a fairly strong base. Reaction 2 requires HY to be a strong acid and reaction 3 requires the silver salt AgY to be chemically stable. In addition to these restrictions, each of these methods has the further disadvantage that a solid is also produced in the reaction; this may act as an initiator of decomposition reactions, either because of the absorption of traces of base, as in reactions 1 and 2, or because of local overheating, as in reaction 3.

We report now, as a convenient alternative which avoids most of the disadvantages of reactions 1-3, the reactions of silylphosphine SiH_3PH_2 with a number of amines and imines, which occur in many cases in accordance with equation 4.

$$SiH_3PH_2 + HNRR' \longrightarrow SiH_3NRR' + PH_3 \qquad 4.$$

Both dimethylamine and diethylamine react with silylphosphine in the vapour phase to give essentially quantitative yields of the corresponding silylamine. Similar gas-phase reactions with cyanic acid and thiocyanic acid give good yields (> 80%) of silyl_iso_cyanate and silyl_iso_thiocyanate respectively. Silylphosphine reacts slowly with a dilute solution of hydrazoic acid in di-_n_-butyl ether to yield silyl azide. Reaction of silylphosphine with solid cyanamide at 0°C yields disilylcarbodiimide, $SiH_3NCNSiH_3$ quantitatively; no evidence was found for the formation of any disilylcyanamide, $(SiH_3)_2N{\cdot}CN$.

Methylamine did not react with silylphosphine in the gas phase, but on condensation the mixture yielded an involatile white solid, treatment of which with hydrogen chloride gave mono-, di- and trichlorosilanes, indicating the formation of an extensively cross-linked polymer. Trimethylamine did not react with silylphosphine either in the vapour phase or in chloroform solution, in which the nmr spectrum was that of the two unperturbed reactants.

Attempts were then made to apply this method to the preparation of some hitherto elusive silicon-nitrogen compounds. Aziridine caused extensive decomposition in the gas phase: the resultant white solid was involatile and with hydrogen chloride gave SiH_3Cl, SiH_2Cl_2 and $SiHCl_3$. Thionylimide (HNSO) vapour, prepared _in situ_ (4), did not react with silylphosphine, but on condensation formed a solid polymer apparently basic enough to decompose the silylphosphine. N-methylhydroxylamine and O,N-dimethylhydroxylamine cause complete decomposition of silylphosphine in the gase phase: they also decompose silyl iodide, and this may be an example of the α-effect (5), with the enhanced nucleophile reactivity of the hydroxylamines arising from the unshared electron pairs on the oxygen atom.

Finally, the reactions of a number of similar silyl compounds with cyanamide were investigated to test the generality of this type of reaction. Whereas both silylphosphine and disilyl sulphide react to give excellent yields of disilylcarbodiimide, reactions 5 and 6,

$$2SiH_3PH_2 + NH_2CN \longrightarrow (SiH_3N)_2C + 2PH_3 \qquad 5.$$

$$(SiH_3)_2S + NH_2CN \longrightarrow (SiH_3N)_2C + H_2S \qquad 6.$$

trisilylphosphine gives a rather poor yield of the carbodiimide, accompanied by some decomposition, and silyldimethylphosphine, $SiH_3P(CH_3)_2$ is completely decomposed, with all the silicon appearing as monosilane. While no explanation for these differences can be offered at present, it seems probable that this reaction can be applied to most of those $HN<$ species which are weak acids or weak bases. We have previously observed (6) the similar reaction of silylphosphine with alcohols.

EXPERIMENTAL

Thionylimide was prepared by vapour phase reaction of thionyl chloride and ammonia (4); the hydrazoic acid solution was prepared by treatment of aqueous sodium azide with concentrated sulphuric acid, followed by extraction into di-*n*-butyl ether and drying with calcium chloride. All reactions were monitored by infrared spectroscopy; those in the vapour phase were monitored without condensation of reaction mixtures. Known volatile compounds were identified by their distillation properties in the vacuum system, and by their ir and nmr spectra.

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