Pentaborane(9)-catalysed Condensation of Silylamines

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Summary Trisilylamine and $(SiH_3)_2NMe$ undergo condensation reactions catalysed by B_5H_9 to form $(SiH_3)_2NSiH_2N(SiH_3)_2$ (I) and $SiH_3(Me)NSiH_2N(Me)SiH_3$ (II), *respectively*, in high yields.

TRISILYLAMINE, $(SiH_3)_3N$, and *N*-methyldisilazane, $(SiH_3)_2NMe$, undergo condensation in the liquid phase in the presence of B_5H_9 to yield two new compounds, $(SiH_3)_2NSiH_2N(SiH_3)_2$ (I) and $SiH_3(Me)NSiH_2N(Me)SiH_3$ (II). Although base-promoted condensation reactions are well known,[1] this appears to be the first well documented example of an acid-catalysed condensation which results in volatile, tractable products.

In a typical reaction, $(SiH_3)_3N$ (3·00 mmol) and B_5H_9 (*ca. 0·1 mmol*) were set aside together at 45°. After 5 days, 13% of the $(SiH_3)_3N$ had undergone condensation with the quantitative elimination of SiH_4 and formation of (I) according to equation (1). The product (I) was purified

$$2(SiH_3)_3N \rightarrow (SiH_3)_2NSiH_2N(SiH_3)_2 + SiH_4 \quad .. \quad (1)$$

by fractional condensation (>95% yield): m.p. $<-170°$; vapour pressure at 0°, 2·4 mmHg; ΔH_{vap} 9·50 kcal mol^{-1}; $\Delta S_{\text{vap}} = 23{\cdot}6$ cal mol^{-1} deg^{-1}. Analogously, $(SiH_3)_2NMe$ in the presence of B_5H_9 yields quantitatively the expected SiH_4 and (II) in 16 h at 25 °C, with the consumption of 33% of the $(SiH_3)_2NMe$. (II) has m.p. $<-150°$; vapour pressure at 0°, 5·0 mmHg; ΔH_{vap} 9·94 kcal mol^{-1}; $\Delta S_{\text{vap}} =$ 26·3 cal mol^{-1} deg^{-1}. It is important to note that heating of $(SiH_3)_3N$ or $(SiH_3)_2NMe$ under similar conditions in the absence of B_5H_9 results in no detectable condensation products or SiH_4.

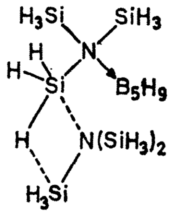
The 100 MHz ^1H n.m.r. spectra exhibit broad singlet resonances which are readily assigned as follows:[2] δ (relative to Me_4Si): (I); 4·75 (2H, SiH_2) and 4·43 (12H, SiH_3) p.p.m.; (II); δ 4·55 (2H, SiH_2), 2·58 (6H, Me), and 4·38 (6H, SiH_3) p.p.m., and the i.r. spectra show characteristic Si–H absorptions[3] for (I) and Si–H and C–H for absorptions for (II). In general the i.r. spectra are similar to those of the parents, differing primarily in peak shapes and intensities. No N–H absorptions are evident. The molecular weights and compound stoicheiometries are established from the mass spectra; (I) and (II) show highest-mass peaks at *m/e* 185 and 153, attributable to $Si_5N_2H_{14}^+$ and $C_2Si_3N_2H_{14}^+$ molecular ions, respectively.

(I) and (II) react rapidly with HBr, resulting in quantitative degradation according to equations (2) and (3).

$$(SiH_3)_2NSiH_2N(SiH_3)_2 + 8HBr \rightarrow 2NH_4Br + SiH_2Br_2 + 4SiH_3Br \quad .. \quad (2)$$

$$SiH_3(CH_3)NSiH_2N(CH_3)SiH_3 + 6HBr \rightarrow 2CH_3NH_3Br + SiH_2Br_2 + 2SiH_3Br \quad .. \quad (3)$$

The role of the B_5H_9 catalyst in promoting condensation and formation of new silicon–nitrogen bonds requires further study. However, it is possible that B_5H_9 with the weakly basic silylamines yields an intermediate in which silyl Si–H bonds are weakened and silyl-group Lewis acidity is increased. Co-ordination of this intermediate with another silylamine molecule and the elimination of SiH_4 *via* a 4-centre transition state, analogous to that reported initially by MacDiarmid,[4] could occur.



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