# Carbamylsilanes: a New Class of Organosilicon Compound

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*Summary* The preparation and properties of *NN*-diethylcarbamylsilane are reported.

IN conjunction with other work it became necessary for us to develop a synthesis of carbamylsilanes. The ready decarbonylation of silanecarboxylic acids and silanecarboxylates[1] appeared to rule out their conversion into carbamylsilanes by the methods usually used to prepare amides.[2] In the course of an attempt to convert methyl trimethylsilanecarboxylate[3] into an amide, each of the following reactions was shown to occur independently at 90°.

$$\underset{(1)}{Me_3SiCO_2Me} + Et_2NH \xrightarrow[\text{slow}]{} \underset{(2)}{Me_3SiOMe} + \underset{(3)}{HCO{\cdot}NEt_2} + \underset{(4)\ \text{(trace)}}{HCO_2Me}$$

$$\underset{(5)}{Me_3SiNEt_2} + \underset{(4)}{HCO_2Me} \xrightarrow{\text{slow}} \underset{(2)}{Me_3SiOMe} + \underset{(3)}{HCO{\cdot}NEt_2}$$

$$(4) + HNEt_2 \xrightarrow{\text{fast}} MeOH + (3)$$

$$(5) + MeOH \xrightarrow{\text{fast}} HNEt_2 + (2)$$

$$(1) + MeOH \xrightarrow{\text{slow}} (2) + (4)$$

*NN*-Diethylcarbamylsilane, (6) (b.p. 50°/5 mm.) was prepared by the addition of hexamethyldisilthiane to bis-*NN*-diethylcarbamylmercury[4] in ether.

$$(Me_3Si)_2S + Hg(CO{\cdot}NEt_2)_2 \rightarrow Me_3SiCO{\cdot}NEt_2\ (6)$$

It was found that (6) was thermally more stable than the ester (1) and showed only slight decarbonylation in 2 hr. at 250°. However, it was more acid-sensitive than (1) and underwent rapid, exothermic decarbonylation when treated with 10% sulphuric acid. Decarbonylation also occurred when (6) was

$$(6) \xrightarrow[H^+]{} (Me_3Si)_2O + CO + Et_2NH_2^+$$

treated with lithium amide, though with weaker bases no decarbonylation was observed and instead rapid cleavage of the Si–CO bond occurred.

$$(6) + NEt_2^- \rightarrow Me_3SiNEt_2 + CO + NEt_2^-$$

$$\begin{tikzcd} (6) + H_2O \arrow[r, "\text{v. fast}", "(\frac{1}{2}\text{ hr. }25^\circ)"'] & Me_3SiOH + HCO{\cdot}NEt_2 \arrow[d, "\text{slow}"] \\ & (Me_3Si)_2O \end{tikzcd}$$

$$(6) + HNEt_2 \xrightarrow{\text{fast}} Me_3SiNEt_2 + HCO{\cdot}NEt_2$$

The i.r. carbonyl group absorption of (6) (1560 cm.$^{-1}$) showed a bathochromic shift of approximately 60 cm.$^{-1}$ relative to that of the carbon analogue *NN*-diethylpivalamide (7). The u.v. absorption of (6) in cyclohexane occurred at 218 nm. (5·69 ev, $\epsilon$ 5300) and 264 nm. (4·70 ev, $\epsilon$ 270) while that of (7) was 201 nm (6·17 ev, $\epsilon$ 9200). The absorption due to the $n\rightarrow\pi^*$ transition of most amides is not observed, because of the proximity of the more intense $\pi\rightarrow\pi^*$ transition,[5] and in (7) it must be below 220 nm. (5·64 ev).

There has been much discussion on the origin of the analogous bathochromic shift in the position of the $n\rightarrow\pi^*$ transition in acylsilanes.[3,6] An approximate energy for the $\pi^*$ orbitals in amides (2·5 ev) and ketones (5·1 ev) can be calculated from the ionization potentials[6d,7] and the energy of the $n\rightarrow\pi^*$ transitions.[6d] Since the energy of the 3*d*-orbitals of silicon has been estimated[6e] to be between 1·6 and 2·6 ev, $d\pi$–$p\pi$ bonding should be much more important in carbamylsilanes than in acylsilanes. Thus the comparatively large bathochromic shift (0·5 ev) observed in the $\pi\rightarrow\pi^*$ transition of (6) relative to (7) may result partially from a lowering in energy of the $\pi^*$-orbital of (6) as a result of $d\pi$–$p\pi$ bonding.

The temperature-dependent $^1$H n.m.r. spectra of (6) and (7) showed typical restricted rotation about the N–CO bond.[8] A higher temperature was required to produce the same rate of exchange in (6) (coalescence, +55—60°) as in (7) (coalescence, −12°).

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