

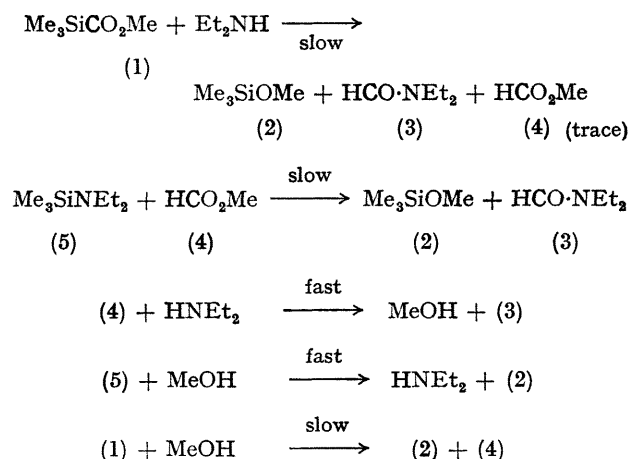
Carbamylsilanes: a New Class of Organosilicon Compound

By G. J. D. PEDDLE* and R. W. WALSHINGHAM

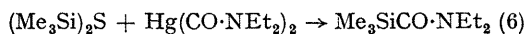
(Department of Chemistry, University of Alberta, Edmonton, Canada)

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

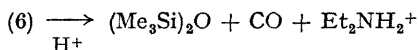
In conjunction with other work it became necessary for us to develop a synthesis of carbamylsilanes. The ready decarbonylation of silanecarboxylic acids and silanecarboxylates¹ appeared to rule out their conversion into carbamylsilanes by the methods usually used to prepare amides.² In the course of an attempt to convert methyl trimethylsilanecarboxylate³ into an amide, each of the following reactions was shown to occur independently at 90°.



NN-Diethylcarbamylsilane, (6) (b.p. 50°/5 mm.) was prepared by the addition of hexamethyldisilthiane to bis-*NN*-diethylcarbamylmercury⁴ in ether.

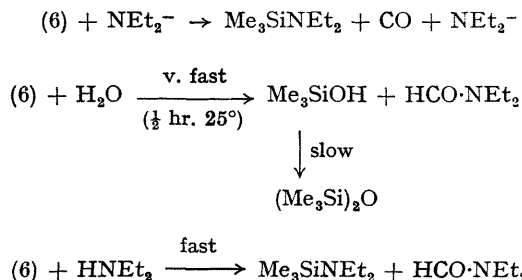


It was found that (6) was thermally more stable than the ester (1) and showed only slight decarbonylation in 2 hr. at 250°. However, it was more acid-sensitive than (1) and underwent rapid, exothermic decarbonylation when treated with 10% sulphuric acid. Decarbonylation also occurred when (6) was



treated with lithium amide, though with weaker bases no

decarbonylation was observed and instead rapid cleavage of the Si-CO bond occurred.



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, ϵ 5300) and 264 nm. (4.70 ev, ϵ 270) while that of (7) was 201 nm (6.17 ev, ϵ 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 π^* 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 π^* -orbital of (6) as a result of $d\pi-p\pi$ bonding.

The temperature-dependent ¹H 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°).

This research was supported by the National Research Council of Canada.

(Received, February 28th, 1969; Com. 284.)

¹ A. G. Brook and H. Gilman, *J. Amer. Chem. Soc.*, 1955, **77**, 2322; A. G. Brook, *ibid.*, 1955, **77**, 4827; 1957, **79**, 971; H. Gilman and W. J. Trepka, *J. Org. Chem.*, 1960, **25**, 2201.

² A. I. Vogel, "Practical Organic Chemistry," 3rd edn., Wiley, New York, 1956, p. 401.

³ G. J. D. Peddle and R. W. Walsingham, *J. Amer. Chem. Soc.*, in the press.

⁴ U. Schöllkopf and F. Gerhart, *Angew. Chem. Internat. Edn.*, 1966, **5**, 664.

⁵ E. B. Nielsen and J. A. Schellman, *J. Phys. Chem.*, 1967, **71**, 2297.

⁶ (a) A. G. Brook, *Adv. Organometallic Chem.*, 1969, **7**, in the press. (b) H. Bock, A. Alt, and H. Seidl, *J. Amer. Chem. Soc.*, 1969, **91**, 355; (c) P. A. Jones and R. West, *ibid.*, 1968, **90**, 6978; (d) G. J. D. Peddle, *J. Organometallic Chem.*, 1968, **14**, 139; (e) F. Agolini, S. Kleimenko, J. G. Cszimadia, and K. Yates, *Spectrochim. Acta*, 1968, **24**, A, 169.

⁷ R. W. Kiser, "Introduction to Mass Spectrometry and its Applications," Prentice-Hall, Englewood Cliffs, New Jersey, 1965, pp. 162–203; 308–318.

⁸ R. C. Neuman and V. Jonas, *J. Amer. Chem. Soc.*, 1968, **90**, 1970.