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Regiospecific Addition of 1,1-Dimethylsilaethene to a Silicon-Oxygen Bond

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Summary The reaction of 1,1-dimethylsilaethene with Me_3SiOMe provides unequivocal evidence for regiospecific addition of $Me_2Si=CH_2$ across the silicon-oxygen bond.

The thermal decomposition of 1,1-dimethylsilacyclobutane (DMSCB) is a ubiquitous route¹ to the generation of the reactive intermediate 1,1-dimethylsilaethene (SE). Flowers and Gusel'nikov² reported that, during the copyrolysis of

DMSCB and MeOH, the expected dimerisation of SE to form 1,1,3,3-tetramethyl-1,3-disilacyclobutane was completely suppressed owing to the concomitant formation of Me₃SiOMe. Sommer and his co-workers³ similarly demonstrated that SE reacts with EtOH and Me₃CCH₂OH rapidly to form the corresponding trimethylsilyl ether, Me₃SiOR, where R = Et or Me_3CCH_2 , respectively.

In a preliminary quantitative study of the gas-phase decomposition kinetics of DMSCB in the presence of MeOH the formation of Me_sSiOMe was unequivocally confirmed (reaction 1).[†]

$$Me_{2}Si=CH_{2}+MeOH \rightarrow Me_{3}SiOMe$$
(1)
(1)

$$Me_2Si=CH_2 + Me_3SiOMe \rightarrow Me_3SiCH_2SiMe_2OMe$$
 (2)
(2)

However, even at the early stages of the reaction (< 5%conversion) the observed silicon mass deficit was accounted for by a rapid secondary addition (reaction 2). Me₃SiOMe is thermally stable under these conditions. Product (2)



FIGURE 1. The ¹H n.m.r. spectrum of (2). Resonances occur at δ 3.40 (3H, s, MeO); 0.12 (6H, s, SiMe_); 0.04 (9H, s, SiMe_3); and -0.14 (2H, s, CH_2). Me_3Si external reference. Spectra were obtained at 100 MHz in CDCl₃ solvent.

G.l.c.-mass spectra of (2) were obtained using a Finnigan 4000 mass spectrometer interfaced to an INCOS data system using a 10 m OV1 glass capillary column. The corresponding mass spectrum is shown in Figure 2. The fragmentation pattern exhibits a base peak at an m/e value corresponding to $[M-CH_3]^+$, which is the highest mass number normally observed for heavily substituted alkylsilanes.⁵



FIGURE 2. Mass-spectral fragmentation pattern (70 eV) of (2).

On pyrolysis of DMSCB with added Me₃SiOMe at 681 K the adduct (2) was formed as a direct result of reaction (2). No reaction occurred, apart from the formation of the normal products,² namely ethene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane, on pyrolysis of DMSCB in the presence of dimethyl ether.

In conclusion, the reaction of SE with MeOH is more complex than proposed hitherto.² Silaethene derivatives are able to add, presumably via a concerted mechanism,³ across a silicon-oxygen bond in a regiospecific manner. This confirms an earlier observation⁶ that SE inserts into the silicon-oxygen bond in hexamethylcyclotrisiloxane. In the present example SE has been shown to react with Me₃SiOMe to yield Me₃SiCH₂SiMe₂OMe. The latter product (2) is a member of the homologous series Me₃Si[CH₂SiMe₂]_nOMe and it is expected that further addition would lead to higher homologues.

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† Trimethylsilyl methyl ether, Me₃SiOMe, was identified by comparison of ¹H n.m.r. and mass spectral data with those of an authentic sample.

- ¹ L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, 1979, **79**, 529. ² M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 1968, 419.

- ^a R. D. Bush, C. M. Golino, G. D. Homer, and L. H. Sommer, J. Organomet. Chem., 1974, 80, 37.
 ⁴ R. Damrauer, Organomet. Chem. Rev., Sect. A, 1972, 8, 67.
 ⁵ H.-P. Schuchmann, A. Ritter, and C. Von Sonntag, J. Organomet. Chem., 1978, 148, 213; F. Aulinger and W. Reerink, Z. Anal. Chem., 1963, 197, 24
- ⁶ C. M. Golino, R. D. Bush, P. On, and L. H. Sommer, J. Am. Chem. Soc., 1975, 97, 1957.