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 route[1] to the generation of the reactive intermediate 1,1-dimethylsilaethene (SE). Flowers and Gusel'nikov[2] 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 Me_3SiOMe. Sommer and his co-workers[3] similarly demonstrated that SE reacts with EtOH and Me_3CCH_2OH rapidly to form the corresponding trimethylsilyl ether, Me_3SiOR, 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_3SiOMe was unequivocally confirmed (reaction 1).†

$$Me_2Si{=}CH_2 + MeOH \rightarrow \underset{\mathbf{(1)}}{Me_3SiOMe} \qquad (1)$$

$$Me_2Si{=}CH_2 + Me_3SiOMe \rightarrow \underset{\mathbf{(2)}}{Me_3SiCH_2SiMe_2OMe} \qquad (2)$$

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). Me_3SiOMe is thermally stable under these conditions. Product (**2**) was isolated, by preparative g.l.c., from accumulated products resulting from several pyrolyses of DMSCB (2·27 kN m^{-2}) in the presence of MeOH (0·267 kN m^{-2}) at 681 K. The ^1H n.m.r. spectrum of the product, shown in Figure 1, is entirely consistent with product (**2**) arising from the addition of SE to a silicon–oxygen bond. The proton chemical shifts are well established[4] for silicon compounds.

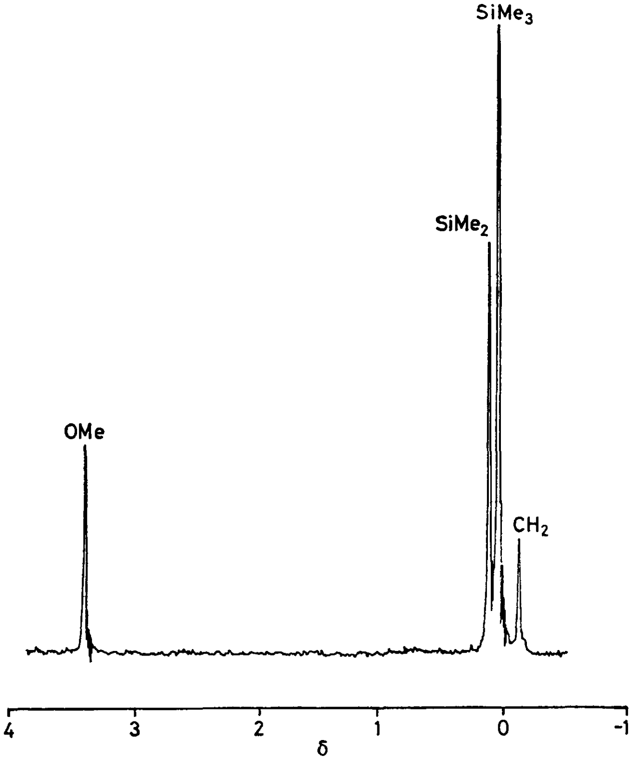

FIGURE 1. The ^1H n.m.r. spectrum of (**2**). Resonances occur at δ 3·40 (3H, s, MeO); 0·12 (6H, s, $SiMe_2$); 0·04 (9H, s, $SiMe_3$); and −0·14 (2H, s, CH_2). Me_4Si external reference. Spectra were obtained at 100 MHz in $CDCl_3$ solvent.

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]

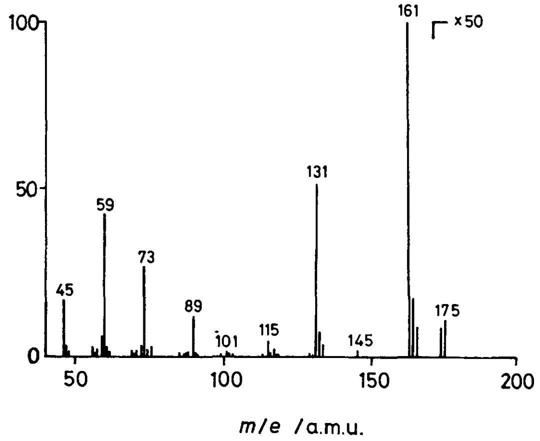

FIGURE 2. Mass-spectral fragmentation pattern (70 eV) of (**2**).

On pyrolysis of DMSCB with added Me_3SiOMe 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 observation[6] that SE inserts into the silicon–oxygen bond in hexamethylcyclotrisiloxane. In the present example SE has been shown to react with Me_3SiOMe to yield $Me_3SiCH_2SiMe_2OMe$. The latter product (**2**) is a member of the homologous series $Me_3Si[CH_2SiMe_2]_nOMe$ and it is expected that further addition would lead to higher homologues.

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† Trimethylsilyl methyl ether, Me_3SiOMe, was identified by comparison of ^1H n.m.r. and mass spectral data with those of an authentic sample.

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