Evidence for the Formation of Diethylsilaneselone: A Reactive Intermediate with a Silicon–Selenium Double Bond

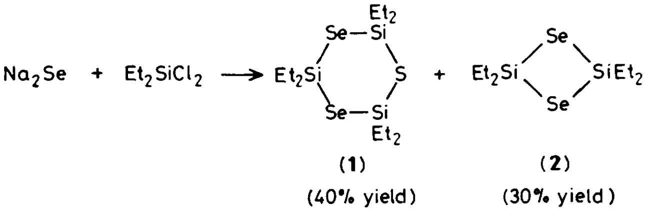
Dennis P. Thompson and Philip Boudjouk*

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105, U.S.A.

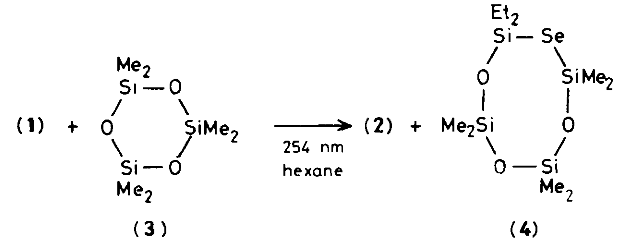
Photolysis of hexaethylcyclotrisilaselenane in the presence of hexamethylcyclotrisiloxane produces tetraethylcyclodisilaselenane and 4,4,6,6,8,8-hexamethyl-2,2-diethyl-1,5,7,3,2,4,6,8-trioxatetrasilaselenocane; *diethylsilaneselone is postulated as an intermediate.*

The chemistry of reactive intermediates with multiple bonds to silicon has been sufficiently investigated to justify a number of extensive reviews.[1] Such species as silenes ($R_2Si{=}CR_2$), disilenes ($R_2Si{=}SiR_2$), silanimines ($R_2Si{=}NR$), silaphosphinimines ($R_2Si{=}PR$), silanones ($R_2Si{=}O$), and silanethiones ($R_2Si{=}S$) have been studied. To our knowledge, there are no reports involving the existence of silaneselones ($R_2Si{=}Se$). In this communication we report chemical evidence for the first member of this family, diethylsilaneselone ($Et_2Si{=}Se$).[2]

Recently, bis(trialkylsilyl)selenides and tellurides were prepared in high yield by the reactions of chlorosilanes with Li_2Se and Li_2Te generated *in situ* from the chalcogen and lithium triethylborohydride in tetrahydrofuran (THF).[3] Using



Scheme 1



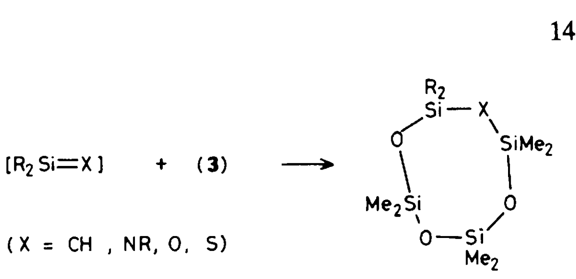
Scheme 2

Na_2Se prepared by a new method[4] and Et_2SiCl_2, we were able to prepare the new heterocycles (**1**) and (**2**) in isolated yields of 40 and 30% respectively (Scheme 1).†

Room temperature photolysis (254 nm) of a hexane solution of (**1**) for 18 h in the presence of an eight-fold excess of hexamethylcyclotrisiloxane produced (**2**), and 4,4,6,6,8,8-hexamethyl-2,2-diethyl-1,5,7,2,4,6,8,3-trioxatetrasilaselenocane (**4**) in 70 and 23% yields respectively (Scheme 2). These products are best explained in terms of the extrusion of $Et_2Si{=}Se$ from (**1**) and the insertion of this new reactive intermediate into the cyclotrisiloxane to form (**4**).

Hexamethylcyclotrisiloxane (**3**) has been used to trap a variety of reactive intermediates with silicon–heteroatom double bonds.[5] Such reactive intermediates undergo a two-atom insertion into a Si–O bond of the cyclotrisiloxane (Scheme 3).

Photolysis of (**1**) in hexane in the absence of (**3**) efficiently produces (**2**). After 18 h photolysis in the absence of a trap, (**1**) is completely consumed, producing (**2**) in >90% yield. The same result occurs when (**1**) is photolysed in an eight-fold excess of Et_3SiH, an efficient silylene trap, indicating that silylene formation is not an important pathway in the photochemical decomposition of (**1**).



Scheme 3

Financial support from the Air Force Office of Scientific Research (Grant Number 84-0008) is gratefully acknowledged. We thank Robert West and Gregory R. Gillete of the University of Wisconsin for the selenium-77 n.m.r. data.

Received, 28th November 1986; Com. 1689§

---

† *Spectral data for* (**1**): *m/z* 495 (M^+, 14.3%), 467 (M^+ − Et, 6.1%), 303 ($Et_3Si_2Se_2^+$, 100%); with appropriate isotope distribution; ^1H n.m.r. at 90 MHz (CCl_4); δ 1.05 (s, CH_2Me, signal begins to separate in C_6D_6); ^{13}C n.m.r. ($CDCl_3$), δ 13.4 ($-CH_2$), 7.6 (Me); ^{29}Si n.m.r. ($CDCl_3$, *vs.* Me_4Si), δ 25.7 p.p.m.; ^{77}Se n.m.r. ($CDCl_3$, *vs.* Me_2Se), δ −81.7 p.p.m.; *For* (**2**): *m/z* 332 (M^+, 27.1%), 303 (M^+ −29, 100%), with appropriate isotope distribution; ^1H n.m.r., 90 MHz (CCl_4), δ 1.00 (s, CH_2Me); ^{13}C n.m.r. ($CDCl_3$), δ 14.4 ($-CH_2$), 7.4 (Me); ^{29}Si n.m.r. ($CDCl_3$), δ 8.7 p.p.m.; ^{77}Se n.m.r. ($CDCl_3$), δ −99.9 p.p.m. Satisfactory elemental analyses were obtained. Yields were calculated assuming that 1 mol of $(Et_2SiSe)_3$ could produce 3 mol of $Et_2Si{=}Se$, which could then dimerize or insert into (**3**).

Spectral data for (**3**): *m/z* 388 (M^+, 2.3%), 373 (M^+ − Me, 9.7%), 359 (M^+ − Et, 100%), with appropriate isotope distribution; ^1H n.m.r., 300 MHz ($CDCl_3$), δ 1.05—0.8 (m, 10 H, CH_2Me), 0.5 (s, 6 H, $Se-SiMe_2$), 0.12 and 0.11 (2s, 12 H, $O-SiMe_2$); ^{13}C n.m.r. ($CDCl_3$), δ 11.74 (CH_2), 7 and 6.8 ($-CH_2CH_3$ and $Se-SiCH_3$), 9.1 and 8.8 ($O-SiCH_3$); ^{77}Se n.m.r. ($CDCl_3$) δ −138.1 p.p.m. Satisfactory elemental analyses were obtained.

References

1 G. Bertrand, G. Trinquier, and P. Mazerolles, *J. Organomet. Chem. Libr.*, 1981, **12**, 1; L. E. Gusel'nikov, and N. S. Namekin, *Chem. Rev.*, 1979, **79**, 529; A. H. Cowley, *Polyhedron*, 1984, **3**, 389; G. Raabe and J. Michl, *Chem. Rev.*, 1985, **85**, 419.

2 For a recent review on selenium chemistry see: 'The Chemistry of Organic Selenium and Tellurium Compounds,' vol. 1, eds S. Patai and Z. Rappoport, Wiley, Great Britain, 1986.

3 J. A. Gladysz, J. L. Hornby, and J. E. Garbe, *J. Org. Chem.*, 1978, **43**, 1204; M. R. Detty and M. D. Seidler, *ibid.*, 1982, **47**, 1354.

4 D. P. Thompson and P. Boudjouk, unpublished results.

5 R. D. Golino, P. O. Bush, and L. H. Sommer, *J. Am. Chem. Soc.*, 1975, **97**, 1957, 7371; H. Okinoshima and W. P. Weber, *J. Organomet. Chem.*, 1978, **149**, 279; D. R. Parker and L. H. Sommer, *J. Am. Chem. Soc.*, 1976, **98**, 618; L. H. Sommer and J. McLick, *J. Organomet. Chem.*, 1975, **101**, 171; H. S. Dilanjan Soysa and W. P. Weber, *J. Organomet. Chem.*, 1979, **165**, C1.

---

§ Revised manuscript received, 1 June 1987.