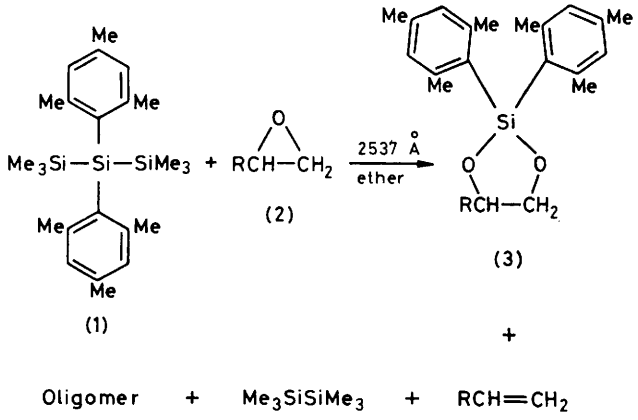
Reaction of Dimesitylsilylene with Epoxides. Silanone–Epoxide Adducts

By Wataru Ando,* Masayuki Ikeno, and Yoshitaka Hamada

(*Department of Chemistry, The University of Tsukuba, Niiharigun, Ibaraki* 305, *Japan*)

Summary Dimesitylsilylene, generated by photolysis of 2,2-dimesitylhexamethyltrisilane (**1**), reacts with epoxides to give dimesitylsilanone–epoxide adducts.

Recently, considerable interest has been focused on highly reactive unsaturated silicon intermediates.[1] However, since silanones show a tendency for cyclic oligomerization and insertion into the Si–O bond of, for example, hexamethylcyclotrisiloxane, dimethyldimethoxysilane, and 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane,[2] only limited information is available concerning the chemical behaviour of silanones towards organic substrates. We thought that studies of silanones with bulky substituents might be of interest, because the steric hindrance due to the substituents on the silicon atom might restrict the extent of cyclic oligomerization and lead to different behaviour from that of sterically less hindered silanones. Recently, it has been found that the reactions of silylene epoxides provide a useful method for silanone synthesis by olefin elimination.[3] We report here the first isolation of dimesitylsilanone–epoxide adducts in the reaction of the dimesitylsilylene intermediate† with epoxides.



In a typical experiment, an ethereal solution of (**1**) (0·5 mmol) and propylene oxide (10 mmol) was irradiated in a quartz tube with a low-pressure mercury lamp for 6 h. G.l.c. analysis of the reaction mixture showed the presence of 1,1-dimesityl-3-methyl-2,5-dioxa-1-silacyclopentane (**3b**) (16%), propene (65%), hexamethyldisilane (90%), and

---

† The photochemical extrusion of dimesitylsilylene from (**1**) on irradiation with a low-pressure mercury lamp was confirmed by trapping with triethylsilane.

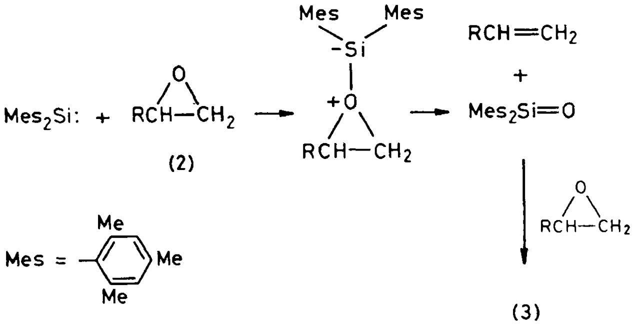
TABLE. Irradiation of (**1**) in the presence of epoxides (**2**).

Epoxide (**2**)	(**3**)[a]	Product and % yield Olefin	Disilane
a; R = H[b]	24		100
b; R = Me	16	65	90
c; R = Et	9	70	92
d; R = Ph	11	39	82

[a] Compounds (**3a**—**d**) were identified by comparison (n.m.r., i.r., and mass spectra) with authentic samples prepared by independent routes, and by elemental analysis. [b] The reaction was carried out at 0 °C.

oligomers of dimesitylsilanone. The results for several other epoxides are shown in the Table. However, irradiation of (**1**) in the presence of cyclohexene oxide gave cyclohexene (44%), but no dioxasilacyclopentane derivative. The variation in the yields of (**3**) may be due to the steric hindrance of the substituent R and steric effects may also explain the different behaviour of cyclohexene.

Compounds are presumably formed by the reaction of dimesitylsilanone with the epoxide (Scheme), and this provides the first example of silanone insertion into the C–O bond of an epoxide; the analogous reaction of a germanone has been reported, however.[4]



SCHEME

(*Received*, 1*st April* 1981; *Com.* 376.)

---

[1] L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, 1979, **79**, 529.

[2] H. Okinoshima and W. P. Weber, *J. Organomet. Chem.*, 1978, **155**, 165.

[3] D. Tzeng and W. P. Weber, *J. Am. Chem. Soc.*, 1980, **102**, 1451; T. J. Barton, *Pure Appl. Chem.*, 1980, **52**, 615; W. F. Groure and T. J. Barton *J. Organomet. Chem.*, 1980, **199**, 33.

[4] H. Lavayssiere, J. Barrau, G. Dousse, J. Satge, and M. Bouchaut, *J. Organomet. Chem.*, 1978, **154**, C9.