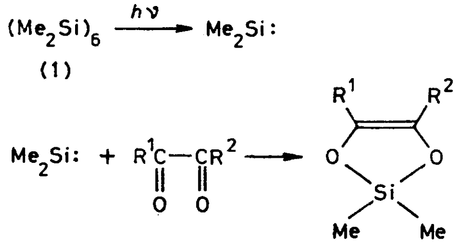
Reaction of Dimethylsilylene with α-Diketones.[1] Formation and Reaction of 1,3-Dioxa-2-silacyclopent-4-enes

By Wataru Ando* and Masayuki Ikeno

(*Department of Chemistry, The University of Tsukuba, Niiharigun, Ibaraki* 300-31, *Japan*)

Summary Photolysis of dodecamethylcyclohexasilane (**1**) in biacetyl, pentane-2,3-dione, bi-n-butyryl, bi-isobutyryl, and 3,5-di-t-butyl-*o*-benzoquinone gave substituted 1,3-dioxa-2-silacyclopent-4-enes, the thermal and chemical properties of which are reported.

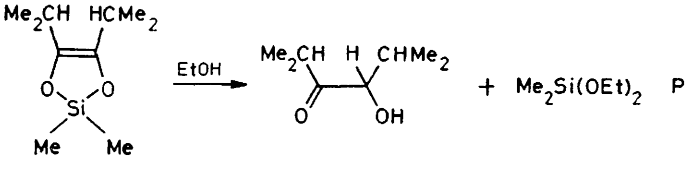
There has been considerable recent attention on the use of silylenes as synthetic intermediates, and we have reported the formation of silyl enol ethers and 1,3-dioxa-5-silacyclopentane derivatives in the reaction of dimethylsilylene with various types of ketones.[1-3] In an extention of this work we now report a convenient synthesis of 1,3-dioxa-2-silacyclopent-4-enes from α-diketones under mild and neutral conditions which is analogous to the formation of 1-silacyclopent-3-ene derivatives from 2,3-dimethylbutadiene.[4] An attempted preparation of compound (**2**) by the modified acyloin reaction of dimethyldichlorosilane with ethyl acetate in the presence of sodium, conditions which have been successfully used to prepare the 1,2-bis(trimethylsiloxy)alkene, resulted in failure.[5] To our knowledge, our method is the first report of the formation of 4,5-dialkyl-1,3-dioxa-2-silacyclopent-4-enes.[6]



(**2**) $R^1 = R^2 = Me$ 41%
(**3**) $R^1 = Et, R^2 = Me$ 38%
(**4**) $R^1 = R^2 = Pr^n$ 45%
(**5**) $R^1 = R^2 = Pr^i$ 67%

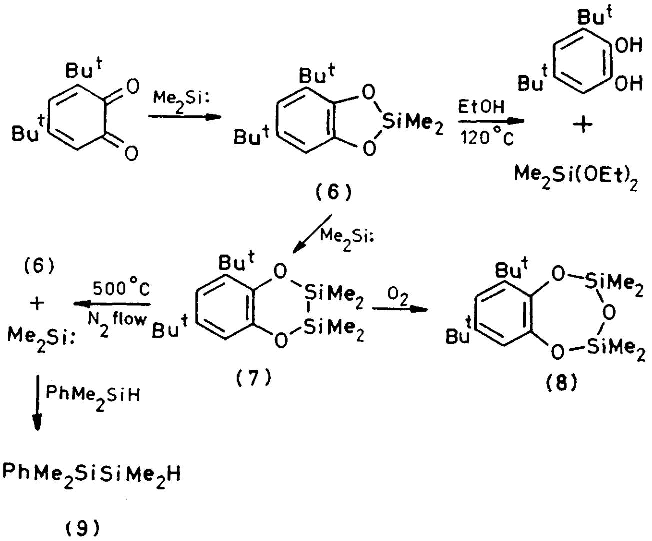
In a typical experiment, irradiation of an ethereal solution of dodecamethylcyclohexasilane (**1**) (1 mmol) and biacetyl (1 mmol) in a quartz tube with a low-pressure mercury lamp until almost all the biacetyl had been consumed yielded (**2**) in 41% yield. The progress of the reaction was shown by the disappearance of yellow colour of biacetyl. Compound (**2**) was isolated as a colourless liquid by preparative g.l.c.; it is extremely sensitive to moisture, and its structure was confirmed by mass (*m/e* 144), i.r. (ν_{max} 1260, 1208, 1125, 988 cm^{-1}), and ^{1}H n.m.r. spectroscopy [δ 0·30 (Me_2Si, s, 6H) and 1·73 (Me–C=C, s, 6H)].

Photolysis of (**1**) in the presence of pentane-2,3-dione under similar conditions gave (**3**) (M^+, *m/e* 158) in 38% yield, and photolysis of (**1**) with bi-n-butyryl and bi-iso-butyryl afforded (**4**) and (**5**) (M^+ at *m/e* 200 for each) in 45 and 67% yield, respectively. The n.m.r. spectra of (**3**)—(**5**) were analogous to the spectrum of (**2**). Compound (**5**) was ethanolysed easily to give dimethyl(diethoxy)silane (87%) and iso-butyroin (51%).



(5)

Furthermore, irradiation of (**1**) (0·3 mmol) with 3,5-di-t-butyl-*o*-benzoquinone (0·3 mmol) in 2·5 ml of dry ether for 1·5 h gave (**6**) quantitatively, and further photolysis gave (**7**), the product of insertion of dimethylsilylene into the Si–O bond of (**6**), in 85% yield (M^+, *m/e* 278). Compound (**6**) was ethanolysed with difficulty at room temperature, but at 120 °C for 6 h it was easily ethanolysed to give dimethyl(diethoxy)silane (67%), 3,5-di-t-butylcatechol (78%), and recovered (**6**) (13%). Compound (**7**) is air-sensitive, giving the corresponding disiloxane (**8**).



Gas-phase flow pyrolysis of the cyclic alkoxy-disilane (**7**) in the presence of a ten-fold excess of dimethylphenylsilane with benzene gave (**6**) in 95% yield and the disilane (**9**) in 56% yield. Compound (**7**) may produce dimethylsilylene which reacts with dimethylphenylsilane to give (**9**).

(*Received*, 26*th April* 1979; *Com.* 433.)

---

[1] For previous paper in the series 'Chemistry of Oxasilacyclopropane,' see W. Ando, M. Ikeno, and A. Sekiguchi, *J. Amer. Chem. Soc.*, 1977, **99**, 6447.

[2] W. Ando, M. Ikeno, and A. Sekiguchi, *J. Amer. Chem. Soc.*, 1978, **100**, 3613.

[3] W. Ando and M. Ikeno, *Chem. Letters*, 1978, 609.

[4] W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, 1968, **90**, 3438.

[5] C. M. Cookson and G. H. Whitham, *J.C.S. Perkin I*, 1975, 806.

[6] E. Hengge and B. Weinhardt, *Monatsh.*, 1974, **105**, 1275.