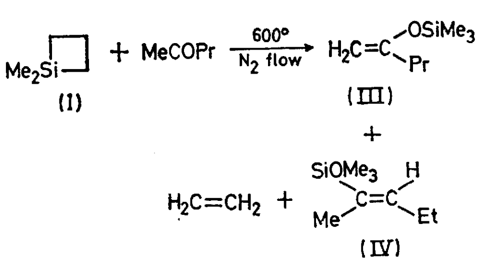
# Reactions of Silicon–Carbon Double-bonded Intermediates with Aldehydes and Ketones

By David N. Roark and Leo H. Sommer*
(*Department of Chemistry, University of California, Davis, California* 95616)

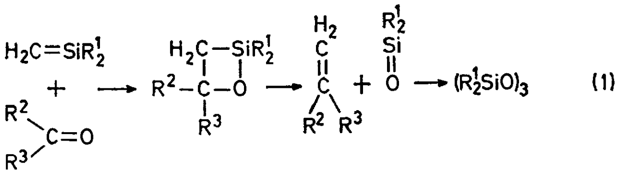
*Summary* $R_2Si{=}CH_2$ intermediates are shown to react with aldehydes and ketones by two different reaction pathways to give either a Wittig-type product or a silyl enol ether.

In 1967 Gusel'nikov and Flowers reported that a silicon–carbon double-bonded intermediate, $Me_2Si{=}CH_2$, was formed on the vapour-phase pyrolysis of 1,1-dimethyl-1-silacyclobutane (I).[1] The probable polar nature of the Si=C bond suggested a similarity with phosphonium ylides and that the reaction of such intermediates with aldehydes and ketones would be of interest.

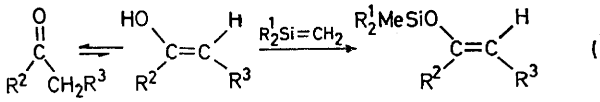


Recently we reported that $Me_2Si{=}CH_2$ generated by thermolysis of (I) at 600° in a stream of $N_2$ reacted with a 3-fold excess of heptanal to give moderate yields (35—40%) of oct-1-ene and $(Me_2SiO)_3$.[2] This reaction was postulated to proceed *via* pathway (1).

We now report both on the generality of pathway (1) and on a second pathway (2) for the reactions of Si=C intermediates with carbonyl-containing compounds.



(1)



(2)

Generation of $Ph_2Si{=}CH_2$ [by vapour-phase pyrolysis of 1,1-diphenyl-1-silacyclobutane (II)[3] at 600° in a stream of $N_2$] in the presence of a 3-fold excess of heptanal gives oct-1-ene† (35%) and a solid tentatively identified as $(Ph_2SiO)_3$. Thus it appears that substitution of Ph for Me on silicon has little or no effect.

---

† Identified by comparison (g.l.c., n.m.r., and i.r.) with an authentic sample.

Similar reaction of (I) with pentan-2-one gave only traces of 2-methylpent-1-ene and $(Me_2SiO)_3$, the expected products from pathway (1). The two major products were identified as 2-(trimethylsiloxy)pent-1-ene (III) and 2-trimethylsilyloxy)pent-2-ene‡ (IV) by their n.m.r. and i.r. spectra and by their ready reaction with aqueous acid.

Similar reaction with cyclohexanone gave 1-(trimethylsilyloxy)cyclohex-1-ene (> 35%),† indicating a new pathway (2) for the reaction of $Si=CH_2$ intermediates with *enolizable* ketones. In order to test this hypothesis benzophenone, a non-enolizable ketone, was allowed to react with (I) similarly, and 1,1-diphenylethylene† and $(Me_2SiO)_3$† were obtained (> 70%).

We thank the National Science Foundation for support, Dr. G. D. Homer for helpful discussions, and Dr. R. B. Miller and Mr. C. Gutierrez-Mena for a gift of 1-(trimethylsiloxy)-cyclohex-1-ene.

(*Received*, 17*th November* 1972; *Com.* 1926.)

---

‡ May be a mixture of *cis*- and *trans*-isomers.

[1] For a detailed discussion of $Me_2Si=CH_2$ see: L. E. Gusel'nikov and M. C. Flowers, *Chem. Comm.*, 1967, 864; M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc.* (*B*), 1968, 419.

[2] D. N. Roark and L. H. Sommer, submitted for publication.

[3] (a) We have found that (II) gives 1,1,3,3-tetraphenyl-1,3-disilacyclobutane when treated under identical conditions in the absence of a trap. (b) We recently reported that (II) gives $Ph_2Si=CH_2$ on photolysis; see: P. Boudjouk and L. H. Sommer, *J.C.S. Chem. Comm.* 1973, 54.