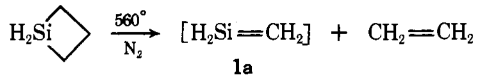
Communications to the Editor

Silicon-Carbon Multiple-Bonded (p_π-p_π) Intermediates. The First Generation and Reactions of Silaethene [$H_2Si{=}CH_2$] and Silanone [$H_2Si{=}O$]

Sir:

In spite of considerable evidence in support of the transient existence of substituted silaethenes,[1] direct evidence for the intermediacy of the parent compound, [$H_2Si{=}CH_2$] (**1a**), is lacking. Since **1a** has been implicated as a product in the vacuum-ultraviolet photolysis of methylsilane,[2] and since it has been the subject of several theoretical studies,[3] definitive evidence for just the formation of **1a** would be of considerable value. Additional information concerning the chemical behavior of **1a** would help to answer the following question: "Is the general chemical behavior of [$H_2Si{=}CH_2$] similar to that reported for its di-, tri-, and tetrasubstituted derivatives?"

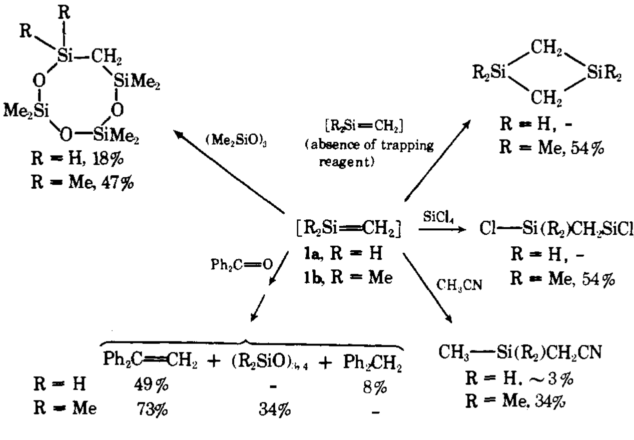
We wish to report the first generation of **1a**, a very reactive transient intermediate, which can be chemically trapped when generated in the presence of a suitable substrate. Gas phase thermolysis (560°, nitrogen flow system) of silacyclobutane[4] generates **1a** as indicated in eq 1. When generated in the absence of a trapping reagent **1a** forms an intractable, high molecular weight polymer. However, if silacyclobutane is copyrolyzed with a suitable trapping reagent, reasonable yields of 1:1 adducts (or their derivatives) are obtained as indicated in Scheme I. The reaction products[5] of [$H_2Si{=}CH_2$], presented in Scheme I together with those of the more thoroughly studied 1,1-dimethyl-1-silaethene,[1b] in our opinion provide convincing evidence for the existence of [$H_2Si{=}CH_2$] as a transient intermediate.



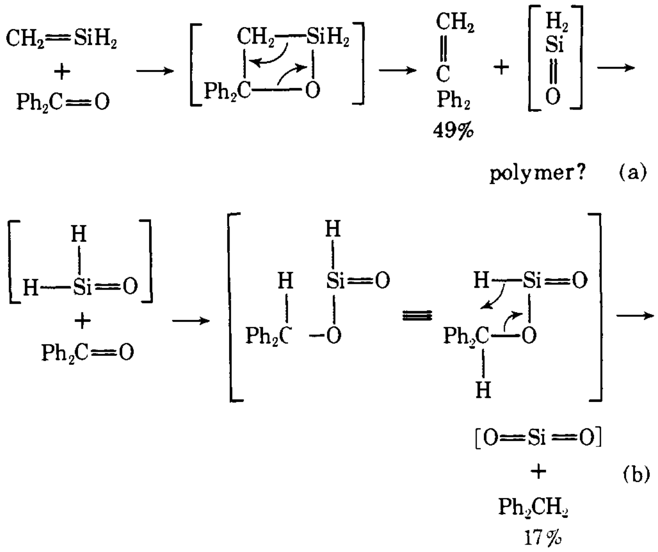
(1)

The reactions summarized in Scheme I indicate that both [$H_2Si{=}CH_2$] (**1a**) and [$Me_2Si{=}CH_2$] (**1b**) show similar behavior toward more reactive trapping reagents such as $Ph_2C{=}O$ and $(Me_2SiO)_3$.[6] However, **1a** reacts differently than **1b** when generated either in the presence of less reactive substrates such as CH_3CN or $SiCl_4$ or in the absence of a trapping reagent. Under these conditions **1a** does not form appreciable quantities of either a 1:1 adduct or volatile self-condensation products such as $(H_2SiCH_2)_n$ (n = 2, 3, or 4), but rather reacts to form an intractable, presumably polymeric, yellow solid.[8] It seems unlikely that the dimer of **1a**, $(H_2SiCH_2)_2$, is formed and then undergoes thermal decomposition since very similar compounds such as 1,1-dimethyl-1,3-disilacyclobutane and 1,3-dimethyl-1,3-disilacyclobutane are stable under similar reaction conditions.[9] The absence of dimer formation may indicate that the high reactivity and/or very short lifetime of **1a** makes polymerization rather than dimerization the predominant reaction pathway.

Scheme I



Scheme II



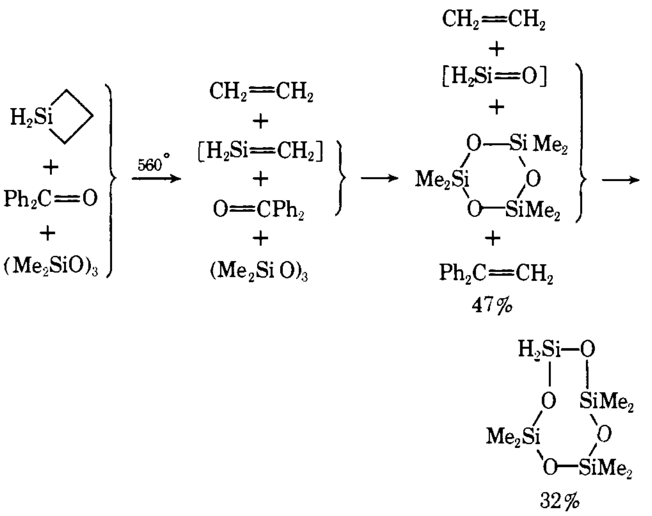
Although the reactions of **1a** and **1b** with benzophenone are similar inasmuch as they both afford reasonable yields of $Ph_2C{=}CH_2$ via a pseudo-Wittig mechanism (Scheme II), two significant differences should be noted. First, the trimer and tetramer of unsubstituted silanone [$H_2Si{=}O$] are not observed. This is not surprising since the trimer, $(H_2SiO)_3$, has never been reported and the tetramer, $(H_2SiO)_4$, which decomposes at room temperature,[11] would probably not survive our reaction conditions.

Second, the reaction between **1a** and $Ph_2C{=}O$ produces diphenylmethane in addition to 1,1-diphenylethylene. When this reaction is carried out using 1,1-dideuteriosilacyclobutane[4] (isotopic purity ~95%) a mixture[12] of Ph_2CD_2, Ph_2CHD, and Ph_2CH_2 (~64% total deuteration of the methylene position) is obtained. This indicates that an $=SiH_2$ moiety[14] is responsible for at least a substantial amount of the reduction.

Since the ratio of $Ph_2C{=}CH_2$:Ph_2CH_2 was observed to be independent of the extent of reaction (i.e., the pyrolysis temperature) it seems reasonable to assume that **1a** is a common precursor for both of these products. This assumption, the larger yield of $Ph_2C{=}CH_2$ relative to that of Ph_2CH_2, and the observation that both $Ph_2C{=}CH_2$ and Ph_2CH_2 are stable under the reaction conditions strongly implicates [$H_2Si{=}O$] as the species responsible for most, if not all, of the observed reduction of $Ph_2C{=}O$. A tentative mechanism which explains these observations is outlined by eq b in Scheme II.

Additional evidence for the intermediacy of [$H_2Si{=}O$]

Scheme III



(silanone) is provided by the following experiment. Pyrolysis of a benzene solution of silacyclobutane (2.2 mmol), benzophenone (4.0 mmol), and hexamethylcyclotrisiloxane (10.0 mmol), followed by resolution by preparative GLPC, afforded 1,1,3,3,5,5-hexamethylcyclotetrasiloxane (32%) and 1,1-diphenylethylene (47%) as the only major reaction products[15] (Scheme III).

The products reported in Schemes II and III, the facile insertion of [$Me_2Si{=}O$] into the Si-O bond of $(Me_2SiO)_3$ under similar reaction conditions,[16] and the observation that $(Me_2SiO)_3$ is stable under the reaction conditions constitute convincing evidence for the existence of [$H_2Si{=}O$] as a transient intermediate.

We are currently attempting to verify the intermediacy of an [O=Si=O] species by means of chemical trapping experiments.

Acknowledgments. We thank the National Science Foundation for generous support of this research and Mr. Kei Miyano for mass spectral studies.

References and Notes

(1) (a) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968); (b) C. M. Golino, R. D. Bush, P. On, and L. H. Sommer, *J. Am. Chem. Soc.*, **97**, 1957 (1975); (c) T. J. Barton, G. Marquardt, and J. A. Kilgor, *J. Organomet. Chem.*, **85**, 317 (1975); (d) P. B. Valkovich and W. P. Weber, *J. Org. Chem.*, **40**, 229 (1975); (e) L. E. Gusel'nikov, N. S. Nametkin, and V. M. Vdovin, *Acc. Chem. Res.*, **8**, 18 (1975), and references therein; (f) R. D. Bush, C. M. Golino, G. D. Homer, and L. H. Sommer, *J. Organomet. Chem.*, **80**, 37 (1974).

(2) (a) O. P. Strausz, K. Obi, and W. K. Duholke, *J. Am. Chem. Soc.*, **90**, 1359 (1968); (b) K. Obi, A. Clement, H. E. Gunning, and O. P. Strausz, *J. Am. Chem. Soc.*, **91**, 1622 (1969).

(3) (a) M. D. Curtis, *J. Organomet. Chem.*, **80**, 63 (1973); (b) R. Damrauer and D. R. Williams, *ibid.*, **66**, 241 (1974); (c) M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *J. Am. Chem. Soc.*, **97**, 1311 (1975); (d) C. M. Golino, W. H. Fink, R. D. Bush, and L. H. Sommer, unpublished results.

(4) J. Laane, *J. Am. Chem. Soc.*, **89**, 1144 (1967).

(5) All new compounds reported were fully characterized by an exact mass determination and their ir, NMR, and mass spectra. This information will be reported in detail in the full paper.

(6) The observed substrate reactivity order toward [$Me_2Si{=}CH_2$] is: $Ph_2C{=}O > (Me_2SiO)_3 > CH_3CN, SiCl_4$.[1f,7]

(7) C. M. Golino and R. D. Bush, unpublished results.

(8) Elemental analysis of this yellow solid (Anal. Calcd for CH_4Si: C, 27.2; H, 9.13; Si, 63.6. Found: C, 25.41; H, 4.86; Si, 55.28.) indicates a considerable loss of hydrogen, probably due to the fact thet this material condensed at the relatively warm (ca. 200°) ends of the pyrolysis tube. The observed carbon:silicon mole ratio of 1.08:1.0 supports the proposed decomposition reaction given in eq 1. The infrared spectrum (KBr) of this material showed only a very strong band at ~2080 cm^{-1} (Si–H stretch) and a weak band at 1248 cm^{-1} (Si–Me stretch). The insolubility of this material has prevented further investigation of its structure.

(9) 1,1-Dimethyl-1,3-disilacyclobutane has been obtained in 30% yield from a pyrolysis carried out at 500°;[10] 1,3-dimethyl-1,3-disilacyclobutane undergoes only minor (< 15%) decomposition under our reaction conditions.

(10) D. N. Roark and G. J. D. Peddle, *J. Am. Chem. Soc.*, **94**, 5837 (1972).

(11) H. J. Campbell-Ferguson, *J. Inorg. Nucl. Chem.*, **27**, 212 (1965).

(12) Ph_2CD_2[13] did not undergo observable H–D exchange when copyrolyzed with $Ph_2C{=}O$, $Ph_2C{=}CH_2$, and benzene at 560°. In pyrolyses which produce Ph_2CD_2, the $Ph_2C{=}CH_2$ which was also formed contained less then 10% deuterium at the 2-positions. The isotopic impurity of the Ph_2CD_2 is likely due to prior Si–H formation via an unknown pathway which is currently under investigation.

(13) K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960).

(14) A dihydro (p_π–p_π) multiply bonded silicon species ([$H_2Si{=}X$], X = CH_2 or O) appears to be necessary for the occurrence of this reduction. The reaction between $Ph_2C{=}O$ and [$CH_2{=}Si(H)Me$] at 611° afforded a 74% yield of $Ph_2C{=}CH_2$, but did not produce detectable quantities of Ph_2CH_2.[7]

(15) Diphenylmethene (0.18 mmol, 8%), benzophenone (1.4 mmol), and $(Me_2SiO)_3$ (8.4 mmol) were also recovered from the pyrolysate.

(16) (a) L. E. Gusel'nikov, N. S. Nametkin, T. H. Islamov, A. A. Sobtsov, and V. M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 84 (1971); (b) I. M. T. Davidson and J. F. Thompson, *Chem. Commun.*, 251 (1971); (c) C. M. Golino, R. D. Bush, and L. H. Sommer, Abstracts, 167th National Meeting of The American Chemical Society, Los Angeles, Calif., April 1975, No. ORGN 005.

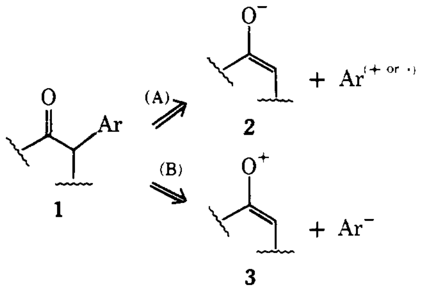
C. M. Golino, R. D. Bush, L. H. Sommer*
Department of Chemistry, University of California
Davis, California 95616

Received June 30, 1975

α-Arylation of Carbonyl Groups. Utilization of the *p*-Toluenesulfonylazo Olefin Functional Group as an Enolonium Synthon

Sir:

In connection with a synthetic study, we required substrates bearing an α-aryl ketone moiety (**1**). Methodology involving the α-arylation of ketones is one conceptual approach for the synthesis of such systems. Analysis of this problem suggests two primary modes of synthesis: (A) the combination of an enolate **2** (or its equivalent) with some electron-deficient aryl species or (B) reaction of an enolonium (α-keto cation) synthon **3** with an electron-rich aryl species.



Although the reaction of enolates and enamines with strongly activated arenes, diphenyliodonium chloride, or benzyne has been shown to produce α-arylated ketones,[1-9] it appears that a more promising approach to enolate arylation is the method of Rossi and Bunnett involving the reaction of enolates with photogenerated aryl radicals.[10-12] An intramolecular variant of this latter procedure has recently been used to great advantage by Semmelhack et al. in their total synthesis of cephalotaxine.[13,14]

In assessing the enolate method for natural product synthesis, complications can be anticipated in those cases where intramolecular condensations (aldol, Claisen) or β-eliminations can occur. Additionally, it has yet to be conclusively demonstrated that a kinetically generated enolate can be regiospecifically arylated.[11,15]

Whereas, a priori, methodology based on mode (B) might avoid some of these difficulties, there has been essentially no effort to utilize such a strategy.[16,17]

Superficial consideration of this problem suggests that the reaction of α-halo ketones with lithium diarylcuprate