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(33) NSF Predoctoral Fellow; Danforth Fellow.

Dale G. Kalina, Tobin J. Marks,*[32] William A. Wachter[33]
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

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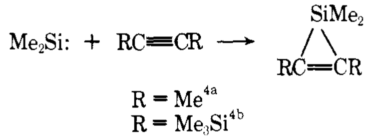
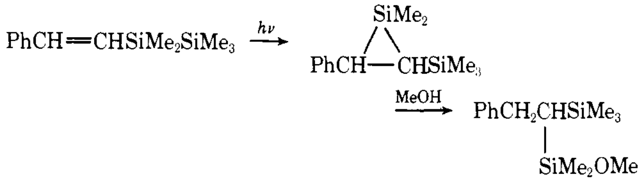
Photochemical Generation of Silacyclopropene[1]

Sir:

Isolation of the first silacyclopropene, 1,1-dimethyl-2,3-diphenyl-1-silacycloprop-2-ene, from the addition of the dimethylsilylene to diphenylacetylene was claimed by Volpin and co-workers in 1962,[2] although the product was demonstrated to be the dimer later.[3] Very recently, Conlin and Gaspar[4a] and Seyferth, Annarelli, and Vick[4b] have reported that the addition of dimethylsilylene to acetylene really resulted in the formation of silacyclopropene.

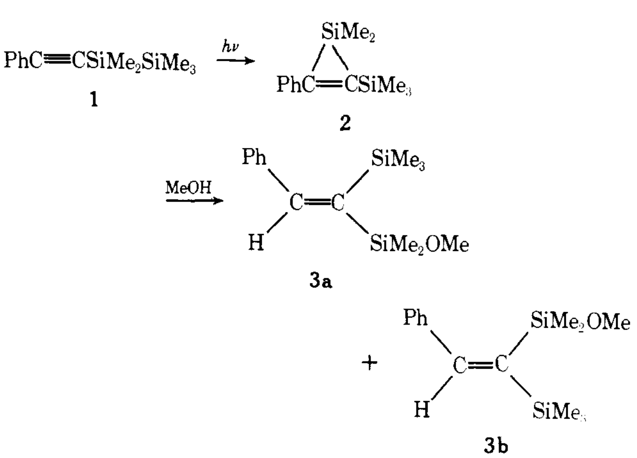


In a recent paper,[5] we demonstrated that photolysis of styrylpentamethyldisilane gave silacyclopropane which afforded 1-trimethylsilyl-1-methoxydimethylsilyl-2-phenylethane upon methanolysis.



As a logical consequence, we have examined the photolysis of (pentamethyldisilanyl)phenylacetylene (**1**) which led to an entirely new route to silacyclopropene. We have also studied a variety of reactions of the photochemically generated silacyclopropene, which open a fascinating new field in organosilicon chemistry.

Irradiation of a methanol solution of **1**[6] in a quartz tube for 1.5 h with a 450-W high-pressure mercury arc lamp[7] afforded a mixture of **3a** and **3b** in 50–90% yield.[8] Both **3a** and **3b** gave 1,1-bis(trimethylsilyl)-2-phenylethylene by treatment with methylmagnesium bromide.



The ratio of each isomer was in favor of **3a** at the early stage of the reaction, but approached 1:1 after prolonged irradiation. Independent irradiation of each isomer gave the same 1:1 isomeric mixture.

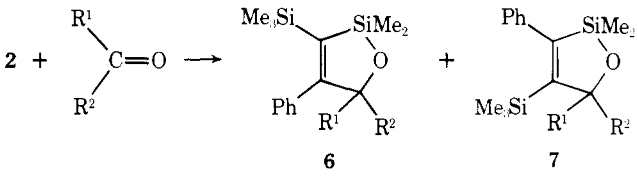
The structure of **3a** is consistent with the intermediacy of 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacycloprop-2-ene (**2**),[4,9] and **2** can be prepared as a fairly thermally stable compound in solution. Irradiation of **1** (0.3 mmol) in benzene (0.3 mL) in a quartz tube afforded a solution containing ca. 75% of **2**. The proton NMR spectrum of the solution displays two sharp singlets of SiMe at δ 0.32 and 0.39 in ratio of peak areas 3:2 in addition to Si–Me signals of **1** at δ 0.29 and 0.40 (ca. 13%). The solution also contains ca. 12% of (trimethylsilyl)phenylacetylene (**4**), the SiMe signal of which appears at δ 0.39.[10] Addition of methanol to the solution destroys **2** within a minute to give **3a** quantitatively.[11]

Although quite reactive toward air and moisture, **2** is thermally stable and unchanged by irradiation through a Pyrex filter. However, **2** gave **4** quantitatively upon irradiation through quartz; the ejected dimethylsilylene was trapped by diethylmethylsilane to give 1,1,2-trimethyl-2,2-diethyldisilane (**5**).

$$\mathbf{2} \xrightarrow{h\nu} \underset{\mathbf{4}}{\mathrm{PhC{\equiv}CSiMe_3}} + \mathrm{:SiMe_3} + \xrightarrow{\mathrm{Et_2MeSiH}} \underset{\mathbf{5}}{\mathrm{Et_2MeSiSiMe_2H}}$$

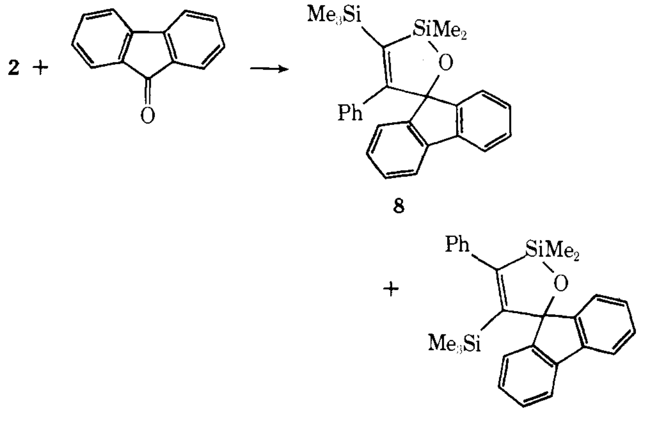
Irradiation of **1** (0.4 mmol) in a mixture of methanol (2 mL) and diethylmethylsilane (2 mL) gave only **3a** and **3b** in 44.0% yield with a trace of **5**. The thermal and photochemical behavior of silacyclopropene contrast interestingly to those of silacyclopropanes,[12] which are photochemically stable but thermally unstable, ejecting silylenes.[13]

We report in this paper two spectacular examples of reactions of **2**. The reaction of **2** with ketones gave products with the general structure 1-sila-2-oxacyclopent-4-ene, but reactivities are quite different depending on the structure of ketones. Aliphatic ketones such as acetone and cyclohexanone gave a mixture of **6** and **7** only upon irradiation (with a high-pressure Hg arc lamp for 0.5 h). No dark reaction occurred for **2** with these ketones.



a, $R^1 = R^2 = CH_3$
b, $R^1 = R^2 = \text{-}(CH_2)_5\text{-}$
c, $R^1 = R^2 = Ph$

The yield of **6** and **7** was 30–60% and the ratio of **6** to **7** varied from 6/1 to 2/1.[14] In contrast to aliphatic ketones, fluorenone reacts with **2** in the dark at room temperature to give **8** and **9** (**8**/**9** = 1/3) in 42-51% yield[14] after 30 min.



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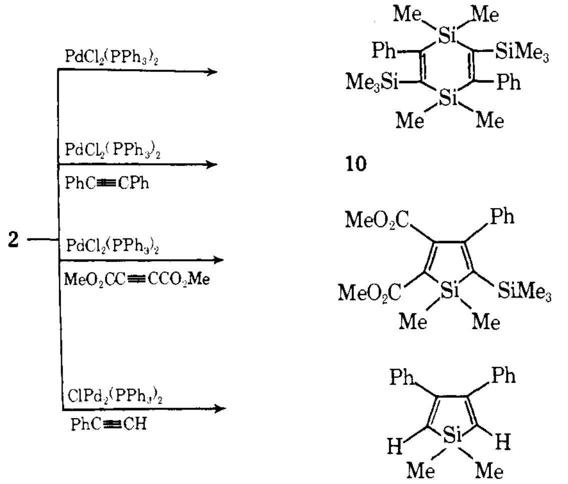
The reactivity of benzophenone is in between aliphatic ketones and fluorenone. Thus, a slow dark reaction gave **6c** and **7c** (**6c**/**7c** = 1/3) in 7.2% yield after 50 min. Irradiation of **2** and benzophenone through a Pyrex filter resulted in the formation of **6c** and **7c** (**6c**/**7c** = 1/1.4) in 42.4% yield.[14] Interestingly, the photochemical cycloaddition with benzophenone was completely suppressed by addition of piperylene, only the dark reaction being observed.

We have demonstrated that a strained Si-C bond of silacyclobutane can undergo palladium complex-catalyzed cycloaddition with acetylenes.[15] Naturally, the Si-C bond of **2** should be more prone to such a reaction. The course of the reaction was, however, affected dramatically by the structure of the acetylene, as shown by the following scheme.



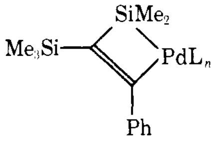
(10)

10

(11)

(12)

These reactions were carried out at 75 °C for 10-30 min, and yields are 30-50%.[14] Mechanisms of these reactions are not necessarily clear, but we believe that they probably involve a common intermediate such as silapalladacyclobutene (**13**).



13

In the absence of acetylenes or even in the presence of an unreactive actylene such as diphenylacetylene, **13** reacts with **2** leading to **10**, while with acetylene dicarboxylic ester the acetylene is incorporated in the product. Although the reaction with phenylacetylene is rather difficult to explain, presumably **13** changes to a silylene complex with extrusion of (trimethylsilyl)phenylacetylene before the reaction, and the silylene complex reacts with 2 mol of acetylene to give **12**.[16] We have evidence for the formation of a silylene complex that will be reported later.

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

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(7) Irradiation of the solution with a 160-W low-pressure mercury arc lamp required 24 h to complete the reaction.
(8) **3a** and **3b** were separated by silica gel TLC, and the stereochemistry was determined by the nuclear Overhauser effect between vinylic hydrogen and methyl groups on silicon. Other products reported in this paper were also isolated by silica gel TLC.
(9) The course of the reaction was not affected by the addition of acetic acid, piperylene, and *m*-xylene, but was completely suppressed by a Pyrex filter. Benzophenone did not sensitize the reaction with a Pyrex filter. These facts suggest that the silacyclopropene may arise from the singlet excited state of 1.
(10) The Si-Me signals of both 2 and 4 at δ 0.39 overlap each other in benzene, but can be separated in other solvents.
(11) Although the silacyclopropene (**2**) could be isolated by fractional distillation or by VPC from the reaction mixture, separation of **2** from the isomeric acetylene (1) was not easy. We hope to succeed in the purification of **2** with a large scale experiment. However, the chemistry of **2** can be done perfectly with the mixture as described in the text since both 1 and 4 are inactive in the reactions.
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Hideki Sakurai,* Yoshiyasu Kamiyama, Yasuhiro Nakadaira
Department of Chemistry, Faculty of Science
Tohoku University
Sendai 980, Japan

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Templated Syntheses of Cyclic Acetylacetone Hosts, Their Affinities for Divalent Ions, and an Example of a Slow Proton Transfer from Enol to Hydroxide Ion[1]

Sir:

We report here the first β-diketone-templated syntheses of macrocycles from acac, the effects of gathering and orienting the units on their affinities for ten different metal dianions, and a surprisingly slow proton transfer from C-OH to OH^- which is on the human time scale.[2,3]

Treatment of acac in THF successively with NaH,[4] BuLi,[4] and either diethylene glycol ditosylate or 1,3-bis(bromomethyl)benzene at 0 °C gave, after 20 h at 20 °C and acidification, **1** (70%)[5] or **2** (95%),[5] respectively. Treatment of **1** under N_2 with CaH_2 gave its calcium salt. The calcium salt in a solution of THF and HMPA was added to lithium diisopropylamide in THF followed by diethylene glycol ditosylate (20 h, 20 °C, solution 0.01 M). Acidification of the mixture and separation of the products by gel permeation chromatography gave macrocycle **3** (16%),[5] mp 32-34 °C, and the dimer of **3** (2%), polymer (3.5%), and recovered **1** (75%). When the Mg^{2+} complex of **1** (Mg turnings plus **1**) was simi-