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Preliminary communication

PHOTOLYSIS OF ORGANOPOLYSILANES. FORMATION AND REACTIONS OF NEW SILACYCLOPROPENE DERIVATIVES

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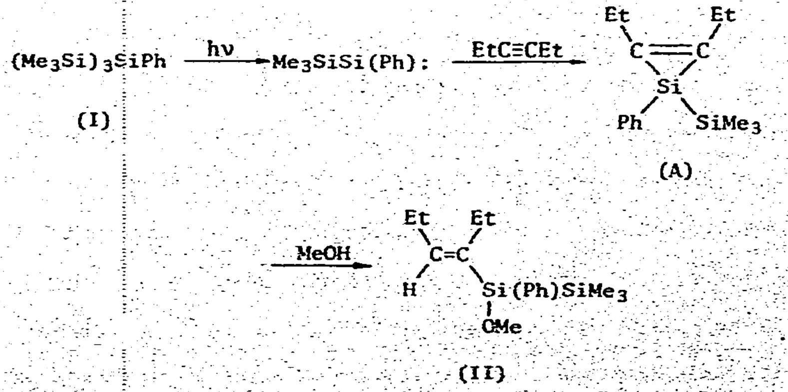
Summary

The photolysis of tris(trimethylsilyl)phenylsilane (I) in the presence of diethylacetylene resulted in formation of a silacyclopropene, which could be trapped by reaction with methanol to give 3-(methoxytrimethylsilylphenylsilyl)-3-hexene in moderate yield. Similarly, irradiation of I in the presence of 1-hexyne, trimethylsilylacetylene and bis(trimethylsilyl)acetylene led to the formation of the respective silacyclopropenes. In these cases, however, silyl-substituted alkynes arising from photorearrangement of the initially formed silacyclopropenes were obtained after methanolysis, in addition to the expected methoxysilylalkenes.

Considerable attention has been focused in recent years on the possible existence of silacyclopropene derivatives [1,2]. Recently, Gaspar and Conlin have reported that dimethylsilylene, generated by thermolysis of 1,2-dimethoxytetramethyldisilane, reacts with 2-butyne to give tetramethyl-1-silacycloprop-2-ene whose formation could be confirmed by its proton NMR spectroscopic analysis [3]. More recently, Seyferth and his co-workers have reported the isolation and characterization of a stable silacyclopropene which was produced by thermolysis of hexamethylsilirane in the presence of bis(trimethylsilyl)acetylene [4]. In a previous communication we reported the first example of the photochemical formation of a silacyclopropene derivative from phenylethynylpentamethyldisilane [5].

In 1970 we found that the photolysis of cyclic and acyclic organopolysilanes affords a convenient route to divalent organosilicon intermediates [6]. Subsequently, we also demonstrated that photochemically generated methylphenylsilylene reacts with various olefins to give silacyclopropane derivatives which, however, readily undergo photorearrangement with a 1,3-hydrogen shift from carbon to silicon [7,8]. However, all attempts to produce silacyclopropenes by adding a silylene to the triple bond of an alkyne were unsuccessful. We have now discovered that photochemically generated trimethylsilylphenylsilylene adds readily to alkynes. In this communication we report the reaction of this novel silylene with some mono- and disubstituted acetylenes and photorearrangement of the silacyclopropenes thus formed.

When tris(trimethylsilyl)phenylsilane (I) was photolyzed by irradiation with a low-pressure mercury lamp in n-hexane under a nitrogen atmosphere, trimethylsilylphenylsilylene was extruded. Thus, the photolysis of I (3.1 mmol) in the presence of diethylacetylene (48 mmol) as a trapping agent in 100 ml of dry n-hexane for 2 h, followed by treatment of the resulting mixture with 5 ml of dry methanol, gave 3-(methoxytrimethylsilyl-



phenylsilyl)-3-hexene (II) in 48% yield as the sole reaction product, in addition to 10% of unchanged I.

The IR [(neat)(cm^{-1}) 1080 (νSi-OMe), 1610 (νC=C)], NMR (δ) [0.15 (CH_3-$SiMe_2$, s, 9H), 0.88 (CH_3-C, t, 3H), 1.05 (CH_3-C, t, 3H), 2.02-2.37 (CH_2, m, 4H), 3.48 (CH_3-O, s, 3H), 5.87 (H-C=C, broad t, 1H) and 7.25-7.55 (ring protons, m, 5H)] and mass spectra [(m/e 292 (M$^+$)] were completely consistent with the proposed structure. The production of II in moderate yield provides convincing evidence for the formation of a rather stable silacyclopropene (A).

Interestingly, photolysis of I (3.0 mmol) in the presence of 1-hexyne (42 mmol) under the same conditions, followed by addition of methanol, afforded a wholly unexpected compound, n-butyl(trimethylsilylphenylsilyl)-acetylene (IVa) in 14% yield [NMR (δ) 0.17 (CH_3-$SiMe_2$, s, 9H), 0.93 (CH_3-C, broad t, 3H), 1.54 (CH_2, m, 4H), 2.33 (CH_2-C≡C, m, 2H), 4.44 (H-Si, s, 1H), 7.20-7.60 (ring protons, m, 5H); IR (cm^{-1}) 2110 (νSi-H), 2170 (νC≡C); m/e 260 (M$^+$)], in addition to the expected 2-(methoxytrimethylsilylphenylsilyl)-1-hexene (IIIa) (21% yield) [NMR (δ) 0.14 (CH_3-$SiMe_2$, s, 9H), 0.86 (CH_3-C, broad t, 3H), 1.32 (CH_2, m, 4H), 2.11 (CH_2-C=C, m, 2H), 3.48 (CH_3-O, s, 3H), 5.46 (H-C=C, broad s, 1H), 5.78 (H-C=C, broad s, 1H), 7.25-7.55 (ring protons, m, 5H); IR (cm^{-1}) 1080 (νSi-OMe), 1590 (νC=C); m/e 292 (M$^+$)].* Similarly, the photolysis of I in the presence of a tenfold excess of a trimethylsilylacetylene, followed by treatment with methanol, gave 1-trimethylsilyl-1-(methoxytrimethylsilylphenylsilyl)ethene (IIIb) [NMR (δ) -0.02 (CH_3-$SiMe_2$, s, 9H), 0.15 (CH_3-$SiMe_2$, s, 9H), 3.50 (CH_3-O, s, 3H), 6.45 (H_2C=C, AB quart., J_{gem}=5.0 Hz), 7.20-7.55 (ring protons, m, 5H); IR (cm^{-1}) 1080 (νSi-OMe); 308 (M$^+$)] and trimethylsilyl(trimethylsilylphenylsilyl)acetylene (IVb) [NMR (δ) 0.19 (CH_3-$SiMe_2$, s, 9H), 0.22 (CH_3-$SiMe_2$, s, 9H), 4.45 (H-Si, s, 1H), 7.25-7.60 (ring protons, m, 5H); IR (cm^{-1}) 2100

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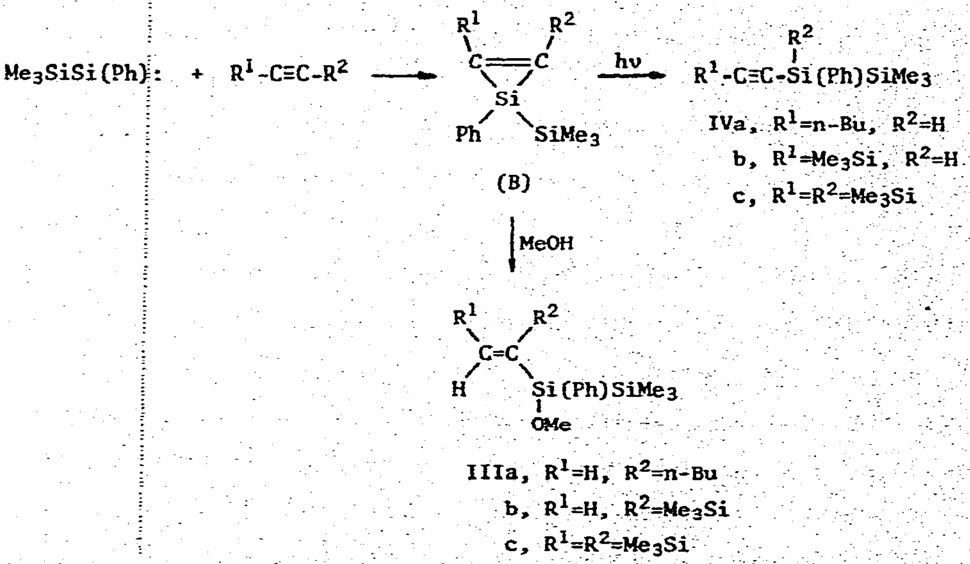
* In this reaction, 4% yield of an isomer of IIIa identified by mass spectrometric analysis was also produced, however, we could not isolate it in a pure form.

(νSi-H); m/e 276 (M^+)] in 16 and 40% yield, respectively.

We believe that compounds IVa and IVb are formed by photorearrangement of the initially formed silacyclopropenes by a 1,2-hydrogen shift from carbon to the ring silicon as shown in Scheme I. The following experiment supports this idea. When I (3.1 mmol) was photolyzed in the presence of methanol(6.4 mmol) as well as trimethylsilylacetylene (31.4 mmol) in 100 ml of dry n-hexane for 2 h, the product IIIb, a result of the fast reaction of the silacyclopropene with methanol, was obtained in 30% yield, where 52% of I was photolyzed. Compound IVb was produced in only 4% yield, together with unidentified products (less than 4%).

The production of silyl substituted alkynes by addition of thermally generated silylene species to acetylene or propyne recently has been reported [9,10]. The formation of silyl alkynes was attributed to rearrangement of initial adducts, silacyclopropenes, but no chemical evidence was provided to support this assumption. The present results clearly indicate that compound IVb must come from the photoisomerization of the silacyclopropene (B).

Scheme 1



In the photolysis of I in the presence of bis(trimethylsilyl)acetylene photoisomerization of the silacyclopropene produced involved migration of a trimethylsilyl group from ethylenic carbon to the ring silicon. Thus, after addition of methanol to the reaction mixture, 1,2-bis(trimethylsilyl)-1-(methoxytrimethylsilylphenylsilyl)ethene (IIIc) [NMR (δ) 0.04 (CH$_3$-SiMe$_2$, s, 9H), 0.13 (CH$_3$-SiMe$_2$, s, 9H), 0.24 (CH$_3$-SiMe$_2$, s, 9H), 3.50 (CH$_3$-O, s, 3H), 7.60 (H-C=C, s, 1H), 7.20-7.50 (ring protons, m, 5H); IR (cm^{-1}) 1080 (νSi-OMe); m/e 365 (M-15)] and trimethylsilyl[bis(trimethylsilyl)phenylsilyl]acetylene (IVc) were isolated in 4 and 6% yield, respectively. The NMR and IR spectra of these products were consistent with those of an authentic sample which was prepared from 2-chloro-2-phenylhexamethyltrisilane and lithium trimethylsilylacetylide in n-hexane [NMR (δ) 0.18 (CH$_3$-SiMe$_2$, s, 18H), 0.23 (CH$_3$-SiMe$_2$, s, 9H), 7.10-7.50 (ring protons, s, 5H); IR (cm^{-1}) 2090 (νC≡C); m/e 348 (M$^+$)].

Recently, we have found the reverse photorearrangement in which a trimethylsilyl group migrates from silicon to carbon in phenylethynylpentamethyldisilane to give a silacyclopropene [5]. However, no rearrangement analogous to the one reported here has been described to date.

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