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SILACYCLOPROPENES

I. SYNTHESIS AND PROPERTIES OF SOME SILACYCLOPROPENES *,**

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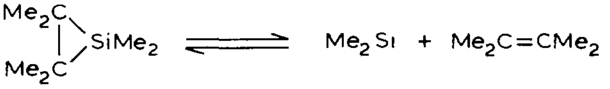
Summary

The thermal decomposition of hexamethylsilirane in the presence of selected disubstituted acetylenes ($Me_3SiC{\equiv}CSiMe_3$, $Me_2HSiC{\equiv}CSiMe_2H$, $Me_3SiC{\equiv}CCH_3$, $Me_3SiC{\equiv}CCMe_3$, $Me_3CC{\equiv}CCH_3$) resulted in Me_2Si addition to the C≡C bonds to give the respective silacyclopropenes. These are thermally stable but are extremely reactive toward atmospheric oxygen and moisture and react readily with methanol and ethanol at room temperature with Si–C (ring) bond cleavage. The very high field ^{29}Si NMR resonance (-87 to -106 ppm) is a characteristic feature of the silacyclopropene ring.

Introduction

During the course of our studies of the hyperreactive silacyclopropane, hexamethylsilirane, we found that this compound decomposes thermally at 65–70 °C to release dimethylsilylene (eq.1) [2].



(1)

When this thermolysis was carried out in the presence of internal olefins, the dimethylsilylene added to the C=C bond of the olefin to give a new silacyclopropane (eq.2) [2c,3].

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* Dedicated to Professor Sei Otsuka in recognition to his many contributions to organometallic chemistry.

** Preliminary communications see ref. 1.

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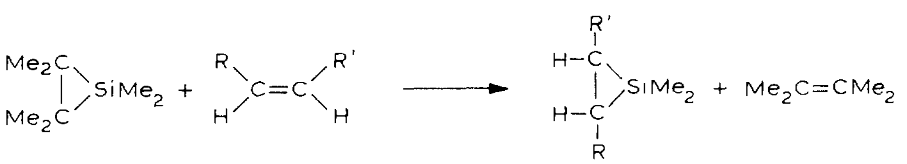
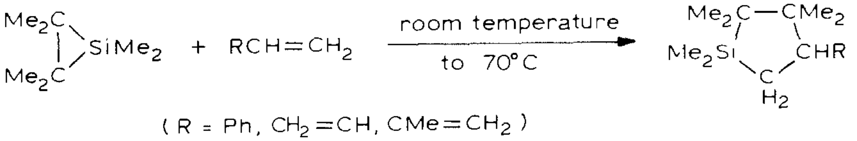


(2)

With styrene and α-methylstyrene and with terminal 1,3-dienes and terminal conjugated acetylenes hexamethylsilirane reacted in another way (eq.3 and 4) [4]. In the

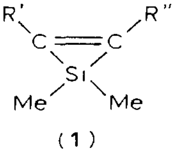


(3)

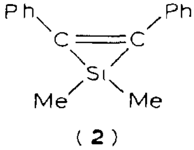
(4)

thermal reactions of hexamethylsilirane with styrene and α-methylstyrene and some 1,3-dienes the Me_2Si adduct was a by-product. Although the isolated products of Me_2Si transfer in these latter cases were not silacyclopropanes, their formation could be rationalized in terms of an initial Me_2Si addition to a C=C bond.

In view of this demonstrated addition of hexamethylsilirane-derived Me_2Si to C=C bonds, it was of interest to see if Me_2Si addition to the C≡C bond of an acetylene could be effected. This was of special interest since the expected products, silacyclopropenes, **1**, were unknown at the time we began our experiments.

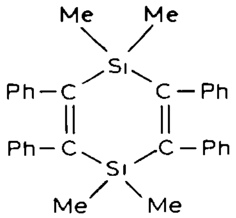


(**1**)



(**2**)

The existence of stable silacyclopropenes had been predicted by Vol'pin et al. in 1961 [5] on the basis of analogies to the cyclopropenium cation. Although the preparation of 1,1-dimethyl-2,3-diphenyl-1-silirene (**2**) had been claimed by these authors, subsequent studies by other workers showed this not to be the case [6]. Rather than **1**, the product obtained by Vol'pin et al. when they generated Me_2Si by $(Me_2Si)_n$ pyrolysis in the presence of diphenylacetylene, was shown to be its dimer **3**. Atwell and coworkers later reported two reactions of dimethylsilylene (generated by 1,2-dimethoxytetramethyldisilane pyrolysis) which very likely involved a silacyclopropene intermediate. In one reaction, Me_2Si was generated in the gas phase in the presence of 2-butyne and methanol [7]. The product, *cis*-MeCH=C(Me)SiMe$_2$OMe, was the one expected if tetramethylsilirene (**4**) had been formed and subsequently cleaved by methanol. In the other reaction, gas phase pyrolysis of the same Me_2Si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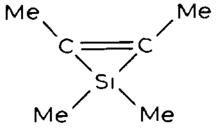
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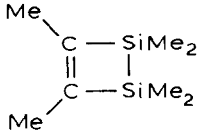

(5)

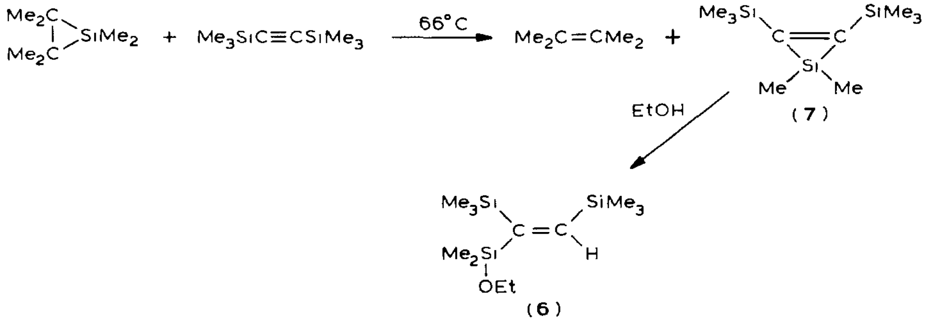
precursor in the presence of 2-butyne alone gave hexamethyl-1,2-disila-3-cyclobutene (**5**) [8]. The formation of the latter could be rationalized in terms of Me_2Si insertion into the Si–C bond of tetramethylsilirene. At the time our investigation of silacyclopropenes was already in progress, Gaspar and Conlin provided convincing evidence for the formation of **4** in the flow pyrolysis of 1,2-dimethoxytetramethyldisilane in the presence of 2-butyne [9]. Silirene **4** was shown to be stable in solution but it could not be isolated in pure form.

Results and discussion

The addition of dimethylsilylene to the $C\equiv C$ bond of several internal acetylenes (e.g., 3-hexyne and 4-octyne) was attempted, using reaction conditions which had been successful in the transfer of Me_2Si from hexamethylsilirane to olefins [2]. No evidence for the formation of a stable silacyclopropene was obtained. However, when the acetylene used was bis(trimethylsilyl)acetylene, we were able to isolate and characterize a stable silacyclopropene.

In an initial experiment, a solution of 1.3 mmol of hexamethylsilirane [2a] in 4 ml of bis(trimethylsilyl)acetylene was heated under nitrogen at 66 °C for 15 h. The reaction mixture subsequently was treated with 0.5 ml of anhydrous ethanol. The exothermic reaction which occurred indicated the presence of a highly reactive product in the solution. Analysis by GLC showed the presence of tetramethylethylene in quantitative yield, as well as of a higher-boiling product in 75% yield which was identified as **6**. Thus the formation of a silacyclopropene, **7**, was indicated (Scheme 1). Further work showed that this silacyclopropene, 1,1-dimethyl-2,3-bis(trimethysilyl)silirene (**7**), could be isolated by gas chromatography. This compound, like the siliranes which we had prepared earlier [2,10], was found to be highly reactive. A GLC-isolated sample fumed profusely in air and strict precautions to

SCHEME 1



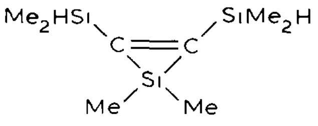
exclude atmospheric oxygen and moisture were required during its preparation, isolation and subsequent handling.

Bis(trimethylsilyl)acetylene is an exceptionally good silylenophile. Usually in silylene trapping reactions a considerable excess of the trapping reagent is used to ensure good product yields. However, in a 1/1 reaction of hexamethylsilirane with this acetylene (in benzene solution at 70 °C for 18 h) a good yield of silirene 7 was obtained, as indicated by a 59% yield of $Me_3SiCH{=}C(SiMe_3)(SiMe_2OMe)$ after methanolysis of the reaction mixture. Even when the solvent used was tetramethylethylene (which is very reactive toward Me_2Si [2c,3]), a 42 h reaction time resulted in a 47% yield of $Me_3SiCH{=}C(SiMe_3)(SiMe_2OMe)$ (after methanolysis). Silirene 7 may be prepared on a larger, more useful scale. For instance, after a reaction of 60 mmol of hexamethylsilirane with 120 mmol of $Me_3SiC{\equiv}CSiMe_3$ (18 h at 70 °C) the product silirene was distilled using a 4″ Vigreux column. A colorless liquid, b.p. 92–94 °C at 30 mmHg, was obtained in 64% yield. Bulk samples of silirene 7, it was found, are spontaneously flammable in air. Despite this high reactivity, a satisfactory C/H analysis could be obtained. Such high reactivity toward air is highly unusual for a compound containing a silicon atom bonded to four carbon atoms. However, silirene 7 is thermally stable and can be stored without decomposition under a protective argon atmosphere. Benzene solutions of 7 are stable for weeks at room temperature and at 70–75 °C in benzene solution the half-life of 7 is greater than 60 h. (We suspect that much of the measured "decomposition" was due to slow intrusion of air through the rubber septum used.)

All spectroscopic data were in full accord with the silacyclopropene structure proposed for the hexamethylsilirane/bis(trimethylsilyl)acetylene product. The IR spectrum showed two bands of moderate intensity at 1505 and 1500 cm^{-1} which were attributed to ring C=C stretching frequencies [11]. The ^1H NMR spectrum of 7 consisted of two $Si{-}CH_3$ signals in 3/1 integrated ratio, in line with expectation. The proton-decoupled ^{13}C NMR spectrum also was unexceptional: three singlets at $\delta(C)$ 189.6, 0.40 and -2.2 ppm. The low field resonance is due to the ring carbon atoms and is rather low for an olefinic carbon atom, very possibly due to the extensive silyl substitution [12]. The ^{29}Si NMR spectrum of silirene 7 showed the resonance due to the Me_3Si group Si atoms at $\delta(Si)$ -8.5 ppm [13], with 8 of the 10 expected lines being observed in the fully coupled spectrum. The resonance of the silicon atom in the ring was found at unexpectedly high field: at $\delta(Si)$ -106.2 ppm as a 3 line pattern (7 lines theoretical), atop the "broad hump" of the glass signal! This resonance is ~ 50 ppm upfield from the silicon resonances of the silacyclopropanes, and, as will be shown later, is diagnostic of the silirene ring. It was expected that the silicon atom in 7 is more highly shielded than the silicon atom in a silacyclopropane ($\delta(Si)$ in hexamethylsilirane -49.7 ppm [2a]), but such a large upfield shift was surprising.

The UV spectrum of silirene 7 showed weak ($\epsilon = 37$) absorption at 345 nm, very likely due to the $\pi \rightarrow \pi^*$ transition of the C=C bond. In the 70 eV mass spectrum the molecular ion was observed at $m/z = 228$ (14%). The most intense fragments corresponded to Me_3Si^+ and $Me_3SiC{\equiv}CSiMe_2^+$.

1,1-Dimethyl-2,3-bis(trimethylsilyl)silirene (7), was the first silacyclopropene which could be isolated as a pure compound. Further studies showed that the preparative route used for 7 could be applied to the synthesis of other silacyclopropenes.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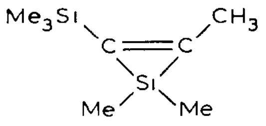
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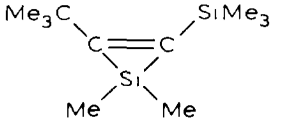
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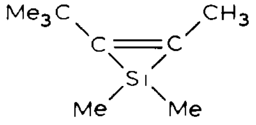

(**11**)

Thermolysis of hexamethylsilirane in the presence of bis(dimethylsilyl)acetylene, propynyltrimethylsilane, t-butyl(trimethylsilyl)acetylene, and 4,4-dimethyl-2-pentyne gave silirenes **8**–**11**, respectively. Silirenes **8** and **10** were isolated by GLC; the other two were not. Only **8** and **10** were analyzed but all were characterized by ^{29}Si NMR spectroscopy and by alcoholysis reactions. All, like silirene **7**, were exceedingly reactive toward atmospheric oxygen and moisture. The formation of **8** from $HMe_2SiC{\equiv}CSiMe_2H$ provides a striking sample of the high reactivity of silylacetylenes in the Me_2Si transfer reaction from hexamethylsilirane. The Si–H bond is an effective "trap" for Me_2Si generated by this method [2], but in the case of $HMe_2SiC{\equiv}CSiMe_2H$ the Me_2Si adds to the C≡C bond rather than inserting into the Si–H bonds.

The ^{29}Si NMR spectra of **8**–**11** showed characteristic resonances for the ring Si atoms far upfield from tetramethylsilane: **8**, −102.1; **9**, −88.6; **10**, −91.9; **11**, −87.0 ppm. Figure 1 shows the ^{29}Si NMR spectrum of the $Me_3CC{\equiv}CSiMe_3$-derived silirene **10** in $Me_3CC{\equiv}CSiMe_3$ solution. The intense resonance at −20 ppm is due to

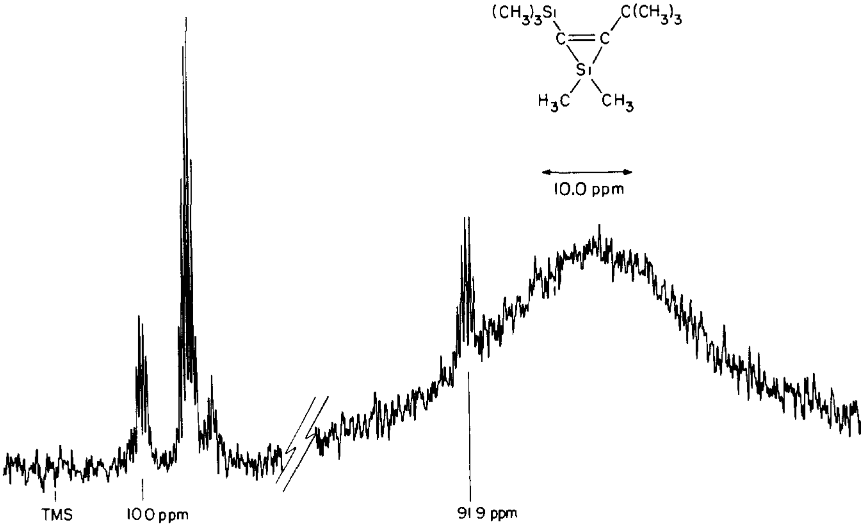


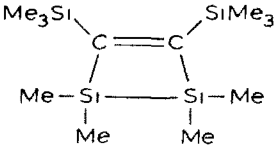
Fig. 1. ^{29}Si NMR spectrum of $Me_3CC{\equiv}CSiMe_3$-derived silirene **10** in $Me_3CC{\equiv}CSiMe_3$ solution.

the Me_3Si silicon atom of the solvent; that at −10 ppm is due to the Me_3Si group of the silirene. The high-field resonance at −91.9 ppm is due to the silicon atom of the silirene ring. The broad, high-field resonance is the "glass peak" due to the silicon atoms in the glass NMR tube.

The oxidation and some simple ring cleavage reactions of silirenes **7**–**11** were studied. All reactions which were observed involved cleavage of the Si–C bond of the silirene ring.

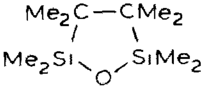
As noted, the air oxidation of bulk samples of silirene **7** results in ignition of the sample, so the oxidation is a vigorous, very exothermic reaction. When oxygen was bubbled through a dilute solution of silirene **7** in benzene at room temperature, an exothermic reaction was observed, and cooling was necessary. The solution became blue and this color persisted for 5 h, ultimately fading to yellow. GLC analysis of such oxidized solutions showed the presence of $Me_3SiC{\equiv}CSiMe_3$ in 76–100% yield and no other volatile products. The fate of the Me_2Si unit was not determined.

In the preparation of 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene by the thermolysis of hexamethylsilirane in the presence of bis(trimethylsilyl)acetylene the use of an excess of the silirane must be avoided since the Me_2Si extruded in the thermal decomposition of the silirane can insert into the Si–C bond of the silirene. This was shown in an experiment in which a mixture of ~ 5 mmol of hexamethylsilirane and 1.34 mmol of silirene **7** in benzene was heated at 70 °C for 18 h. Two products were obtained: octamethyl-1,2-disilacyclobutane (36% based on the silirane), the product of the insertion of Me_2Si into hexamethylsilirane [2a] and 1,1,2,2-tetramethyl-3,4-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene, (**12**) (55% based on **7**). The latter is the product of Me_2Si insertion into a Si–C bond of silirene **7**. Thus the suggestion of Atwell and Uhlmann [8] that **4** had been formed by Me_2Si insertion into tetramethylsilirene is given credence.



(12)

Identification of **12** is based on spectroscopy. In its ^{29}Si NMR spectrum the resonance due to the ring silicon atoms is in the "normal" range, $\delta(Si)$ 12.5 ppm (vs. $\delta(Si)$ 11.6 for octamethyl-1,2-disilacyclobutane [2a]). Its mass spectrum showed the molecular ion and the most intense fragment ion corresponded to $Me_4Si_2^+$. Like octamethyl-1,2-disilacyclobutane, disilacyclobutene **12** is very sensitive to oxygen. When such a hexamethylsilirane/silirene **7** thermolysis reaction mixture was exposed to oxygen the observed products were the cyclic disiloxanes **13** [2a] and **14**. The very



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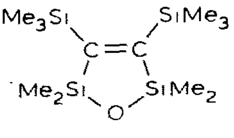
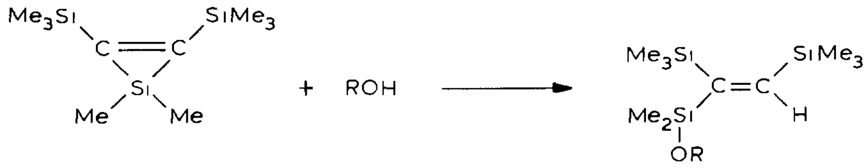


(14)

air-sensitive, disilacyclobutene **12** is very stable thermally, surviving a heating period of 20 h at 175 °C without decomposition.

1,1-Dimethyl-2,3-bis(trimethylsilyl)silirene reacted exothermally with water, methanol, ethanol and n-propanol (eq. 5). With the more sterically hindered isopropanol the reaction with **7** was slow at room temperature; after 24 h the yield of **15** ($R = Me_2CH$) was 41%. In another experiment, after **7** and isopropanol had been allowed to react at room temperature for 2 h, methanol was added; **15** ($R = Me_2CH$) was obtained in only 18% yield while **15** ($R = Me$) was obtained in 45% yield. Silirene **7** was cleaved also by acetic acid in a strongly exothermic reaction to give $Me_3SiCH{=}C(SiMe_3)(SiMe_2OAc)$ in 79% yield.

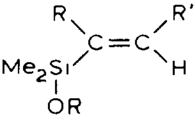


(5)

(R = H, CH_3, Et, n-Pr, i-Pr)

(15)

All the other silirenes (**8**–**11**) react exothermally with water, methanol and ethanol. In the case of **9**, **10** and **11**, all of which are unsymmetrically substituted on the C=C bond, two products are, in principle, possible, **16** and **17**. In some cases these reactions were regioselective; in other cases they were not (Scheme 2, eq. 6–8).



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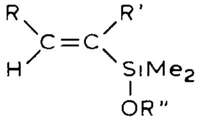

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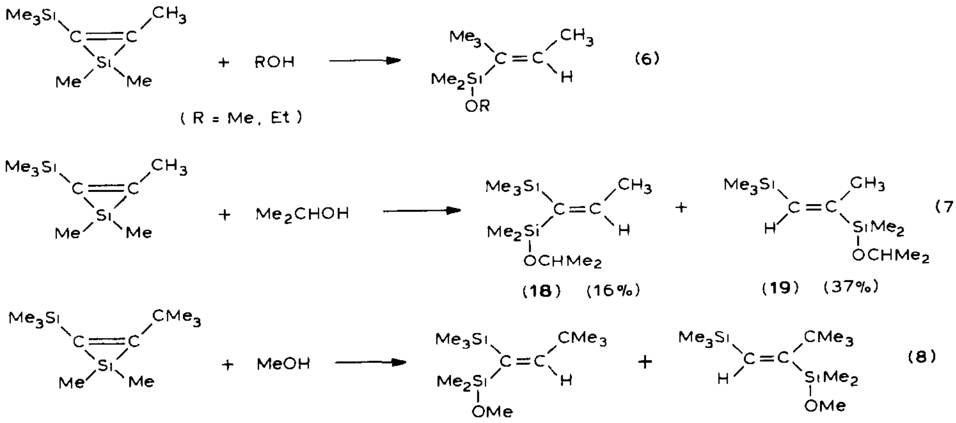
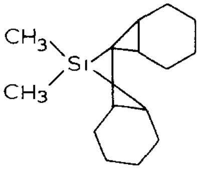
SCHEME 2



It would appear that steric factors are of importance in these reactions, but not enough examples are available to permit useful discussion.

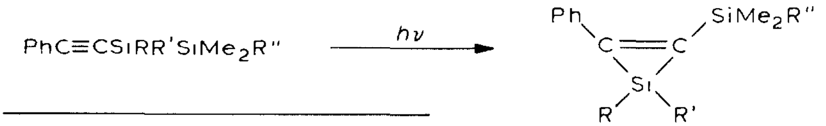
The identification of products of type **15** and **16** is based on their proton NMR spectra. In the spectrum of **18**, the $=CCH_3$ and the $=CH$ protons are coupled with J 6.6 Hz (characteristic of such *gem*-coupling [14]) and the $=CH$ resonance is at δ 6.8 ppm. In the ^1H NMR spectrum of **19**, the $=CCH_3$ and $=CH$ protons also are coupled, but with J 2 Hz (characteristic of *trans*-allylic coupling [14]), and $\delta(=CH)$ 6.1 ppm. This difference in $=CH$ chemical shifts in the NMR spectra of **18** and **19** was useful in assignment of structures to **20** and **21** since the vinyl proton resonances were singlets.

This study has demonstrated the hyperreactivity of silacyclopropenes in which the ring silicon atom bears two methyl substituents (i.e., **7**–**11**). That the silirene ring should be strained and highly reactive is suggested by a simple calculation of the C–Si–C angle in the SiC_2 ring. If one assumes, as a first approximation, Si–C and C=C bond distances as found for $Me_3SiCH=CH_2$ (1.853 and 1.347 Å, respectively) [15], then one may calculate the C–Si–C angle in a silacyclopropene to be ~ 43°. This angle is smaller than the 49.2° found for the endocyclic C–Si–C angle in the silacyclopropane **22** for which structural data are available [16]. All of our previous studies of silacyclopropanes have shown them to have exceptionally reactive Si–C bonds [2,4,17], so that silirenes **7**–**11** are so highly reactive is not at all surprising.



(**22**)

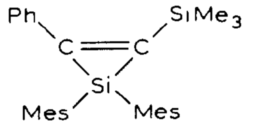
After our initial reports of the isolation and chemistry of silirene **7**, Kumada, Ishikawa and their coworkers have reported a second, fairly general route to silicyclopropenes as typified by the reaction shown in eq. 9 [18]. These compounds



(9)

R	R'	R''
Me	Me	Me
Me	Ph	Me
Ph	Ph	Me
mesityl	mesityl	Me
Me	Me	Et
Me	Me	Me_3C
Me	Me	Ph
Me	mesityl	Me
Me	Me_3Si	Me

were characterized by proton NMR spectroscopy and, in some cases, by high resolution mass spectrometry. None were submitted to combustion analysis and, unfortunately, ^{29}Si NMR data were not reported. The X-ray crystal structure of **23** was determined [19]. The C–Si–C bond angle was found to be 43.5°, in surprisingly



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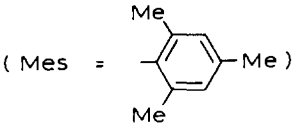
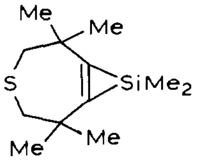


good agreement with our "back-of-the-envelope" calculation. The C=C bond distance was determined to be 1.349 Å and the Si–C bonds were of unequal length (1.800 and 1.839 Å). A theoretical study [20] determined the C–Si–C ring angle of silacyclopropenes to be 42.5°. While most of these silacyclopropenes appeared to be sensitive toward atmospheric oxygen and reactive toward methanol, **20** was very sterically hindered as a result of the two mesityl substituents, so that this compound could be purified by recrystallization from ethanol.

This photochemical route to silacyclopropenes was reported independently by another Japanese group [21]. Kumada, Ishikawa and their coworkers also prepared some other silacyclopropenes by the photochemical generation of phenyl(trimethylsilyl)silylene (from $(Me_3Si)_3SiPh$) in the presence of internal acetylenes [22]. More recently, Krebs and Berndt prepared silirene **24** by the generation of Me_2Si (via



(24)

hexamethylsilirane thermolysis or cyclo-$[Me_2Si]_6$ photolysis) in the presence of the appropriate cycloalkyne [23].

The elusive silacyclopropenes thus can be prepared by two general routes: silylene addition to appropriate acetylenes and the photochemically induced rearrangement of suitable alkynyldisilanes. Their thermal and kinetic stability may be "fine-tuned" by varying the substituents on the carbon atoms and the silicon atom of the silirene ring. The silirenes which we describe here are hyper-reactive and a further account of their exceptional reactivity is in preparation.

Experimental

General comments

Infrared spectra were recorded using a Perkin–Elmer Model 457A infrared spectrophotometer, proton magnetic resonance spectra using either a Varian Associates T60, a Perkin–Elmer R-20 or R-22 spectrometer. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Chloroform and dichloromethane often were used as alternative internal standards. ^{13}C NMR spectra were obtained with a Jeol FNM HFX-60Q spectrometer. ^{29}Si NMR spectra using a Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 computer. Gas–liquid chromatography (GLC) was used routinely for isolation of pure samples, determination of purity of distilled samples and for yield determinations by the internal standard method. All columns were packed on acid-washed, dimethyldichlorosilane-treated Chromosorb W. In the case of the silirenes, it was not found necessary to condition the column with large amounts of material in order to obtain consistent results. The silirene samples were collected in a U-shaped glass capillary tube, using a Dry-Ice/acetone bath to condense the sample. Immediately after removing the capillary from the exit port of the GLC column the ends of the tube were plugged with high vacuum stopcock grease and the capillaries then were sealed in a flame about 1 inch from the ends. Samples for spectroscopy were prepared in an inert atmosphere box.

All solvents used were rigorously dried. All reactions were carried out under an atmosphere of prepurified nitrogen, or more usually, argon. All glassware was flame-dried under a stream of nitrogen before use. Reactive reagents were transferred by syringe or cannula.

The preparations of hexamethylsilirane and its precursors have been described in detail, as have the methods used for the determination of the yield of hexamethylsilirane, for the preparation of solutions of hexamethylsilirane in solvents other than THF and for the handling hexamethylsilirane and its solutions [2]. We stress again the high reactivity of hexamethylsilirane and of the silirenes prepared in this study towards atmospheric oxygen and moisture and the absolute need to perform all operations involving these compounds with complete exclusion of air in rigorously dried glassware using rigorously dried and degassed solvents.

Preparation of silacyclopropenes

1,1-Dimethyl-2,3-bis(trimethylsilyl)silirene (7)

A solution of 1.3 mmol of hexamethylsilirane in 4 ml (2.8 g, 28 mmol) of bis(trimethylsilyl)acetylene (Silar) in a 50 ml three-necked flask (equipped with a reflux condenser topped with an argon inlet tube, a magnetic stir-bar, a glass stopper and a no-air rubber septum) was heated at 66 °C for 15 h. GC examination of the solution indicated the presence of one major product. This was collected (3 ft, 20% SE-30 on Chromosorb W, 125 °C) and identified as 7. Small samples of this product fumed vigorously on exposure to air and it was necessary to handle it under an inert atmosphere at all times. Analysis. Found: C, 52.19; H, 10.51. $C_{10}H_{24}Si_3$ calcd.: C, 52.55; H, 10.58%.

IR (thin film, cm^{-1}): 2960(vs), 2895(m), 2780(w), 1520(sh), 1505(m), 1500(m), 1435(w), 1400(w), 1250(vs), 1055(w), 975(vs), 865(vs), 840(vs), 780(vs), 755(s), 690(s), 625(s). (The IR spectrum of a sample which had been exposed to air developed a broad, medium intensity band at 1680 cm^{-1} and a broad band at 1050 cm^{-1}.)

^{1}H NMR (benzene-d_6, cyclohexane): δ 0.19 (s, 6H, ring Me_2Si), and 0.30 (s, 18H, Me_3Si).

^{13}C NMR (benzene-d_6), proton-decoupled: δ(C) −2.2 (ring $Si(CH_3)_2$, 0.40 ($Si(CH_3)_3$, and 189.6 (C=C). In the fully proton-coupled spectrum the Si–CH_3 resonances split into two overlapping quartets with $J(^{13}C-^1H)$ 119 Hz.

^{29}Si NMR (in $Me_3SiC{\equiv}CSiMe_3$ solution), proton-coupled: 8 of the expected 10 lines centered at −8.50 ppm for the $Si(CH_3)_3$ group Si atoms and 3 of the expected 7 lines centered at −106.2 ppm for the ring Si atom. In a fully decoupled spectrum, both of these resonances were singlets, with the 106.2 ppm signal inverted due to the negative nuclear Overhauser effect of the Si nucleus.

UV (pentane, ~ 0.0002 M): λ_{max} 345 nm ($\epsilon = 37$), 215 nm ($\epsilon = 2850$) and 205 nm ($\epsilon = 3450$).

Mass spectrum (70 eV), m/z (relative intensity): 230 (2, $M^+ + 2$), 229 (4, $M^+ + 1$), 228 (14, M^+), 214 (4), 213 (14), 170 (4), 157 (6), 156 (14), 155 (67), 1414 (5), 140 (16), 139 (3), 133 (3), 125 (8), 99 (4), 97 (11), 85 (3), 83 (13), 81 (4), 75 (5), 74 (9), 73 (100), 67 (7), 59 (9), 55 (6), 53 (5).

In another experiment, a solution of 1.96 mmol of hexamethylsilirane and 1.97 mmol of $Me_3SiC{\equiv}CSiMe_3$ in 3 ml of benzene was heated at 70 °C for 18 h. Addition of 400 μl of MeOH resulted in an exothermic reaction. GLC analysis showed the presence of tetramethylethylene (86% yield), $Me_2CHCMe_2SiMe_2OMe$ (10% yield), $Me_3SiCH{=}C(SiMe_3)(SiMe_2OMe)$ (59% yield) and some $Me_3SiC{\equiv}CSiMe_3$. Thus even in a 1/1 reaction the silacyclopropene yield is substantial.

In order to explore its chemistry, larger amounts of silirene **7** were needed and its preparation was carried out on a larger scale. A typical reaction is described.

A solution of 59.0 mmol of hexamethylsilirane in 26.5 ml (120 mmol) of $Me_3SiC{\equiv}CSiMe_3$ was stirred and heated at 70 °C for 18 h. The reaction mixture then was distilled (4 in. Vigreux column) at reduced pressure. A clear, colorless liquid boiling at 92–94 °C at 30 mmHg was collected in 64% yield and identified (^1H NMR, GLC retention time) as silirene **7**). Such larger samples, it was found, are spontaneously flammable in air.

*1,1-Dimethyl-2,3-bis(dimethylsilyl)silirene (**8**)*

A solution of 7.0 mmol of hexamethylsilirane in 2.5 ml of bis(dimethylsilyl)acetylene [24] was stirred and heated under argon at 70 °C for 18 h. GLC analysis of the reaction mixture (4.5 ft 20% SE-30, MIT isothermal GLC instrument, 108 °C) showed the presence of one product, **8**, which was collected. This compound, like **7**, is an extremely air- and moisture-sensitive liquid, which requires extreme care in all handling and transfer operations. The product yield (~ 50%) was determined indirectly by means of a methanolysis reaction (see below). Analysis. Found: C, 47.68; H, 10.10. $C_8H_{20}Si_3$ calcd.: C, 47.92; H, 10.05%.

IR (thin film, cm^{-1}): 2960(s), 2900(m), 2700(w), 2120(vs), 1520(sh), 1510(m), 1505(m), 1490(sh), 1425(m), 1410(w), 1250(vs), 1075(m), 980(s), 880(broad, s), 830(s), 810(m), 780(s),760(m), 725(m), 700(m), 655(m), 630(m). Upon exposure of the sample to air, a new band at 1689 cm^{-1} as well as a strong, broad band at 1050 cm^{-1} developed in the IR spectrum.

^1H NMR (benzene-d_6): δ 0.17 (s, 6H, ring Me_2Si), 0.37 (d, J 3.8 Hz, 12H, Me_2HSi) and 4.87 (hept., J 3.8 Hz, 2H, Me_2SiH).

^{29}Si NMR (in $Me_2HSiC{\equiv}CSiMe_2H$) (coupled spectrum): d of hept. centered at δ(Si) −25.3, J(Si–H) 200 Hz (MeHSi); 3 of the expected 7 lines (broadened) centered at δ(Si) −102.1 (ring Si).

Mass spectrum (m/z, relative intensity): 210 (11, $M^+ + 1$), 200 (33, M^+), 186 (13), 185 (56), 155 (20), 142 (18), 141 (100), 127 (20), 126 (18), 125 (13), 116 (87), 111 (19), 102 (17), 83 (30), 73 (53), 59 (34).

*1,1,2-Trimethyl-3-trimethylsilylsilirene (**9**)*

A solution of 6.0 mmol of hexamethylsilirane in 2.5 ml of propynyltrimethylsilane [25] was stirred and heated under argon at 70 °C for 18 h. At the end of this time, the ^{29}Si NMR spectrum (proton-coupled) of the solution showed signals (5 of the expected 7 lines) centered at δ(Si) −88.6 ppm (ring Si) and at δ(Si) −88.6 ppm (ring Si) and at δ(Si) −7.8 ppm (8 of the expected 10 lines, Me_3Si), indicative of the presence of silirene **9**. The GLC retention time of **9** is approximately the same as those of the ubiquitous minor by-products of the hexamethylsilirane preparation [2]. Thus pure samples of **9** could not be isolated although it appeared to be stable to the GLC conditions used. On the basis of a separate methanolysis experiment (see below) the yield of **9** is around 55%.

1,1-Dimethyl-2-tert-butyl-3-trimethylsilylsilirene (10)

A solution of 6.0 mmol of hexamethylsilirane in 2.25 ml of 2,2-dimethylpropynyltrimethylsilane [24] was stirred and heated under argon at 70 °C for 18 h. GLC analysis of the reaction mixture showed the presence of one product, **10**, which was collected (3 ft 20% SE-30, MIT isothermal, 125 °C). The product is extremely air- and moisture-sensitive. Analysis. Found: C, 62.02; H, 11.39. $C_{11}H_{24}Si_2$ calcd.: C, 62.18; H, 11.39%.

IR (thin film, cm^{-1}): 2960(s), 2930(m), 2900(s), 2865(m), 1575(sh), 1570(s), 1565(sh), 1475(m), 1457(m), 1405(w), 1385(m), 1360(s), 1300(w), 1255(sh), 1248(vs), 1215(w), 1200(w), 1055(m), 1015(m), 850(broad, vs), 780(s), 755(m), 690(m), 660(m), 610(m).

^1H NMR (benzene-d_6): δ 0.27 (s, 6H, Me_2Si), 0.39 (s, 9H, Me_3Si) and 1.34 (s, 9H, Me_3C).

^{29}Si NMR (in $Me_3CC{\equiv}CSiMe_3$) (proton-coupled): 5 of the expected 7 lines centered at δ(Si) −91.9 ppm (ring Si) and 6 of the expected 10 lines centered at −10.0 ppm (Me_3Si).

Mass spectrum, m/z (relative intensity): 213 (3, $M^+ + 1$), 212 (13, M^+), 197 (6), 156 (14), 155 (79), 139 (31), 125 (8), 124 (70, 123 (13), 109 (14), 97 (42), 83 (21), 73 (100), 69 (13), 67 (17), 59 (20).

The yield of **10**, based on a separate methanolysis experiment, was about 75% (see below).

1,1,2-Trimethyl-3-tert-butylsilirene (11)

A solution of 7.5 mmol of hexamethylsilirane in 2.5 ml of 4,4-dimethyl-2-pentyne, $Me_3CC{\equiv}CMe$, prepared by reaction of $Me_3CC{\equiv}CLi$ with dimethyl sulfate, was stirred and heated under argon at 70 °C for 18 h. At the end of this time, the ^{29}Si NMR spectrum of the reaction mixture showed a signal (3 lines of the expected 7) centered at δ(Si) −87.0 ppm, attributable to the ring silicon atom of silirene **11**. Pure samples could not be isolated by GLC. A separate methanolysis experiment (see below) indicated that the yield of **11** was around 30%.

Thermolysis of hexamethylsilirane in the presence of 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene

A solution of 5.11 mmol of hexamethylsilirane and 1.34 mmol of silirene **7** in 3 ml of dry benzene was stirred and heated at 70 °C under argon for 18 h. GLC analysis showed that two products had been formed. The product of shorter retention time was collected (1.5 ft 20% SE-30, 117 °C) and was identified as octamethyl-1,2-disilacyclobutane, m.p. 71–71.5 °C, by comparison with the authentic sample [2a]. The yield was 36% based on the hexamethylsilirane charged.

The product of longer retention time was collected (3.5 ft 20% SE-30, 117 °C) and identified as 1,1,2,2-tetramethyl-3,4-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene (**12**) m.p. 61–61.5 °C. The yield, as determined by GLC, was 0.74 mmol, 55% based on silirene charged. Analysis Found: C, 50.20; H, 10.53. $C_{12}H_{30}Si_4$ calcd.: C, 50.27; H, 10.55%.

IR (solid film, cm^{-1}): 2960(s), 2900(s), 2970(sh), 1460(m), 1425(w), 1395(m), 1307(w), 1257(sh), 1245(s), 944(s), 865(s, broad), 850(s, broad), 830(s, broad), 760(m), 718(w), 685(m), 660(m), 623(w).

Raman (capillary, cm^{-1}): 2968(s), 2891(vs), 1424(m), 1399(m, broad), 1260(w), 1243(m), 947(w), 866(w), 835(w), 755(w), 729(w), 675(sh), 662(vs), 617(s), 425(vs), 374(vs), 282(w), 250(m).

^1H NMR (benzene-d_6): δ 0.32 (s, 18H, $SiMe_3$), 0.46 (s, 12H, $SiMe_2$).

^{13}C NMR, proton decoupled (benzene-d_6): $\delta(C)$ 200.8 (s, C=C), 1.4 (s, Me_3Si), 0.6 (s, Me_2Si). (A delay between pulses of 4 sec was required in order to observe the ring carbon atom signal.)

^{29}Si NMR, proton-coupled (benzene-d_6): $\delta(Si)$ 12.5 (3 of expected 7 lines, ring Si), 10.2 (8 of expected 10 lines, Me_3Si).

Mass spectrum, 70 eV, m/z (relative intensity): 287 ($M^+ + 1$, 4), 286 (M^+, 12), 271 ($M^+ - 15$, 5), 213 ($M^+ - Me_3Si$, 8), 155(8), 117 (15), 116 ($Me_4Si_2^+$, 100), 101 (7), 73 (58), 59 (5).

In another such reaction, upon completion of the thermolysis, oxygen was bubbled through the solution for 1 h. There was an immediate exothermic reaction which subsided within 15 min, as well as the appearance of an immediate blue color which turned pale green after 30 min. GLC analysis showed the presence of two products. The product with the shorter retention time was collected (1.5 ft 20% SE-30, 117 °C) and identified as cyclodisiloxane **13** by comparison of its GLC retention time and its proton NMR spectrum with those of an authentic sample [2]. The yield of **13** was 28% based on hexamethylsilirane charged. The second product was collected (same GLC conditions) and identified as the unsaturated cyclodisiloxane **14**, m.p. 62–64 °C. Found: C, 47.92; H, 10.03. $C_{12}H_{30}OSi$ calcd.: C, 47.61; H, 9.99%.

^1H NMR (CCl_4/CH_2Cl_2): δ 0.20 (s, all $Si-CH_3$). Mass spectrum, 70 eV, m/z (relative intensity): 303 ($M^+ + 1$, 8), 302 (M^+, 22), 288 (11), 287 ($M^+ - 15$, 31), 274 (6), 231 (18), 230 (10), 229 (36), 207 (9), 119 (10), 155 (12), 147 (41), 133 (23), 131 (10), 117 (21), 116 (2), 73 (100), 59 (21).

The analytical sample was obtained by separate oxidation of a benzene solution of pure **12**.

Hydrolysis and alcoholysis reactions

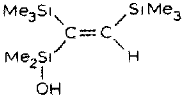
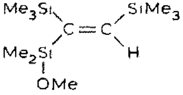
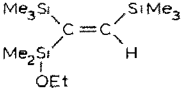
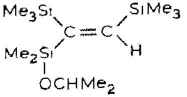
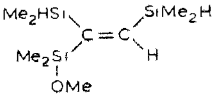
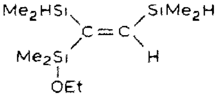
Hydrolysis of 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene. A solution of 1.34 mmol of hexamethylsilirane in 4 ml of bis(trimethylsilyl)acetylene was stirred and heated under argon at 73 °C for 15 h. The reaction mixture was cooled to room temperature and then 0.2 ml of water in 2 ml of THF was added slowly by syringe. An exothermic reaction was noted. GLC analysis showed the presence of one product, the silanol **15** (R = H), n_D^{25} 1.4770, in 70% yield. Analysis. Found: C, 49.10; H, 10.68. $C_{10}H_{26}OSi$ calcd.: C, 48.70; H, 10.63%.

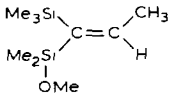
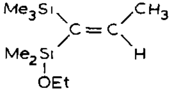
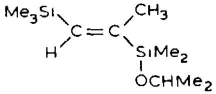
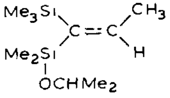
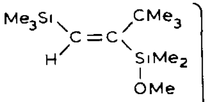
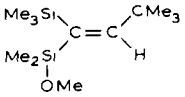
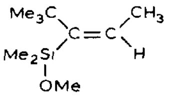
IR (thin film): $\nu(OH)$ 3690 cm^{-1}.

^1H NMR (CCl_4/CH_2Cl_2): δ 0.17 (s, 24H, $Si-CH_3$), 1.30 (s, 1H, OH) and 7.35 (s, 1H, =CH).

(Continued on p. 138)

TABLE 1. SILIRENE HYDROLYSIS AND ALCOHOLYSIS PRODUCTS

Product	From silirene	(Yield) (%)	n_D^{25}	Analysis (Found (calcd.) (%)) C	Analysis (Found (calcd.) (%)) H	^{1}H NMR, δ (CCl_4 solution, CH_2Cl_2 internal standard)
	**7**	70	1.4770	49.10 (48.70)	10.68 (10.63)	0.17 (s, 24H, Si–CH_3), 1.30 (s, 1H, OH), 7.35 (s, 1H, =CH)
	**7**	72	1.4575	50.80 (50.69)	10.98 (10.83)	0.15 (s, 6H, $SiMe_2$), 0.18 (s, 18H, $SiMe_3$), 3.32 (s, 3H, OMe), 7.30 (s, 1H, =CH)
	**7**	75		52.03 (52.47)	10.91 (11.01)	0.03 (s, 6H, $SiMe_2$), 0.07 (s, 18H, $SiMe_3$), 1.10 (t, *J* 6 Hz, CH_3 of Et) 3.58 (q, 2H, OCH_2), 7.25 (s, 1H, =CH)
	**7**	41	1.4548	53.73 (54.09)	11.03 (11.18)	0.15 (s, 6H, $SiMe_2$), 0.18 (s, 18H, $SiMe_3$), 1.13 (d, *J* 6 Hz, CMe_2), 4.08 (hept, *J* 6 Hz, 1H, OCH), 7.38 (s, 1H, =CH)
	**8**	50	1.4554	46.45 (46.48)	10.34 (10.40)	complex pattern, 0.2–0.3 (18H, Si–CH_3), 3.40 (s, 3H, OMe), 4.21–4.48 (m, 2H, SiH), 7.27 (d, *J* 5Hz, 1H, =CH)
	**8**	48	1.4523	48.84 (48.71)	10.59 (10.63)	complex pattern, 0.19–0.3 (18H, Si–CH_3), 1.24 (t, *J* 7 Hz, 3H, CH_3 of Et), 3.64 (q, *J* 7 Hz, 2H, OCH_2) 4.09-4.39 (m, 2H, SiH), 7.32 (d, *J* 5 Hz, 1H, =CH)

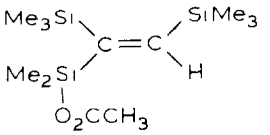
	**9**	56	1.4464	53.22 (53.39)	10.50 (10.96)	0.14 (s, 6H, $SiMe_2$), 0.20 (s, 9H, $SiMe_3$), 1.94 (d, *J* 6 Hz, 3H, $=CCH_3$), 3.34 (s, 3H, OMe), 6 79 (q, *J* 6 Hz, 1H, =CH)
	**9**	59	1.4455	55.60 (55.48)	11.26 (11.18)	0.13 (s, 6H, $SiMe_2$), 0.19 (s, 9H, $SiMe_3$), 1.18 (t, *J* 6.6 Hz, 3H, CH_3 of Et), 1.93 (d, *J* 6.6 Hz, 3H, $=CCH_3$), 3.60 (q, J 6.6 Hz, 2H, OCH_2), 6.84 (q, *J* 6.6 Hz, 1H, =CH)
	**9**	37	1.4342	57.09 (57.32)	11.40 (11.37)	0.25 (s, 15H, $SiCH_3$), 1.17 (d, *J* 6 Hz, 6H, CMe_2), 1.95 (d, *J* 2 Hz, 3H, $=CCH_3$) 3.99 (hept, *J* 6 Hz, 1H, OCH), 6.10 (q, *J* 2 Hz, =CH)
	**9**	16	1.4444	57.08 (57.32)	11.35 (11.37)	0.17 (s, 6H, $SiMe_2$), 0.22 (s, 9H, $SiMe_3$), 1.15 (d, *J* 6 Hz, 6H, CMe_2), 1.95 (d, *J* 6.6 Hz, 3H, $=CCH_3$), 3.95 (hept, *J* 6 Hz, 1H, OCH), 6.82 (q, *J* 6.6 Hz, 1H, =CH)
 (70 parts)  (30 parts)	**10**	75	1.4555	59.02 (58.94)	11.57 (11.54)	0.20, 0.23, 0.27 (15H, $SiCH_3$), 1.15, 1.18 (9H, CCH_3), 3.34, 3.38 (3H, OMe), 6.10, 6.82 (1H, =CH), (the signals at 1.18, 3.38 and 6.10 ppm are attributed to the major isomer).
	**11**	30	1.4466	64.31 (64.44)	12.01 (11.90)	0.12 (s, 6H, $SiMe_2$), 1.17 (s, 9H, CMe_3), 1.82 (d, *J* 7 Hz, 3H, $=CCH_3$), 3.29 (s, 3H, OMe), 5.87 (q, *J* 7 Hz, 1H, =CH)

Alcoholysis reactions. The following general procedure was followed. The silirene was prepared by heating hexamethylsilirane in a large excess of the acetylene (under argon, generally for 18 h at 70 °C). The reaction mixture then was cooled to room temperature and an excess of the respective alcohol was added by syringe. In most cases an exothermic reaction occurred. The product then was isolated by GLC and identified by analysis and spectroscopy. Table 1 gives yields, refractive indexes, analyses and proton NMR spectra.

IR spectra are given in the MIT Ph.D. theses of D.C.A. and S.C.V.

Reaction of silirene 7 with acetic acid

The silirene was prepared by heating 4.72 mmol of hexamethylsilirene in 3.0 ml of bis(trimethylsilyl)acetylene at 70 °C for 18 h. The solution was cooled to room temperature and 400 μl of glacial acetic acid was added by syringe. A strongly exothermic reaction was observed. GLC analysis (1.5 ft 20% SE-30, 117 °C) showed the presence of one product (79%) which was collected and identified as:



n_D^{25} 1 4622

Analysis. Found: C, 49.88; H, 9.88. $C_{12}H_{28}O_2Si$ calcd.: C, 49.94; H, 9.78%.

^{1}H NMR (CCl_4/CH_2Cl_2): δ 0.20 (s, 18H, $SiMe_3$), 0.34 (s, 6H, $SiMe_2$), 2.02 (s, 3H, $C(O)CH_3$), 7.40 (s, 1H, =CH).

IR (film, cm^{-1}): ν(C=O) 1730 cm^{-1}.

References and notes

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