

PHOTOCHEMICALLY GENERATED SILICON–CARBON DOUBLE-BONDED INTERMEDIATES

XII *. SOME PROPERTIES OF SILACYCLOPROPENES AND SILAPROPADIENES PRODUCED BY PHOTOLYSIS OF ETHYNYLPOLYSILANES

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Summary

The photolysis of six ethynyl-substituted polysilanes has been investigated in the presence or absence of methanol. Irradiation of 1-ethynyl-2-phenyl- and 1-ethynyl-1-phenyltetramethyldisilane (I and II), 1-ethynyl-1,1-diphenyltrimethyldisilane (III) and 2-ethynylheptamethyltrisilane (V) in the presence of methanol produced methoxysilanes arising from the corresponding reactive silacyclopropene and silapropadiene intermediates. Irradiation of 1-ethynylheptamethyltrisilane (IV) led to the formation of dimethylsilylene, ethynylpentamethyldisilane and 1,1-dimethyl-2-pentamethyldisilanyl-1-silacyclopropene intermediate. The photolysis of tris(trimethylsilyl)ethynylsilane (VI) in the presence of methanol produced 1-trimethylsilyl-1-bis(trimethylsilyl)methoxysilylethene and hexamethyldisilane. Photolysis of II and III in the absence of a trapping agent gave the respective bis(silyl)acetylenes, via a 1,2-hydrogen shift, from the transient silacycloprenes, in moderate yields, whereas the yields of the rearranged acetylenes from IV and V were low.

Introduction

The chemistry of silacycloprenes constitutes one of the most active areas of current research. In spite of high strain energy, the silacycloprenes isolated to date are thermally rather stable [1–5]. Recently we have demon-

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strated that silacyclopropenes can be produced photochemically by two different methods, viz., one involves the reaction of photochemically generated trimethylsilylphenylsilylene with alkynes [6] and the other comprises the photolysis of phenylethynylpentamethyldisilane [5]. By using these methods, we prepared several types of silacyclopropenes and investigated their chemical behavior [6,7]. As part of a continuing investigation into the chemistry of the silicon-containing small ring compounds, we have now initiated systematic studies of the photochemical behavior of alkynylpolysilanes. In this paper, we report some properties of silacyclopropenes and silapropadienes produced from the photolysis of ethynylpolysilanes.

Results and discussion

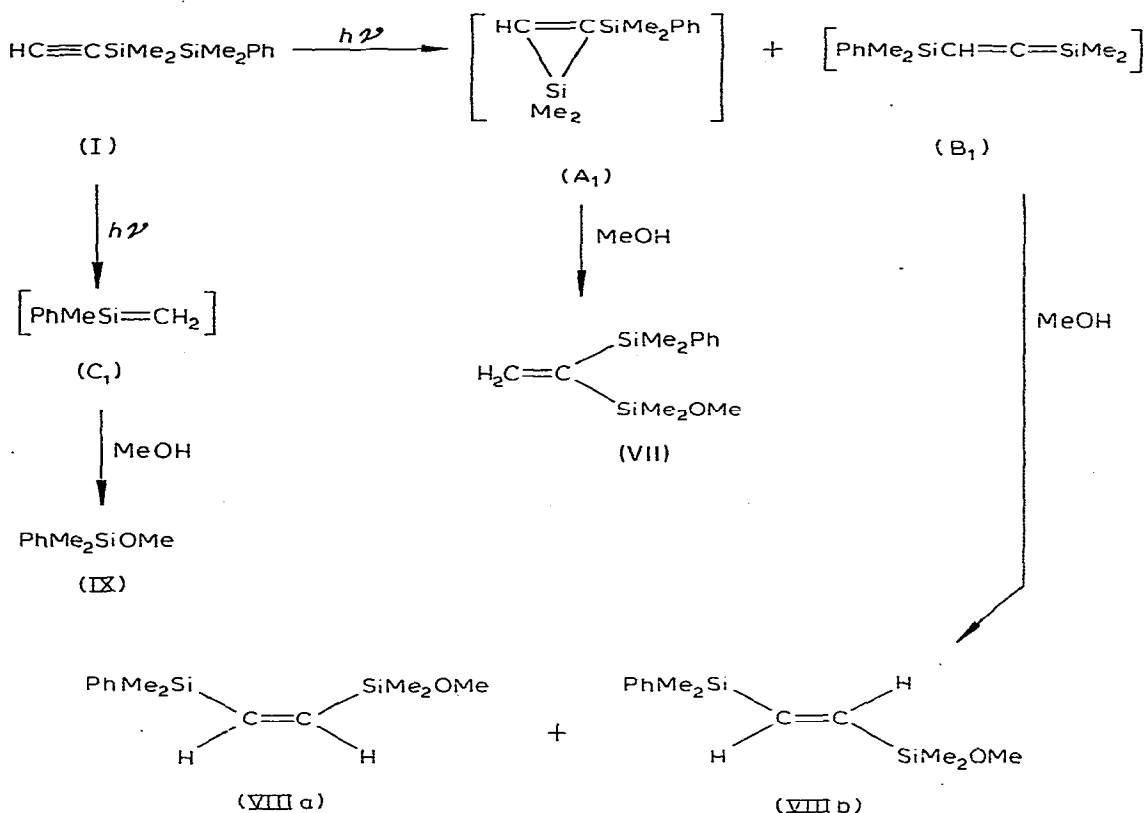
The starting ethynylpolysilanes, 1-ethynyl-2-phenyltetramethyldisilane (I), 1-ethynyl-1-phenyltetramethyldisilane (II), 1-ethynyl-1,1-diphenyltrimethyldisilane (III), 1-ethynylheptamethyltrisilane (IV), 2-ethynylheptamethyltrisilane (V) and tris(trimethylsilyl)ethynylsilane (VI) were prepared by the reaction of ethynylmagnesium bromide with the corresponding chloropolysilanes.

Photolysis of ethynylphenyldisilanes

In marked contrast to photolysis of phenylethynylpentamethyldisilane, which leads to stable 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene [3], photolysis of the ethynyl-substituted disilanes and polysilanes in the present study has proved to produce no stable silacyclopropenes. When a hexane solution of 1-ethynyl-2-phenyltetramethyldisilane (I) was photolyzed with a low-pressure mercury lamp in the presence of methanol for 3 h at room temperature, four products, 1-methoxydimethylsilyl-1-dimethylphenylsilyl-ethene (VII), *cis*- and *trans*-1-methoxydimethylsilyl-2-dimethylphenylsilyl-ethene (VIIIa and VIIIb) and methoxydimethylphenylsilane (IX), were obtained in 11, 10, 6 and 30% yields, respectively, in addition to 16% of the starting ethynyldisilane I. The formation of VII, VIIIa, VIIIb and IX can be best explained in terms of simultaneous production of three different types of intermediate, silacyclopropene (A_1), silapropadiene (B_1) and silaethene (C_1), followed by reaction with methanol, as shown in scheme 1. The reaction of silacyclopropene A_1 with methanol affords product VII, while that of silapropadiene B_1 with methanol gives two products, VIIIa and VIIIb. In the methanolysis of the silacyclopropenes which we have investigated to date, it has always been observed that the less substituted silicon-carbon bond is cleaved preferentially [6]. Consequently, VIIIb is thought to be produced mainly from silapropadiene B_1 , but not from silacyclopropene A_1 . Silaethene intermediate C_1 reacts with methanol to yield IX. The formation of this silaethene was confirmed by the photolysis of I in the presence of methanol- d_1 , which gave mono-deuterated IX of high isotopic purity (88%) in 25% isolated yield, in addition to mono-deuterated VII, VIIIa and VIIIb.

All products with the exception of VII and VIIIb could be isolated by preparative GLC. Attempts to separate VII from VIIIb using several different kinds of columns (polyethylene glycol, SE-30, QF-1, Silicone DC and Apiezon L) were unsuccessful. Therefore, the identification of VII and VIIIb, and the

SCHEME 1

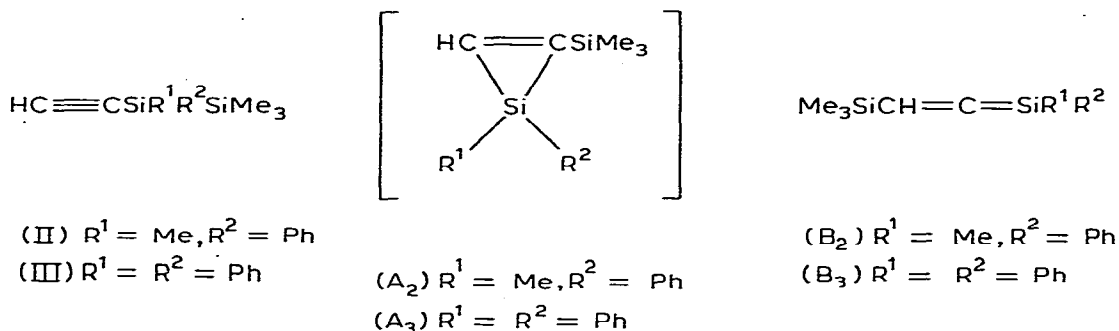


estimation of the ratio of both compounds were done by analyzing the ¹H NMR spectrum of the mixture. Irradiation of I in the absence of methanol under similar conditions, followed by treatment of the resulting mixture with methanol without irradiation, afforded only non-volatile substances. No methoxysilane VII arising from silacyclopropene A₁ was detected either by GLC or by spectroscopic analysis. This result indicates that silacyclopropene A₁ is unstable under the photolysis conditions used. The fact that the photolysis of I in the absence of methanol in isopropylbenzene did not afford bicumyl clearly indicates the absence of radical intermediates* in the reaction mixture. In order to obtain further insight into the process of decomposition of silacyclopropene A₁, we carried out the photolysis of I in the presence of a large excess of diethylmethylsilane as a silylene quencher. No 1,1-diethyl-1,2,2-trimethyldisilane, which would be expected from insertion of dimethylsilylene into the silicon-hydrogen bond, was detected by GLC analysis. This suggests that the photochemical decomposition of A₁ does not involve the extrusion of dimethylsilylene.

Similar photolysis of 1-ethynyl-1-phenyltetramethyldisilane (II) in the pres-

* One referee suggested an alternative mechanism involving diradical intermediates such as Me₂PhSiCH=C-SiMe₂ and HC=C(SiMe₂Ph)SiMe₂ in order to explain the production of compounds VIIa-VIIIb and VII, respectively. However, we have never obtained evidence for this alternative.

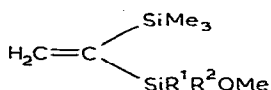
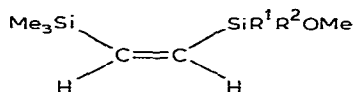
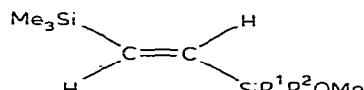
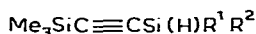
ence of methanol gave 1-trimethylsilyl-1-methoxymethylphenylsilylethene (X), *cis*- and *trans*-1-trimethylsilyl-2-methoxymethylphenylsilylethene (XIa and XIb) * in 29, 19 and 15% yields, respectively, in addition to 10% of the starting disilane II. Trimethylsilyl(methylphenylsilyl)acetylene (XII) was also obtained in 3% yield. One might consider the possibility that some of XIb was produced as an initial product by reaction of silacyclopropene A₂ with methanol. However, in the photolysis of 1-ethynylheptamethyltrisilane (IV) in the presence of methanol, only 1-pentamethyldisilanyl-1-methoxydimethylsilylethene (XVII) from the silacyclopropene (A₄) was formed, but not *trans*-1-pentamethyldisilanyl-2-methoxydimethylsilylethene (*vide infra*). This fact suggests that XIb is produced mainly from the methanolysis of silapropadiene B₂. The formation of compound XII may be rationalized in terms of a photochemical 1,2-hydrogen shift from a ring carbon to the silicon atom in silacyclopropene A₂. Again, products X and XIb could not be separated by GLC. However, the proton chemical shifts to be ascribed to XIb in the NMR spectrum of the mixture of X and XIb were identical with those of the authentic sample prepared by three-step reactions, viz., (i) hydrosilylation of trimethylsilylacetylene with methyl-dichlorosilane, (ii) partial phenylation of the resulting hydrosilylation product and (iii) methanolysis of the product. The hydrosilylation of trimethylsilylacetylene with dimethylchlorosilane in the presence of chloroplatinic acid has recently been reported [8].



In contrast to I, when II was photolyzed in the absence of methanol, trimethylsilyl(methylphenylsilyl)acetylene (XII) was produced in 25% yield as the sole volatile product. Treatment of the resulting photolysis mixture with methanol after irradiation was stopped did not afford methoxysilane X arising from silacyclopropene A₂.

Recently, we have reported that many of the silacyclopropenes produced from the reaction of photo-generated trimethylsilylphenylsilylene with alkynes can readily be trapped by methanol, even at room temperature [6]. An attempt to trap silacyclopropene A₂ by way of the photolysis of II at -78°C for 9 h in the absence of methanol, followed by methanolysis of the photolysis product at the same temperature, only resulted in the formation of 13% yield of XII. None of the expected methoxysilanes was detected.

* The photochemical isomerization of *cis* and *trans* was also observed. Thus the photolysis of XIa in hexane for 30 h afforded an equilibrium mixture consisting of XIa and XIb in the ratio of 4/6.

(X) $\text{R}^1 = \text{Me}, \text{R}^2 = \text{Ph}$ (XIII) $\text{R}^1 = \text{R}^2 = \text{Ph}$ (XIa) $\text{R}^1 = \text{Me}, \text{R}^2 = \text{Ph}$ (XIVa) $\text{R}^1 = \text{R}^2 = \text{Ph}$ (XIb) $\text{R}^1 = \text{Me}, \text{R}^2 = \text{Ph}$ (XIVb) $\text{R}^1 = \text{R}^2 = \text{Ph}$ (XII) $\text{R}^1 = \text{Me}, \text{R}^2 = \text{Ph}$ (XV) $\text{R}^1 = \text{R}^2 = \text{Ph}$

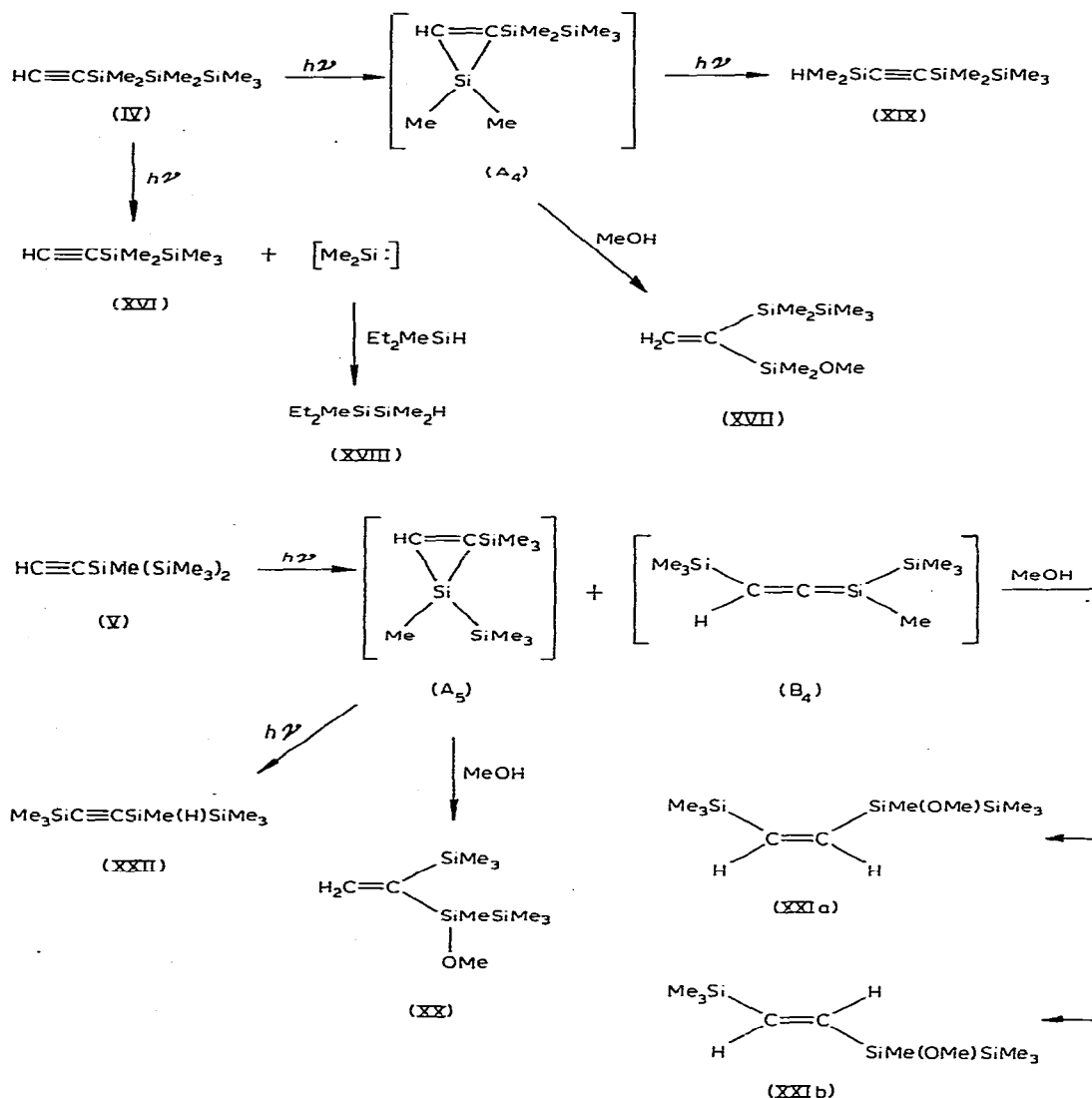
Photolysis of 1-ethynyl-1,1-diphenyltrimethyldisilane (III) afforded both silacyclopropene A_3 and silapropadiene B_3 which could be trapped by methanol. Thus, irradiation of III in the presence of methanol with a low-pressure mercury lamp gave 1-trimethylsilyl-1-methoxydiphenylsilylethene (XIII), and *cis*- and *trans*-1-trimethylsilyl-2-methoxydiphenylsilylethene (XIVa and XIVb) in 21, 23 and 21% yields, respectively, when 80% of the starting ethynyldisilane III was photolyzed. In this case, no trimethylsilyl(diphenylsilyl)acetylene (XV) arising from a 1,2-hydrogen shift in the silacyclopropene was detected by either GLC or NMR spectroscopic analysis, indicating that all of the silacyclopropene A_3 produced was trapped by methanol. Here also, isomers XIII and XIVb could not be separated from each other by GLC. However, since XIVb was obtained in the pure form by an independent route (see Experimental), the structure of XIII could be confirmed by eliminating the signals corresponding to XIVb in the ^1H NMR spectrum of the mixture. Irradiation of III in the absence of methanol under similar conditions produced photoisomerization product XV in 18% yield. No other volatile product was detected by GLC after treating the resulting photolysis products with methanol.

It is of interest to note that the introduction of the phenyl group(s) onto the ethynyl-substituted silicon atom of the disilanes leads to good yields of silapropadiene intermediates B 's, whereas the introduction of a phenyl group onto the other silicon atom results in formation of appreciable amounts of silaethene type intermediate C_1 .

Photolysis of 1-ethynyl- and 2-ethynylheptamethyltrisilane

The photolysis of 1-ethynylheptamethyltrisilane (IV) has been found to proceed simultaneously by two different pathways: one involves extrusion of dimethylsilylene to give photochemically stable ethynylpentamethyldisilane (XVI), and the other comprises a 1,2-shift of the pentamethyldisilanyl group producing silacyclopropene A_4 which is also unstable under the conditions used. Irradiation of a hexane solution of IV in the presence of methanol afforded XVI and 1-pentamethyldisilanyl-1-methoxydimethylsilylethene (XVII) in 22 and 20% yields, respectively, as the volatile products, in addition to 36% of the unchanged ethynyltrisilane IV. None of the silapropadiene intermediate which can be expected from a 1,3-shift of the pentamethyldisilanyl group was observed in this photolysis (scheme 2). The fact that methoxysilane XVII is the only methanolysis product indicates that the less substituted silicon-carbon bond in the silacyclopropene ring is cleaved exclusively. The

SCHEME 2



formation of dimethylsilylene was confirmed by the trapping technique using diethylmethylsilane. In this photolysis, an insertion product, 1,1-diethyl-1,2,2-trimethyldisilane (XVIII) [9], was produced in 16% yield. Irradiation of IV in the absence of methanol afforded a small amount of a volatile product (ca. 10% yield) which was identified as dimethylsilyl(pentamethyldisilanyl)acetylene (XIX). Its IR spectrum showed a strong absorption at 2145 cm^{-1} due to the silicon-hydrogen stretching vibration. Furthermore, the mass spectrum indicated the molecular ion at m/e 214 corresponding to the calculated molecular weight of $\text{C}_9\text{H}_{22}\text{Si}_3$. No other volatile products, such as a dimerization product, 1,4-disilacyclohexa-2,5-diene, were observed, but non-volatile polymeric substances were obtained after distillation of the photolysis mixture.

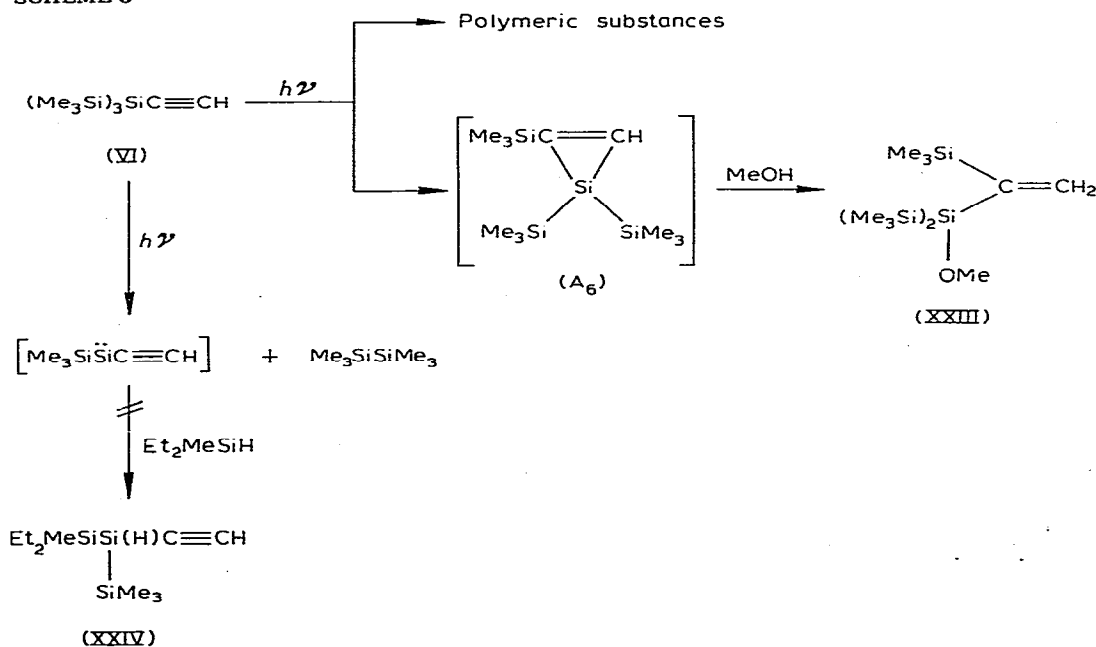
Irradiation of 2-ethynylheptamethyltrisilane (V) with methanol under identical photolysis conditions produced 1-trimethylsilyl-1-(1'-methoxytetramethyldisilanyl)ethene (XX), *cis*- and *trans*-1-trimethylsilyl-2-(1'-methoxytetramethyldisilanyl)ethene (XXIa and XXIb) in 32, 12 and 16% yields, respectively. In the absence of methanol, likewise, silacyclopropene A₅ mainly decomposed to give non-volatile products, in addition to a small amount of an isomerization product (XXII) (less than 6% yield) which was confirmed by its IR and mass spectrometric analysis.

Photolysis of tris(trimethylsilyl)ethynylsilane

Photolysis of a hexane solution of tris(trimethylsilyl)ethynylsilane (VI) in the presence of methanol gave only 5% yield of 1-trimethylsilyl-1-bis(trimethylsilyl)methoxysilylene (XXIII), along with 16% yield of hexamethyldisilane. When VI was photolyzed in the presence of diethylmethylsilane under similar conditions, none of the silicon-hydrogen bond insertion product was detected by GLC analysis, although hexamethyldisilane was obtained as the sole volatile product, in 12% yield (Scheme 3).

In conclusion, all of the silacyclopropene intermediates produced from ethynylpolysilanes described in this paper are photochemically unstable. We could detect none of these by either the GLC or the NMR technique. The silacyclopropene intermediates which have at least one phenyl substituent on the ring silicon atom, A₂ and A₃, underwent, if a quenching agent was absent, photoisomerization to give bis(silyl)acetylene derivatives in high yields (based on the silacyclopropene), whereas the silacyclopropenes whose ring silicon atom bears no phenyl group, A₄ and A₅, also afforded the rearranged acetylenes but only in low yields.

SCHEME 3



Experimental

Spectra

^1H NMR spectra were determined with a JEOL Model JNM MH-100 spectrometer in carbon tetrachloride solution containing cyclohexane as an internal standard. IR spectra of thin liquid films were determined using a Hitachi Model EPI-G3 grating spectrometer. Mass spectra were obtained on a JEOL Model JMS-D 300 equipped with a JNA-2000 data processing system. Ionising voltage was 24 eV for all compounds. An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separating the reaction products.

Preparation of 1-ethynyl-2-phenyltetramethyldisilane (I)

In a 300-cm³ three-necked flask fitted with a stirrer, dropping funnel, condenser and inlet tube for introducing acetylene was placed 200 cm³ of dry THF. To this was slowly added ethylmagnesium bromide in ether (15 cm³, 2.9 M) at room temperature with a stream of acetylene bubbling through the mixture, according to the reported method [10]. A solution of 4.0 g (17.5 mmol) of 1-chloro-2-phenyltetramethyldisilane [11] in 10 cm³ of THF was added to the ethynyl Grignard reagent and the mixture was refluxed for 5 h. The mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the water layer was extracted with ether. The organic layer and extracts were combined and washed with water. The mixture was dried over potassium carbonate. The solvents were evaporated and the residue was distilled under reduced pressure to give 3.1 g (81% yield) of I, b.p. 67°C/1 Torr, n_D^{20} 1.5226; IR (cm⁻¹) 3290, 2040, 1433, 1410, 1253, 1108; NMR (δ , ppm) 0.18 (s, 6H, Me₂Si), 0.40 (s, 6H, Me₂Si), 2.32 (s, 1H, HC $\equiv$ C) and 7.2–7.5 (m, 5H, ring protons) Found: C, 66.22; H, 8.47. C₁₂H₁₈Si₂ calcd.: C, 65.98; H, 8.31%.

Preparation of 1-ethynyl-1-phenyltetramethyldisilane (II)

A THF solution of 2.5 g (10.9 mmol) of 1-chloro-1-phenyltetramethyldisilane [12] was added to ethynylmagnesium bromide (29 mmol) prepared as described above. The mixture was refluxed for 5 h and hydrolyzed with dilute hydrochloric acid. The organic layer was washed with water and dried over potassium carbonate. Distillation gave 2.3 g (97% yield) of II, b.p. 70°C/2 Torr, n_D^{20} 1.5187; IR (cm⁻¹) 3290, 2040, 1435, 1255, 1108; NMR (δ , ppm) 0.13 (s, 9H, Me₃Si), 0.47 (s, 3H, MeSi), 2.48 (s, 1H, HC $\equiv$ C) and 7.2–7.7 (m, 5H, ring protons) Found: C, 65.70; H, 8.49. C₁₂H₁₈Si₂ calcd.: C, 65.98; H, 8.31%.

Preparation of 1-ethynyl-1,1-diphenyltrimethyldisilane (III)

This compound was prepared from 6 g (20.7 mmol) of 1-chloro-1,1-diphenyltrimethyldisilane [13] and ethynylmagnesium bromide (43.3 mmol) in 59% yield, b.p. 145–147°C/2 Torr, n_D^{20} 1.5715; IR (cm⁻¹) 3295, 2035, 1490, 1433, 1255, 1106; NMR (δ , ppm) 0.22 (s, 9H, Me₃Si), 2.64 (s, 1H, HC $\equiv$ C) and 7.2–7.7 (m, 10H, ring protons) Found: C, 72.63; H, 7.29. C₁₇H₂₀Si₂ calcd.: C, 72.79; H, 7.19%.

Preparation of 1-ethynylheptamethyltrisilane (IV) and 2-ethynylheptamethyltrisilane (V)

A solution of 22.5 g (0.1 mmol) of 1-chloroheptamethyltrisilane [11] in 50 cm³ of THF was treated with ethynylmagnesium bromide (0.15 mol) in THF. The reaction and work-up was similar to that described above. Distillation gave 16 g (78% yield) of IV, b.p. 77°C/22 Torr, n_D^{20} 1.4744; IR (cm⁻¹) 3300, 2040, 1405, 1252; NMR (δ , ppm) 0.13 (s, 9H, Me₃Si), 0.14 (s, 6H, Me₂Si), 0.24 (s, 6H, Me₂Si), 2.33 (s, 1H, HC≡C) (Found: C, 50.58; H, 10.09. C₉H₂₂Si₃ calcd.: C, 50.39; H, 10.33%). Similarly, compound V was prepared in 70% yield from 22.5 g (0.1 mol) of 2-chloroheptamethyltrisilane [11] and ethynylmagnesium bromide (0.15 mol) in THF, b.p. 75°C/19 Torr, n_D^{20} 1.4738; IR (cm⁻¹) 3300, 2040, 1405, 1255; NMR (δ , ppm) 0.16 (s, 18H, Me₃Si), 0.20 (s, 3H, MeSi), 2.30 (s, 1H, HC≡C) Found: C, 50.49; H, 10.24. C₉H₂₂Si₃ calcd.: C, 50.39; H, 10.33%.

Preparation of tris(trimethylsilyl)ethynylsilane (VI)

A solution of 1.9 g (6.7 mmol) of tris(trimethylsilyl)chlorosilane [14] in 10 cm³ of THF was added to 10 cm³ of THF solution of ethynylmagnesium bromide (29 mmol). After work-up in the usual manner, distillation gave 1.4 g (77% yield) of VI, m.p. ca. 45°C; IR (cm⁻¹) 3300, 2020, 1395, 1245; NMR (δ , ppm) 0.22 (s, 27H, Me₃Si), 2.19 (s, 1H, HC≡C) Found: C, 48.47; H, 10.62. C₁₁H₂₈Si₄ calcd.: C, 48.45; H, 10.35%.

Preparation of trans-trimethylsilyl(dichloromethylsilyl)ethane

In a 200-cm³ two-necked flask was placed a mixture of 22 g (0.22 mol) of trimethylsilylacetylene dissolved in 60 cm³ of THF and 180 μ l of an isopropyl alcohol solution of chloroplatinic acid (0.01 M). To this was added 27 g (0.24 mol) of dichloromethylsilane at ca. 50°C for 20 min. The mixture was heated to reflux for 2 h, the solvent THF evaporated, and the residue distilled under reduced pressure to give 33 g (70% yield) of *trans*-trimethylsilyl(dichloromethylsilyl)ethene, b.p. 66–68°C/16 Torr; NMR (δ , ppm) 0.15 (s, 9H, Me₃Si), 0.83 (s, 3H, MeSi), 6.53 and 6.97 (d, J = 22.5, HC≡CH) Found: Cl, 33.68. C₆H₁₄Si₂Cl₂ calcd.: Cl, 33.25%.

Preparation of trans-trimethylsilyl(chloromethylphenylsilyl)ethene

To a solution of 10 g (46.9 mmol) of *trans*-trimethylsilyl(dichloromethylsilyl)ethene in 20 cm³ of THF was added 14.5 cm³ (46.4 mmol) of a phenylmagnesium chloride/THF solution at room temperature. The mixture was heated to reflux for 5 h. The mixture was then filtered off to remove magnesium salts and the solvent was distilled off. The residue was distilled under reduced pressure to give 7 g (59% yield) of *trans*-trimethylsilyl(chloromethylphenylsilyl)ethene, b.p. 67–69°C/1 Torr; NMR (δ , ppm) 0.12 (s, 9H, Me₃Si), 0.72 (s, 3H, MeSi), 6.72 and 6.85 (d, J = 22 Hz, HC≡CH), 7.3–7.7 (m, 5H, ring protons) Found: Cl, 13.43. C₁₂H₁₉Si₂Cl calcd.: Cl, 13.91%.

Preparation of trans-trimethylsilyl(methoxymethylphenylsilyl)ethene (XIb)

To a mixture of 3.03 g (11.9 mmol) of *trans*-trimethylsilyl(chloromethylphenylsilyl)ethene and 1.2 g (15.2 mmol) of pyridine in 10 cm³ of ether was

added 0.57 g (17.7 mmol) of dry methanol at room temperature. The reaction mixture was stirred for 2 h at room temperature and then the resulting pyridinium salts were filtered off. The filtrate was concentrated and distilled under reduced pressure to give 1.5 g (50% yield) of colorless liquid, b.p. 73–74°C/1.5 Torr, exact mass 250.1199 (calcd.: 250.1209) (Found: C, 62.89; H, 8.60. $C_{13}H_{22}OSi_2$ calcd.: C, 62.34; H, 8.85%).

Preparation of trans-trimethylsilyl(trichlorosilyl)ethene

This compound was prepared in 67% yield from 16.7 g (0.17 mol) of trimethylsilylacetylene and 25.4 g (0.19 mol) of trichlorosilane in the presence of a catalytic amount of chloroplatinic acid in THF in a similar way to that described above; b.p. 61–63°C/13 Torr; NMR (δ , ppm) 0.17 (s, 9H, Me_3Si), 6.51 and 7.17 (d, $J = 22$ Hz, $HC\equiv CH$) Found: Cl, 45.75. $C_5H_{11}Si_2Cl_3$ calcd.: Cl, 45.52%.

Preparation of trans-trimethylsilyl(chlorodiphenylsilyl)ethene

This compound was prepared in 42% yield from 9.2 g (39.4 mmol) of *trans*-trimethylsilyl(trichlorosilyl)ethene and phenylmagnesium chloride (83 mmol) in THF; b.p. 134–136°C/3 Torr; NMR (δ , ppm) 0.13 (s, 9H, Me_3Si), 6.87 and 6.89 (d, $J = 22$ Hz, $HC\equiv CH$), 7.2–7.7 (m, 10H, ring protons); Found: Cl, 10.98. $C_{17}H_{21}Si_2Cl$ calcd.: Cl, 11.18%.

Preparation of trans-trimethylsilyl(methoxydiphenylsilyl)ethene (XIVb)

Compound XIVb was prepared in 72% yield from 4.4 g (13.9 mmol) of *trans*-trimethylsilyl(chlorodiphenylsilyl)ethene and 0.6 g (18.8 mmol) of methanol in the presence of 1.4 g (17.7 mmol) of pyridine in dry ether; b.p. 132–134°C/2 Torr; Found: C, 69.07; H, 7.90. $C_{18}H_{24}OSi_2$ calcd.: C, 69.17; H, 7.74%.

Photolysis of ethynylpolysilanes in the presence of methanol

The following is typical of the procedures used. In a 100 cm³ reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter was placed a mixture of 0.6358 g (2.92 mmol) of 1-ethynyl-2-phenyltetramethyldisilane (I), 0.1641 g (0.97 mmol) of dodecane as an internal standard and 1.0 cm³ of dry methanol in 80 cm³ of dry hexane. The solution was irradiated at room temperature with a slow stream of nitrogen bubbling through the mixture. After 3 h of irradiation, 84% of the starting I was photolyzed. The yields of products, VII, VIIa, VIIb and IX, were determined by analytical GLC. Most of the solvent and unchanged methanol were evaporated. The residue was distilled under reduced pressure to give volatile products boiling up to 200°C/2 Torr. Pure compounds were isolated by preparative GLC. The reaction conditions and yields of the products obtained from photolysis experiments are listed in Table 1.

Photolysis of ethynylpolysilanes in the absence of a trapping agent

A mixture of 0.7068 g (2.52 mmol) of 1-ethynyl-1,1-diphenyltrimethyldisilane (III) and 0.2254 g (1.0 mmol) of cetane in 80 cm³ of dry hexane was placed in a reaction vessel similar to that described above. The mixture was

TABLE 1
PHOTOLYSIS OF ETHYNYLPOLYSILANES IN THE PRESENCE OR ABSENCE OF A QUENCHER
(λ 2537 Å)

Ethynylpolysilane g (mmol)	Quencher (cm ³)	Time (h)	Product (yield %) ^a	Recovered polysilane (%)
HC≡CSiMe ₂ SiMe ₂ Ph 0.6358 (2.92)	MeOH (1)	3	VII(11), VIIIa(10), VIIIb(6), IX(30)	16
HC≡CSiMe(Ph)SiMe ₃ 0.5634 (2.58)	MeOH (1)	3	X(29), XIa(19), XIb (15), XII(3)	10
HC≡CSiMe(Ph)SiMe ₃ 0.0177 (0.081)	—	15	XII(25)	0
HC≡CSiMe(Ph)SiMe ₃ ^b 0.5995 (2.75)	MeOH (0.5)	2.5	X(19), XIa(16), XIb (19), XII(19)	0
HC≡CSiPh ₂ SiMe ₃ 0.7359 (2.63)	MeOH (1)	4	XIII(21), XIVa(23), XIVb(21)	20
HC≡CSiPh ₂ SiMe ₃ 0.7068 (2.52)	—	4	XV(18)	12
HC≡CSiMe ₂ SiMe ₂ SiMe ₃ 0.7659 (3.58)	MeOH (1)	22	XVI(22), XVII(20)	36
HC≡CSiMe ₂ SiMe ₂ SiMe ₃ 0.0225 (0.11)	Et ₂ MeSiH (0.2)	25	XVIII(16), XIX(4)	33
HC≡CSiMe ₂ SiMe ₂ SiMe ₃ 0.2441 (1.14)	—	2	XIX(10)	55
HC≡CSiMe(SiMe ₃) ₂ 0.8410 (3.93)	MeOH (1)	7	XX(32), XXIa(12), XXIb(16)	27
HC≡CSiMe(SiMe ₃) ₂ 0.1815 (0.85)	—	2	XXII(6)	13
HC≡CSi(SiMe ₃) ₃ 0.7149 (2.63)	MeOH (1)	7	XXIII(5)	33

^a Based on unrecovered ethynylpolysilanes. ^b High-pressure mercury lamp.

photolyzed at room temperature for 4 h. After the irradiation was stopped, 1 cm³ of dry methanol was added to the reaction mixture through the condenser by a syringe. The mixture was then analyzed by GLC as being trimethylsilyl(diphenylsilyl)acetylene (XV) (18% yield) and 12% of the starting ethynyl-disilane III. After distilling off the hexane solvent, the residue was flash-distilled under reduced pressure to give volatile products. Pure XV was isolated by preparative GLC.

Low temperature photolysis of 1-ethynyl-1-phenyltetramethyldisilane (II)

A solution of 0.7185 g (3.30 mmol) of II and 0.1842 g (1.1 mmol) of dodecane in 120 cm³ of dry hexane was photolyzed with a low-pressure mercury lamp surrounded by a Vycor vacuum jacket for 9 h at -78°C. At this stage, 69% of II was photolyzed. After irradiation was stopped, 1 cm³ of dry methanol was added to the reaction mixture through the condenser by a syringe at the same temperature. The mixture was then analyzed by GLC as being trimethylsilyl(methylphenylsilyl)acetylene (XII) (13% yield). Pure XII was isolated by preparative GLC after distillation of the photolysis mixture. The IR, mass and ¹H NMR spectra of XII were identical with those of an

authentic sample obtained from the photolysis of II in the absence of methanol at room temperature.

Photolysis of I in the presence of methanol- d_1

A mixture of 0.7659 g (3.5 mmol) of I, 0.2183 g (1.3 mmol) of dodecane and 1 cm³ of methanol- d_1 in 80 cm³ of dry hexane was irradiated at room temperature. After 3 h of irradiation, 89% of the starting I was photolyzed. Most of the solvent was evaporated. The residue that remained was distilled under reduced pressure to give a volatile product boiling up to 180°C/2 Torr. Mono-

TABLE 2
PROTON NMR CHEMICAL SHIFTS FOR SILYL ALKENES

Compound	Chemical shifts (δ , ppm)
VII	0.04(s, 6 H, Me ₂ Si), 0.38(s, 6 H, Me ₂ Si), 3.27(s, 3 H, MeO), 6.31 and 6.41(d, J = 5 Hz, H ¹ H ² C=C), 7.2–7.6(m, 5 H, ring protons).
VIIIa	0.05(s, 6 H, Me ₂ Si), 0.38(s, 6 H, Me ₂ Si), 3.23(s, 3 H, MeO), 6.69 and 6.89(d, J = 20 Hz, H ¹ C=CH ²), 7.2–7.6(m, 5 H, ring protons).
VIIIb	0.15(s, 6 H, Me ₂ Si), 0.35(s, 6 H, Me ₂ Si), 3.37(s, 3 H, MeO), 6.59 and 6.73(d, J = 23 Hz, H ¹ C=CH ²), 7.2–7.6(m, 5 H, ring protons).
IX	0.32(s, 6 H, Me ₂ Si), 3.39(s, 3H, MeO), 7.2–7.6(m, 5 H, ring protons).
X	0.02(s, 9 H, Me ₃ Si), 0.43(s, 3 H, MeSi), 3.44(s, 3 H, MeO), 6.32 and 6.40(d, J = 5 Hz, H ¹ H ² C=C), 7.2–7.6(m, 5H, ring protons).
XIa	0.06(s, 9 H, Me ₃ Si), 0.43(s, 3 H, MeSi), 3.41(s, 3 H, MeO), 6.70 and 6.88(d, J = 21 Hz, H ¹ C=CH ²), 7.2–7.6(m, 5 H, ring protons).
XIb	0.10(s, 9 H, Me ₃ Si), 0.39(s, 3 H, MeSi), 3.44(s, 3 H, MeO), 6.65 and 6.73(d, J = 23 Hz, H ¹ C=CH ²), 7.2–7.6(m, 5 H, ring protons).
XII	0.21(s, 9 H, Me ₃ Si), 0.47(d, 3 H, J = 4 Hz, MeSi), 4.57(q, 1 H, J = 4 Hz, HSi), 7.2–7.7(m, 5 H, ring protons).
XIII	0.01(s, 9 H, Me ₃ Si), 3.54(s, 3 H, MeO), 6.37 and 6.53(d, J = 5 Hz, H ¹ H ² C=C), 7.2–7.6(m, 10 H, ring protons).
XIVa	0.03(s, 9 H, Me ₃ Si), 3.51(s, 3 H, MeO), 6.83 and 7.03(d, J = 20 Hz, H ¹ C=CH ²), 7.2–7.6(m, 10 H, ring protons).
XIVb	0.12(s, 9 H, Me ₃ Si), 3.54(s, 3 H, MeO), 6.83(s, 2 H, H ¹ C=CH ²), 7.2–7.6(m, 10 H, ring protons).
XV	0.25(s, 9 H, Me ₃ Si), 5.09(s, 1 H, HSi), 7.2–7.7(m, 10 H, ring protons).
XVII	0.05(s, 9 H, Me ₃ Si), 0.14(s, 6 H, Me ₂ Si), 0.16(s, 6 H, Me ₂ Si), 3.36(s, 3 H, MeO), 6.22 and 6.34(d, J = 5 Hz, H ¹ H ² C=C).
XIX	0.13(s, 9 H, Me ₃ Si), 0.21(s, 6 H, Me ₂ Si), 0.25(d, 6 H, J = 3.5 Hz, Me ₂ Si), 4.09(septet, 1 H, J = 3.5 Hz, HSi).
XX	0.10(s, 18 H, Me ₃ Si), 0.26(s, 3 H, MeSi), 3.38(s, 3 H, MeO), 6.26 and 6.32(d, J = 5 Hz, H ¹ H ² C=C).
XXIa	0.11(s, 18 H, Me ₃ Si), 0.27(s, 3 H, MeSi), 3.42(s, 3 H, MeO), 6.48 and 6.72(d, J = 20 Hz, H ¹ C=CH ²).
XXIb	0.09(s, 18 H, Me ₃ Si), 0.22(s, 3 H, MeSi), 3.38(s, 3 H, MeO), 6.59(s, 2 H, H ¹ C=CH ²).
XXII ^a	0.19(s, 9 H, Me ₃ Si), 0.21(s, 9 H, Me ₃ Si), 0.28(d, 3 H, J = 4.5 Hz, MeSi), 4.28(q, 1 H, J = 4.5 Hz, HSi).
XXIII	0.10(s, 9 H, Me ₃ Si), 0.13(s, 18 H, Me ₃ Si), 3.47(s, 3 H, MeO), 6.06 and 6.21(d, J = 4 Hz, H ¹ H ² C=C).

^a In deuterobenzene.

TABLE 3
ELEMENTAL ANALYSIS, MASS AND IR DATA FOR ISOLATED COMPOUNDS

Compound		Found(calcd.)(%)		IR (neat) (cm ⁻¹)	M ⁺ (m/e)
		C	H		
VII					
VIIb	C ₁₃ H ₂₂ OSi ₂ ^a	62.48(62.34)	8.73(8.85)	1090	250
VIIIa	C ₁₃ H ₂₂ OSi ₂	62.06(62.34)	9.13(8.85)	1090	250
IX	C ₉ H ₁₄ OSi	65.04(65.00)	8.52(8.49)	1090	166
X					
XIb	C ₁₃ H ₂₂ OSi ₂ ^b	62.13(62.34)	8.91(8.85)	1085	250
XIa	C ₁₃ H ₂₂ OSi ₂	62.34(62.34)	8.74(8.85)	1090	250
XII	C ₁₂ H ₁₈ Si ₂	65.79(65.98)	8.44(8.31)	2160	218
XIII					
XIVb	C ₁₈ H ₂₄ OSi ₂ ^c	69.20(69.17)	7.93(7.74)	1085	312
XIVa	C ₁₈ H ₂₄ OSi ₂	69.03(69.17)	7.83(7.74)	1090	312
XV	C ₁₇ H ₂₀ Si ₂	72.69(72.79)	7.31(7.19)	2150	280
XVII	C ₁₀ H ₂₆ OSi ₃	48.48(48.71)	10.61(10.63)	1090	246
XIX	C ₉ H ₂₂ Si ₃ ^d	—	—	2145	214
XX	C ₁₀ H ₂₆ OSi ₃	48.41(48.71)	10.77(10.63)	1085	246
XXIa	C ₁₀ H ₂₆ OSi ₃	48.43(48.71)	10.78(10.63)	1090	246
XXIb	C ₁₀ H ₂₆ OSi ₃	48.88(48.71)	10.80(10.63)	1080	246
XXII	C ₉ H ₂₂ Si ₃ ^e	—	—	2120	214
XXIII	C ₁₂ H ₃₂ OSi ₄ ^f	46.64(47.30)	10.67(10.58)	1090	304

^a A mixture of VII and VIIb. ^b A mixture of X and XIb. ^c A mixture of XIII and XIVb. ^d Exact mass, found: 214.1009; calcd.: 214.1029. ^e Exact mass, found: 214.1033; calcd.: 214.1029. ^f Exact mass, found: 304.1518; calcd.: 304.1530.

deuteromethylmethoxymethoxyphenylsilane (25% yield) was isolated by preparative GLC; M^+ (m/e) 167 (mol. wt 167.29); NMR (δ , ppm) 0.32 (5H, MeSi and CH₂DSi), 3.39 (s, 3H, MeO) and 7.2–7.6 (m, 5H, ring protons).

Photolysis of I in isopropylbenzene

In a carefully dried 5 cm³ quartz tube was placed a solution of 31.1 mg (0.143 mmol) of I and 0.041 mmol of dodecane as an internal standard in 3 cm³ of dry isopropylbenzene.

The solution was irradiated externally with a low-pressure mercury lamp for 5 h. At this stage, 84% of I was photolyzed. GLC analysis of the resulting solution showed the presence of a small amount of an unidentified product. However, no bicumyl could be detected.

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References

- 1 R.T. Conlin and P.P. Gaspar, J. Amer. Chem. Soc., 98 (1976) 3715.
- 2 D. Seyferth, D.C. Annarelli and S.C. Vick, J. Amer. Chem. Soc., 98 (1976) 6382.

- 3 M. Ishikawa, T. Fuchikami and M. Kumada, J. Amer. Chem. Soc., 99 (1977) 245.
- 4 H. Sakurai, Y. Kamiyama and Y. Nakadaira, J. Amer. Chem. Soc., 99 (1977) 3879.
- 5 M. Ishikawa, T. Fuchikami and M. Kumada, J. Organometal. Chem., 142 (1977) C45.
- 6 M. Ishikawa, K. Nakagawa and M. Kumada, J. Organometal. Chem., 131 (1977) C15.
- 7 M. Ishikawa, T. Fuchikami and M. Kumada, J. Chem. Soc. Chem. Commun., (1977) 352.
- 8 L. Birkofer and T. Kuehn, Chem. Ber., 111 (1978) 3119.
- 9 M. Ishikawa and M. Kumada, J. Organometal. Chem., 42 (1972) 325.
- 10 E.R.H. Jones, L. Skatterbol and M.C. Whiting, J. Chem. Soc., (1956) 4765; Org. Synth. Coll. Vol., 4 (1963) 792.
- 11 M. Kumada, M. Ishikawa and S. Maeda, J. Organometal. Chem., 2 (1964) 478.
- 12 M. Ishikawa, T. Fuchikami and M. Kumada, J. Organometal. Chem., 162 (1978) 223.
- 13 M. Ishikawa, T. Fuchikami and M. Kumada, J. Organometal. Chem., 118 (1976) 139.
- 14 H. Gilman and R.L. Harrell, J. Organometal. Chem., 5 (1966) 199.
- 15 M. Ishikawa, T. Fuchikami and M. Kumada, J. Organometal. Chem., 173 (1979) 117.