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Accounts

Polyorganosilicon Compounds in Strained Carbocyclic Systems

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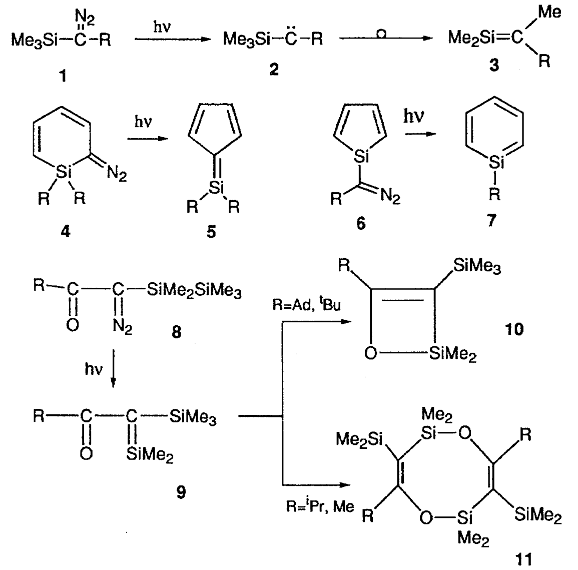
Organosilicon chemistry has been highlighted by the successful construction and thorough characterization of strain carbocyclic systems: 1) silabenzene, silafulvene, and polycyclic polysilane via a silylcarbene rearrangement to silene, 2) a ring-expansion reaction of disilacyclobutene with *exo*-methylene, and 3) cyclic polysilanes containing unsaturated carbon systems, such as acetylene, allene, and fullerene. Some of these numerous compounds, which are now available, are fully substituted with bulky ligands. These compounds permit examinations of: 1) the variation in the physical and chemical properties of a system with polysilane, and 2) how the systems are related thermally and photochemically with carbon analogues. Some cyclic polysilanes may constitute a stepping stone on the way to super-molecules.

Over the past decade significant and exciting progress has been made regarding organosilicon chemistry. Species once thought to exist only as reactive intermediates, such as silylene (carbene-like) species,[1] and molecules containing silicon double bonds and silacyclopropanes have yielded to synthesis.[2] Numerous compounds with silicon embedded in small and highly strained rings have been expanded dramatically.[3] Perhaps most importantly, these accomplishments have greatly enhanced our understanding of bonding in these systems.

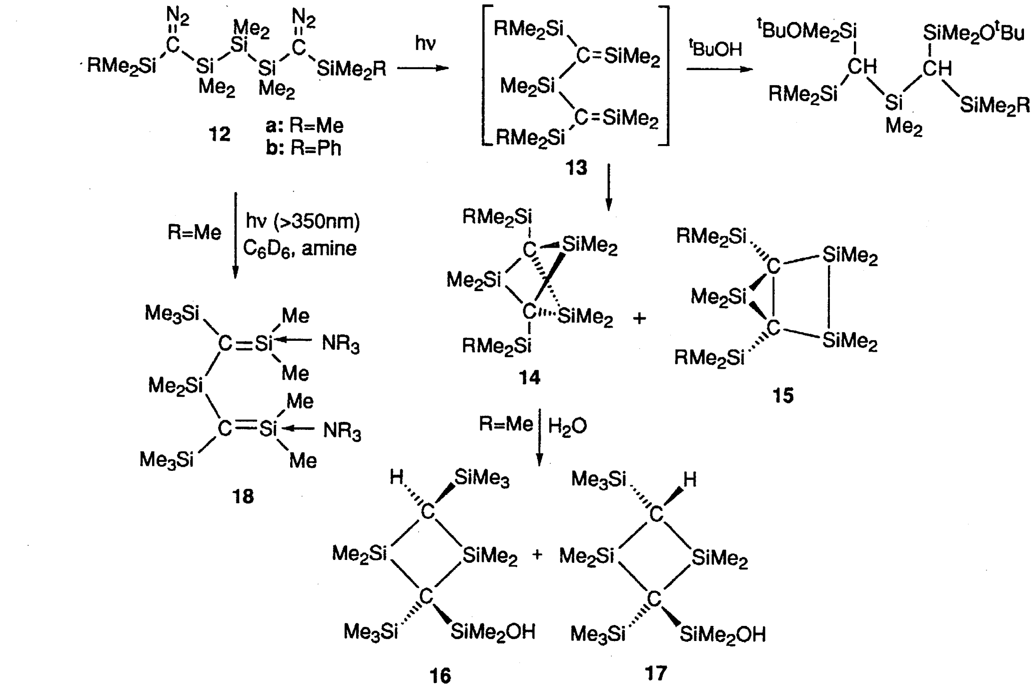
Our research in the field of silicon chemistry was initiated in 1973[4] as an extension of prior work on carbene chemistry. The accumulated results obtained at our and other laboratories since then have clearly demonstrated that: 1) the chemistry of silylene and its related species is intimately related to that of the corresponding carbene chemistry, and 2) polysilanes in a strained ring system can be constructed, and exhibit unique properties often unexpected based on their carbogenic analogues.[5]

Silylcarbene: Formation and Reaction of Silenes. Trimethylsilylcarbene (**2**), generated by the photolysis or thermolysis of trimethylsilyldiazomethane (**1**), forms silenes (**3**) by the migration of a methyl group from the silicon atom to the carbene center (Scheme 1). This silyl carbene-to-silene rearrangement has proven to be a convenient route to a variety of functionalized silenes.[4,6—11] The photolysis of cyclic silyldiazo compounds (**4** and **6**) resulted in the formation of silafulvene (**5**) and silabenzene (**7**) intermediates via the migration of a dienyl group to the carbene center.[12—14] The photochemical generation of the siladienone intermediate (**9**) from disilanyldiazomethyl ketone (**8**) led intramolecular [2+2] cyclization to yield oxasiletene (**10**) quantitatively, which is thermally a very labile molecule.[15] The products were highly dependent on the bulkiness of the substituents on α-keto silene (**9**): oxasiacyclobutene (**10**) from adamantyl and t-butyl groups, and head-to-tail cyclodimers (**11**) from isopropyl and methyl groups.[16]



Scheme 1.

Under these circumstances, the thermal and photochemical decompositions of bis(silyldiazomethyl) compounds were expected to produce two silenes in one molecule, which would undergo intramolecular dimerization. The photolysis of bis(silyldiazomethyl)trisilane (**12**) produces bissilene, (**13**) which afforded trisilabicyclo[1.1.1]pentane (**14**) and trisilabicyclo[2.1.0]pentane (**15**) (Scheme 2).[17] It is surpris-

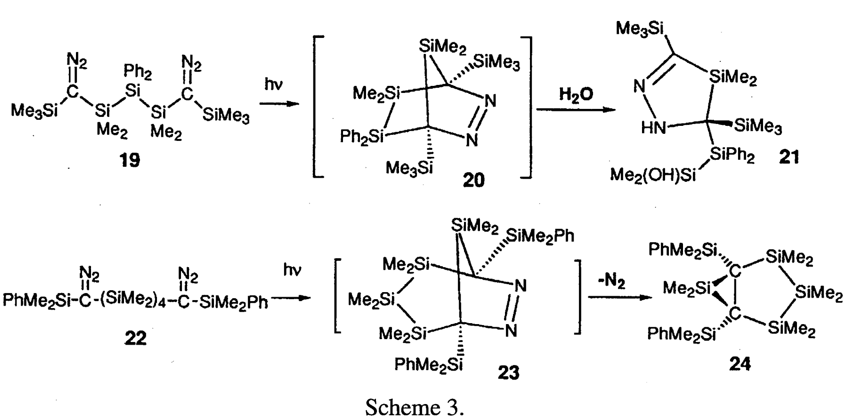


Scheme 2.

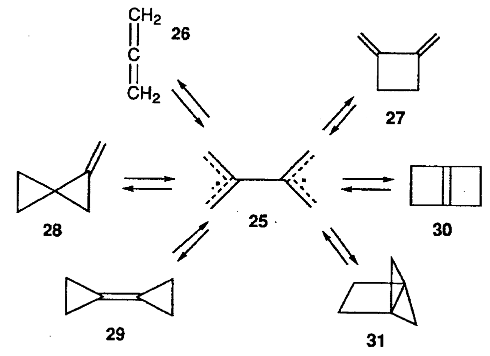
ing to obtain both head-to-head and head-to-tail dimerization products. The cage C–Si bond of **14a** showed a high reactivity to nucleophile, especially moisture, to give ring-opening products (**16**, **17**). This result revealed that the compound has considerable ionic character, as suggested by Streitweiser.[18] The photolysis of **12a** in amines gave the 1,5-disilapentadiene-amine complex (**18**), which has a relatively long lifetime ($t_{1/2}=29$—41 h at r.t.).[19] The reaction pathway was completely changed in the photolyses of 2,2-diphenyltetramethyltrisilane (**19**) and hexamethyltetrasilane (**22**) (Scheme 3). Silanol (**21**) and tetrasilabicyclo[3.1.0]hexane (**24**)[20] are probably obtained from bicyclic azo intermediates (**20**) and (**23**) by the intramolecular [2+3] cycloaddition of silene and the diazo group. Silirane (**24**) is stable towards oxygen and moisture.

Dialkylidenedisilacyclobutanes: Ring-Expansion Reactions. 1,2-Dialkylidenecyclobutane possesses a large strain energy compared with cyclobutane (26.5 kcal mol^{-1}).[21] Tetramethyleneethane, or 2,2′-bis(allyl) diradical (**25**), has been postulated to be an intermediate in the thermal dimerization of allenes (Scheme 4); it could also be a potential intermediate for the interconversion of allene (**26**), 1,2-dimethylenecyclobutane (**27**), methylenespiropentane (**28**), bicyclopropylidene (**29**), $\Delta^{1,4}$-bicyclo[2.2.0]hex-1(4)-ene (**30**), and tricyclo[2.1.1.0^{1,4}]hexane (**31**).[22] A small ring system involving a silicon-silicon bond is interesting because of its high strain energy.[23] Only a few examples concerning the formation of 1,2-disilacyclobutanes (**32**)[24] and 1,2-disilacyclobutenes (**33**) have been reported (Scheme 5).[25]

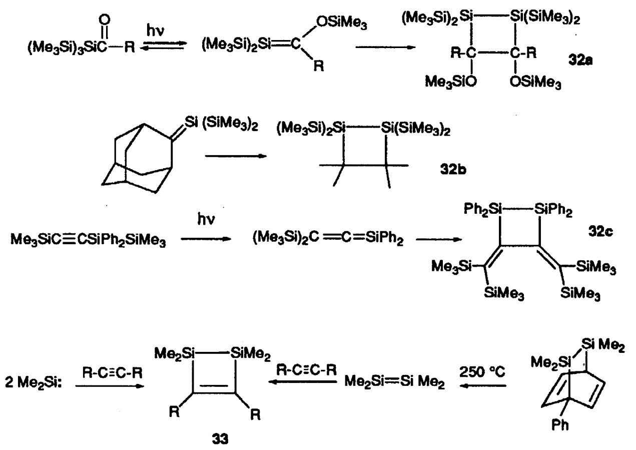
The novel 3,4-dialkylidene-1,2-disilacyclobutanes (**34**), which were synthesized by the treatment of dilithiated tetramethylbutatriene with appropriate halosilane, gave bissilanes that were chlorinated with $PdCl_2/CCl_4$. Reductive coupling of the resulting bis(chlorosilane)s with sodium in toluene afforded the desired disilacyclobutanes **34** as oxygen- and moisture-sensitive liquids (Scheme 6). While **34a** is readily polymerized and must be stored as a dilute solution in order to avoid decomposition, **34b** is stable at room temperature



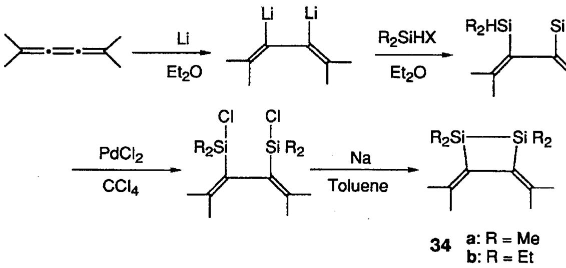
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

for several months, even in the neat form.[26]

The medium-sized ring of alkylidenecyclopolysilane, such as polysila–cyclohexane and –cyclooctane, can be easily synthesized by a transition-metal catalyzed reaction[27—29] of 1,2-disilacyclobutanes. Diisopropylidenedisilacyclobutanes **34a** in the presence of a catalytic amount of $Pd(PPh_3)_4$ was cleanly converted into **35** in 93% yield (Fig. 1). When an equimolar mixture of **34a** and benzo derivatives[30] **36** was treated with catalytic amounts of $Pd(PPh_3)_4$, the corresponding cross-metathesis products **38** were obtained, respectively, with high selectivity in addition to minor amounts of homometathesis products **37**.[26] A favored formation of the cross metathesis product **39** was also observed in the conversion of a mixture of **36a** and **36b**, though with a lower degree of selectivity (Fig. 2). Double silylation product (**40**) was obtained in the reaction of **34a**, and excess alkynes in the presence of a catalytic amount of $Pd(PPh_3)_4$ (Fig. 3). In the

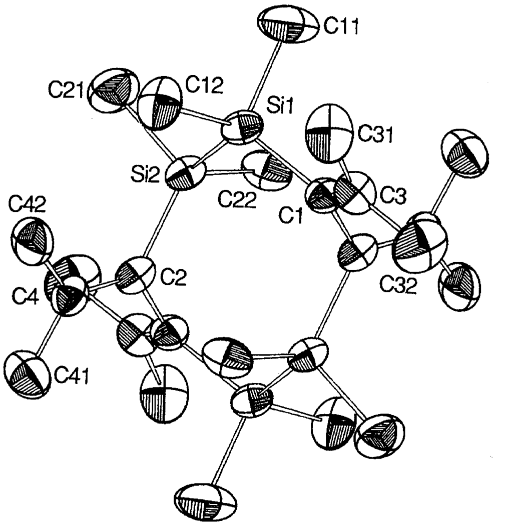


Fig. 1. ORTEP drawing of **35**.

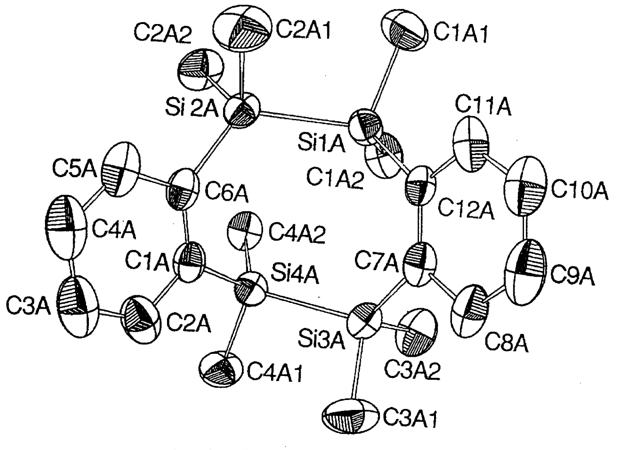


Fig. 2. ORTEP drawing of **39**.

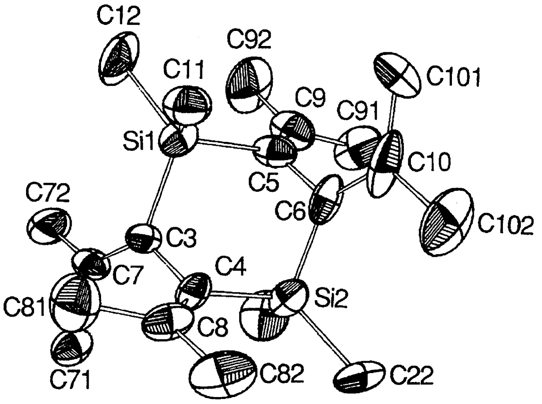
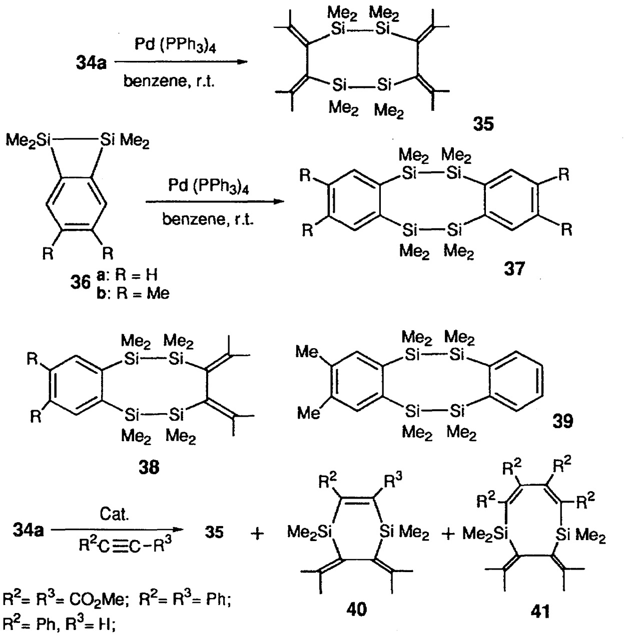


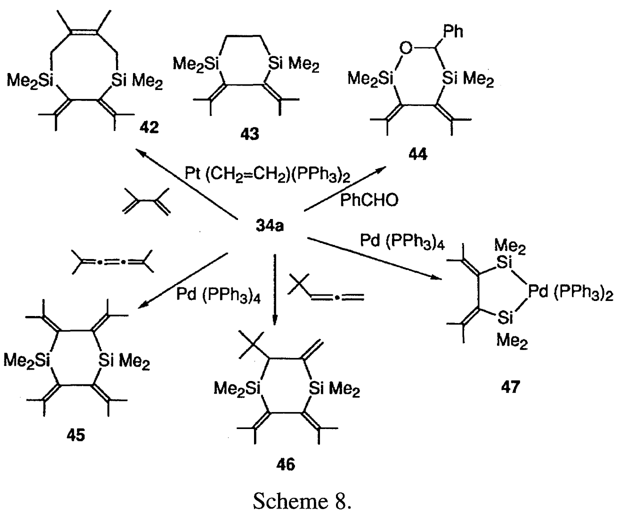
Fig. 3. ORTEP drawing of **40**.

case of diphenylacetylene, disilane metathesis and double silylation products were observed, which showed moderate selectivity. The yield of **40** increased, if the catalyst was changed from the triphenylphosphine ligand to benzonitrile ligands. The product distribution of disilane metathesis (**35**) and acetylene insertion (**40**) depends on the electrophilicity of acetylenes, since in the case of dimethyl acetylenedicarboxylate mono-adduct **40** and a di-adduct **41** are giving, and in the case of phenylacetylene only a mono-adduct **40** is given (Scheme 7).

2,3-Dimethyl-1,3-butadiene and benzaldehyde were not successful in competing with a disilane metathesis reaction even if 5 equiv of unsaturated compound were employed in the presence of Pd(PPh$_3$)$_4$ catalyst at room temperature for 30 min, since only **35** was found in 74 and 80% yield respectively. On the contrary, Pt(CH$_2$=CH$_2$)(PPh$_3$)$_2$ catalyst (80 °C, 3 h) promoted a double silylation to give **42** (41%), **43** (10%), and **44** (60%) (Scheme 8). Of special interest, 2,5-diemthyl-2,3,4-hexatriene moderately inhibited a disilane metathesis reaction to give **35** (15%) and 2,3,5,6-tetraisopropylidene-1,1,4,4-tetramethyl-1,4-disilacyclohexane (**45**) (68%) in the presence of Pd(PPh$_3$)$_4$. The latter was obtained as a 3 : 1 mixture of two conformational isomers, which do not interconvert at room temperature. *t*-Butylallene also inhibited disilane metathesis to give **46** (yield, 85%) in the presence of Pd(PPh$_3$)$_4$. It is evident that in the reaction involves a common intermediate with a double silylation reaction, i.e. bis(silyl)palladium(II) (**47**).[31] Such an intermediate is followed by the insertion of unsaturated compounds. The selectivity of these pathways depends on the reactivity of unsaturated compounds.

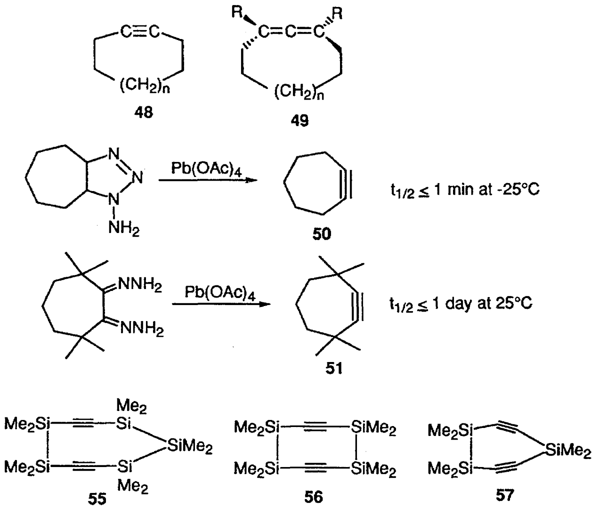


Scheme 7.



Scheme 8.

Polysilacyclic Alkynes and Allenes: Syntheses and Reactions. Decreasing the ring size of cyclic acetylene **48**[32] and allene **49**[33] results in unusual structures and reactivities being exhibited. Witting et al., reported that cycloheptyne **50** was formed by the oxidation of 1,4,5,6,7,8-hexahydrocycloheptatriazole (Scheme 9).[34] The half lifetime of cycloheptyne **50** in dichloromethane at −25 °C is one minute. 3,3,7,7-Tetramethylcycloheptyne **51** was obtained from 3,3,7,7-tetramethyl-1,2-cycloheptanedione by way of the bishydrazone.[35] The introduction of the four CH$_3$ groups leads to a drastic increase in the kinetic stability of the cycloheptyne system; dimerization of **51** proceeded more slowly than **50**. Krebs et al., reported on the syntheses of 5-sila,[36] thio,[37] and 5-sila-, 5-thia-, and 5-oxa-cycloheptyne,[38] **52**—**54**, by way of the bishydrazone. Although cycloheptynes bound with seven carbons are generally unstable at room temperature,[34,35] cycloheptynes which possess one sulfur or silicon atom in the skeleton are thermally stable (Fig. 4). This difference in the stability of medium-ring acetylenes is due to the longer



Scheme 9.

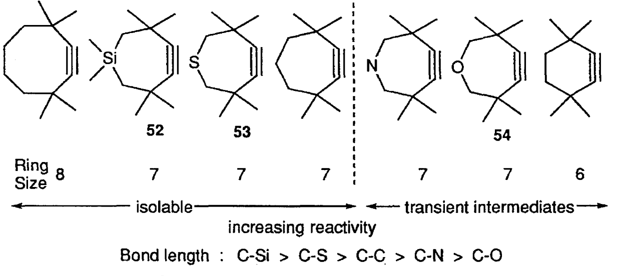
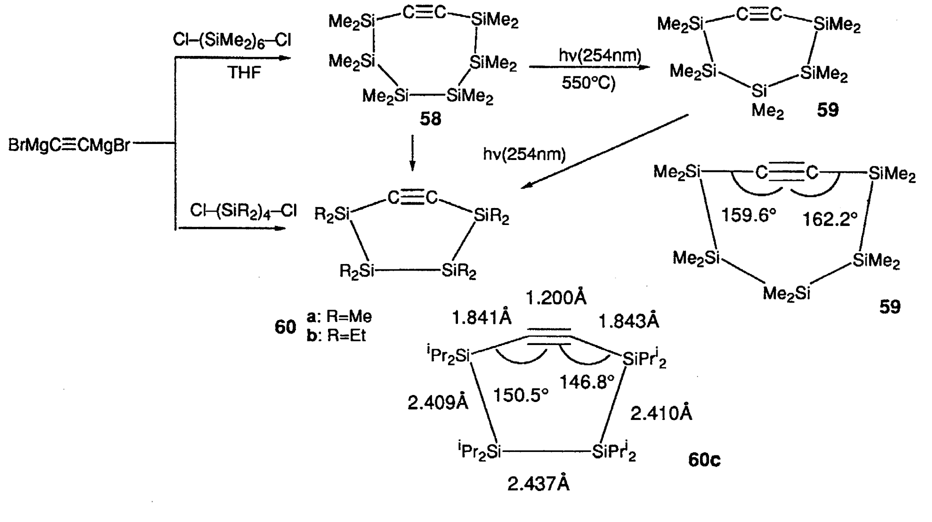


Fig. 4. Stability of cyclic acetylene.

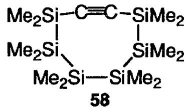
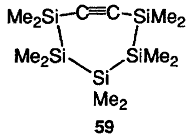
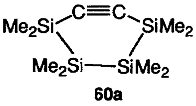


Scheme 10.

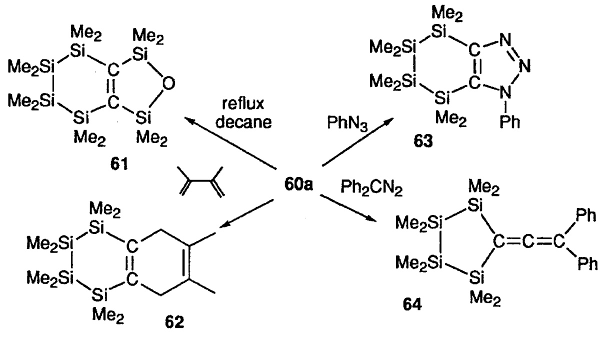
bond lengths of C–S or C–Si than that of C–C. Various examples of the silicon-containing cycloalkynes have already been reported.[39—44] Strained polysilacycloacetylenes and allenes have attracted much interest because of the possibility of a σ–π interaction between the silicon–silicon and carbon–carbon multiple bond in this ring.[45] Sakurai et al., reported that polysilacycloalkynes (**55**, **56**, and **57**) were synthesized by a ring-contraction method (FVP).[41]

Polysilacyclic Alkynes: The synthesis of 6—8 membered polysilacyclic alkynes **58**—**60** was achived by the reaction of 1,ω-dichloropolysilane with acetylenic bis(Grignard reagent) under dilute conditions in moderate yield (Scheme 10).[42,43] Tetrasilacyclohexynes **60a**, **b** were prepared from the corresponding 1,4-dichlorotetrasilane with the acetylenic bis(Grignard reagent) in 52 and 55% yields, respectively; compounds **59** and **60a** were also prepared by the ring-contracted photochemical and thermal reactions of **58** and **59**. Tetrasilacyclohexyne **60a** was thermally stable, even in boiling hexane, but unstable toward atmospheric moisture, and gave a complex mixture. The spectroscopic data of **60a** indicated that the acetylenic carbons are very distorted. In particular, the ^{13}C NMR signal of the acetylenic carbons of **60a** was observed at 135.6 ppm, which is lower value than those of the corresponding cycloheptyne **59** (123.1 ppm) and cyclooctyne **58** (117.7 ppm). The UV absorption of **59** was shown to exist at a maximum of 229 nm, which is a shorter wavelength than those of **58** (235 nm) because of the reduction of the silicon chain (Table 1). However, the UV absorption maximum of **60a** appears at 237 nm, which is a bathochromic shift compared with the case for **59**. Tetrasilacycloalkynes **60a**, **b** were colorless liquids. An X-ray crystallographic analysis was carried out by Barton et al., with more bulky octaisopropyltetrasilacyclohexyne **60c**.[44] The bending angles of the sp carbons of **60c** are 31.4° on the average. Because of a carbon–carbon triple bond **60a** was very distorted, and a Diels–Alder reaction of **60a** with 2,3-dimethyl-1,3-butadiene proceeded easily at room temperature to give the cycloadduct **62** (Scheme 11). Cyclohexyne **60a** reacted with phenyl azide and diphenyldiazomethane to give the corresponding cycloadduct **63** and its rearranged product **64**, respectively. However, hexasilacyclooctyne **58** and cycloheptyne **59** did not react under the conditions used. Hexasilacyclooctyne **58** reacted with dimesitylsilylene to give heptasilabicyclo[6.1.0]non-1(8)-ene **65c** (Scheme 12).

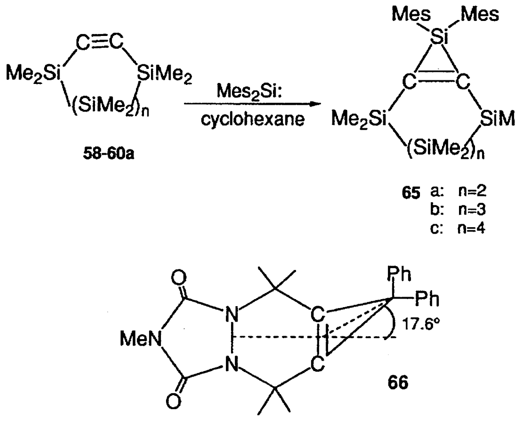
Table 1. Spectral Data of Polysilacycloalkynes

Compounds	NMR (δ/ppm) (C_6H_{12})			UV (C_6H_{12})
	^{1}H	^{13}C	^{29}Si	nm, λ_{max} (ε)
 **58**	0.16 (s, 12H)	−5.8 (q)	−39.6	235 (9700)
	0.17 (s, 12H)	−4.6 (q)	−38.9	
	0.20 (s, 12H)	−2.7 (q)	−35.8	
		117.7 (s)		
 **59**	0.16 (s, 12H)	−5.74 (q)	−38.5	229 (10200)
	0.18 (s, 12H)	−5.66 (q)	−34.6	
	0.19 (s, 6H)	−3.0 (q)	−33.8	
		123.1 (s)		
 **60a**	0.16 (s, 12H)	−6.3 (q)	−30.8	237 (8700)
	0.19 (s, 12H)	−2.9 (q)	−19.2	
		135.6 (s)		

a) Bending angles of C≡C–Si. b) Measured in C_6D_6.



Scheme 11.

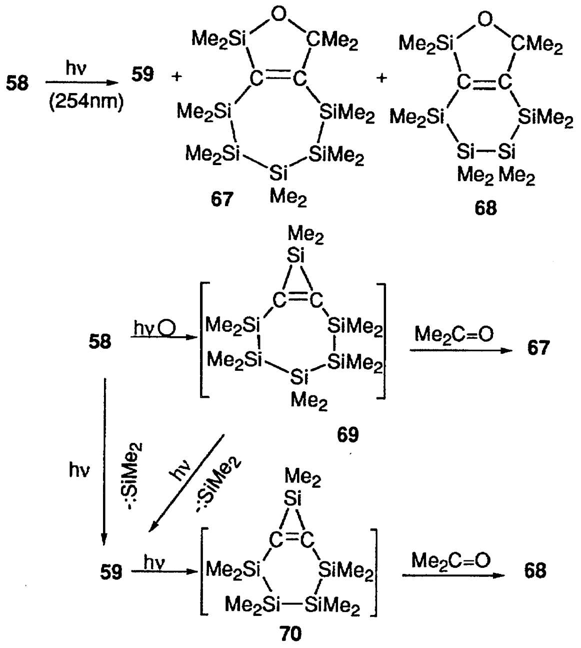


Scheme 12.

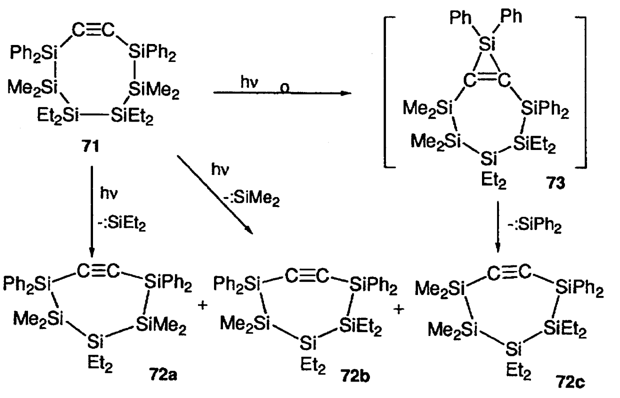
Similar results were obtained concerning the reaction of cycloheptyne **59** and cyclohexyne **60a** to give the corresponding bicyclic compounds, **65a** and **65b**. Bicyclo[n.1.0]alk-1(n+2)-enes have been known to be representatives of highly strained olefins, and several verbal theoretical studies have been conducted.[46—48] Wagner et al.[46] have indicated that the preferred geometries of bicyclo[n.1.0]alk-1(n+2)-enes ($n = 1$—3) are nonplanar and that pyramidalization decreased as the size of the bridging ring was increased. In the most recent calculation using RHF 6-31G*, carried out by Wiberg et al., the strain energies of the planar bicyclo[4.1.0]hept-1(6)-ene was 46 kcal mol^{-1}.[48] On the other hand, Ando et al., previously observed that such bicyclic systems can be effectively stabilized by the introduction of suitable heteroatoms, which enabled us to isolate heteroatom-substituted bicyclo-[4.1.0]hept-1(6)-enes.[49] The X-ray structure revealed that the double-bonded carbons in **66** are pyramidalized, so that the flap angle between the two rings is not 180°, but 162°. The geometry around the double bond is essentially planar, and the torsional angles of Si1–C1–C2–Si5 and Si4–C2–C1–Si5 are 179.4° and 172.2°, respectively.

The photochemical reaction of polysilacyclic alkynes **58** in acetone was carried out using a low-pressure mercury lamp;[43,50] small amounts of bicyclic acetone adducts **67** and **68** were obtained in 4.4 and 1.8% yields (Scheme 13), together with a majority of ring-reduced cycloheptyne **59** (21%). The formation of acetone adducts can be explained by the acetone-trapping process of fused silacyclopropenes, **69** and **70**. These photochemical behaviors indicate that the ring contraction of polysilacycloalkynes seems to occur via polysilabicyclo[n.1.0]alk-1(n+2)-ene derivatives. The photolysis of polysilacyclooctyne **71** led to the formation of the three types of ring contracted cycloheptynes; **72a**, **72b**, and **72c** in 10, 10, and 19% yields (Scheme 14), respectively. These results indicate that the ring contraction of polysilacycloalkynes proceeds via two different routes. One is direct desilylation; the other is a process via silacyclopropene derivatives **73**.

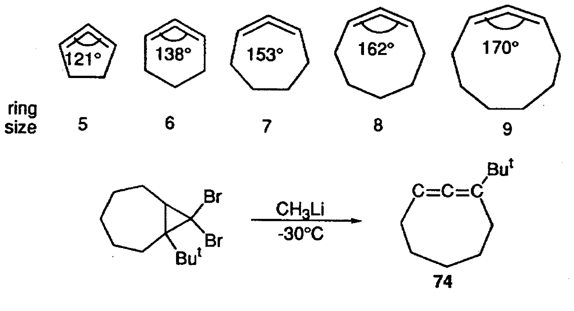
Polysilacyclic Allenes: In smaller cyclic allenes, ring constraints must increase the bending, torsion, and strain. Electron-diffraction studies[51] and the crystal structure[52] of the 1,2-cyclononadiene derivative predict the the allene is bent from linearity by 10°. Semiempirical MNDO calculations indicated a strain energy of < 5 kcal mol^{-1}.[53] The smallest isolable cyclic allene is the 1-t-butyl-substituted cycloocta-1,2-diene **74**, which Johnson et al., reported in 1986 (Scheme 15).[54] Allene **74** was prepared by the carbenoid route, and was found to be stable at room temperature. Seven-[55] and six-membered[56] cyclic allenes are also



Scheme 13.



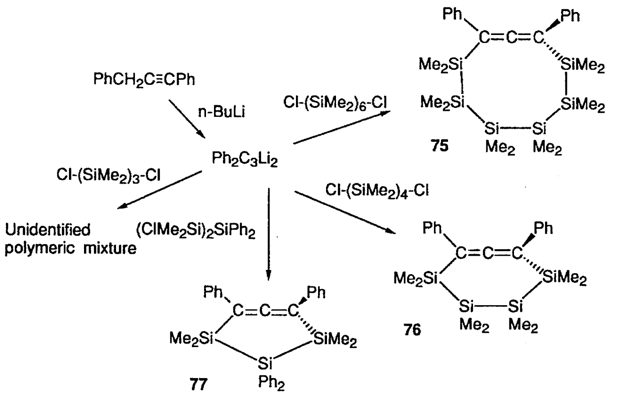
Scheme 14.



Scheme 15.

well known as being important intermediates in organic synthesis, and many synthetic methods have been documented.

Ph_2C_3 dianion, prepared from 1,3-diphenylpropyne and 2 equiv of butyllithium reacted with 1,6-dicholorohexasilane and 1,4-dichlorotetrasilane in THF/hexane, gave hexasilacyclonona-1,2-diene **75** and tetrasilacyclohepta-1,2-diene **76** in 24 and 72% yields, respectively. A reaction of Ph_2C_3 dianion with 1,3-dichlorohexamethyltrisilane gave mainly polymeric products and no 1 : 1 cycloadduct could be detected. The six-membered cyclic allene **77** was obtained from the reaction of 1,3-dichloro-2,2-diphenyltetramethyltrisilane with Ph_2C_3 dianion in 11% yield (Scheme 16). The difference in the reactivities of two types of dichlorotrisilanes might be explained based on the steric effects of two phenyl groups on a central silicon atom, which prevent an intermolecular reaction. This is the first isolated example of seven- and six-membered cyclic allenes.[57] X-Ray crystallographic analyses of **76** and **77** showed that the slightly longer bond lengths of the skeletal C–Si and Si–Si bonds of **77** (1.94 and 2.38 Å as the averages, respectively) compared with those of **76** (1.91 and 2.34 Å) release strain caused by the allenic moiety to a greater extent Figs. 5 and 6. The most interesting point concerning the structures of **76** and **77** is the relationship of the allenic moiety. The bond angle on the sp carbon, (C1–C2–C3) of **77** was found to be highly strained (19°) from linear geometry, while that of **76** is almost strain free (6°). The dihedral geometries around the allenic structures of **76** and **77** are also influenced by the ring strains. The dihedral angle, (Si1–C1–C3–Si3) of **77** is strongly contracted (52.2°) from the normal vertical geometry, while that of **76** is nearly a right angle (85.3°). There have been attempts to synthesize dimeric allenes as well as cyclic bisallenes.[58] The ten-membered cyclic tetraene **78a** was synthesized by Skattebol for the first time as the smallest bisallene (Scheme 17).[58] However, only meso structure **78a** has been characterized, although the dl isomer **78b** does not appear to be seriously strained. An X-ray crystallographic analysis of **78a** shows that the allene unit is bent from linear geometry by 6°. The Ph_2C_3 dianion, prepared from 1,3-diphenylpropyne and 2 equiv of butyllithium, reacts easily with 1,2-dichlorotetramethyldisilane to give the two isomers of 1,2,6,7-tetrasilacyclodeca-3,4,8,9-tetraenes **79a** and **79b**.[59] In **79a** and **79b** the average bent angle on the sp carbons of C2 and C7 was found to be 4°, respectively. The allene unit of bisallenes **79a** and **79b** is slightly spread to 99—102° from the normal vertical geometry of allene. The eight-membered bisallene **80** was synthesized by the reaction of 1,3-dilithio-1,3-bis(trimethylsilyl)allene with dimethyldichlorosilane by Barton et al..[60] An X-ray crystallographic analysis of bisallene **80** shows that the allene unit is bent to 4.8° and twisted to 78.1°; the distances between the allenic central carbons is 2.859 Å.



Scheme 16.

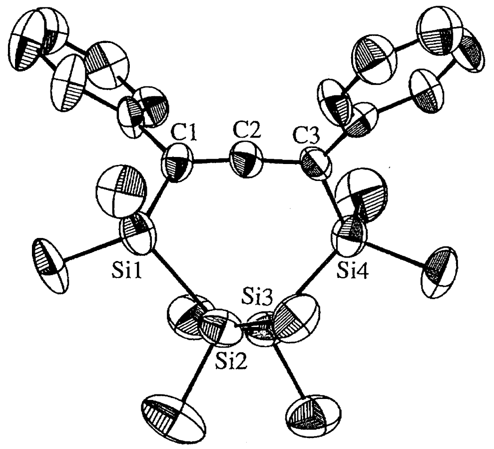


Fig. 5. ORTEP drawing of **76**.

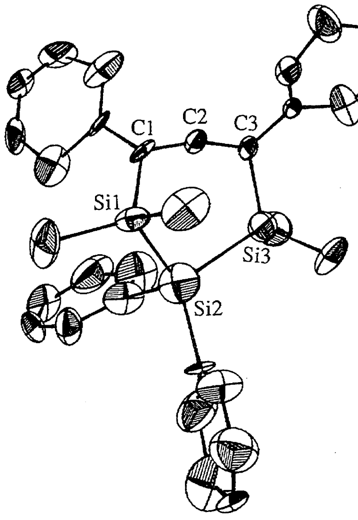
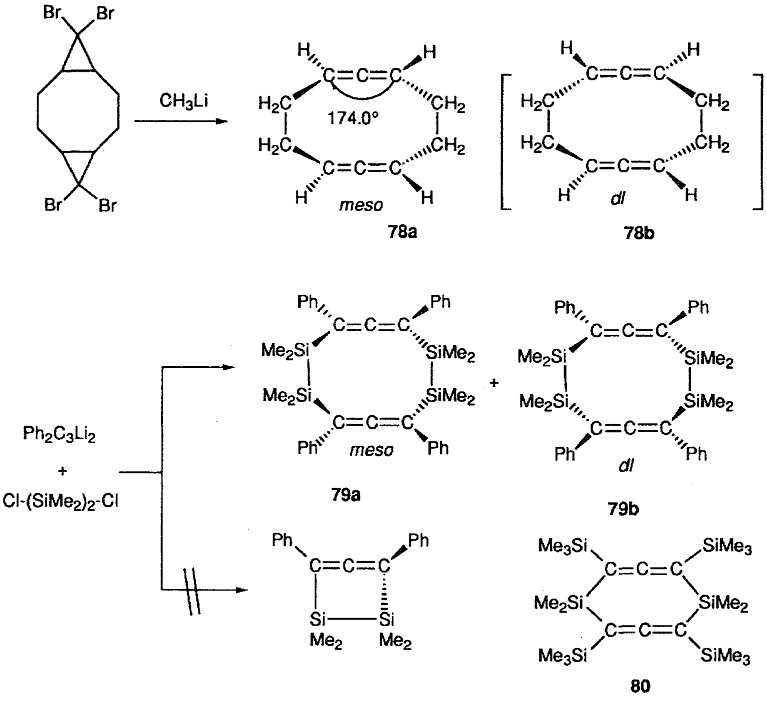
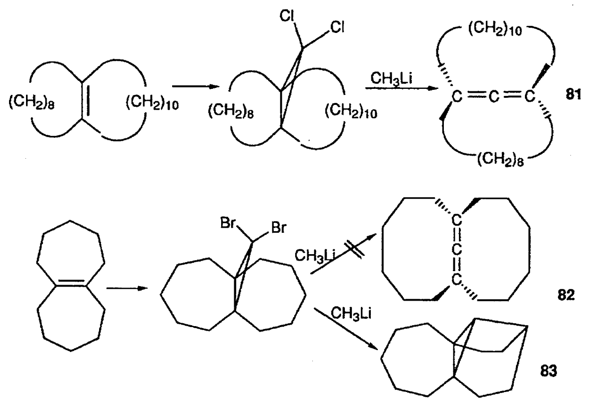


Fig. 6. ORTEP drawing of **77**.

There are few known examples of the bicyclic, doubly-bridged allenes, as betweenallenes. The strained symmetrical betweenallenes can gain no strain relief by bending, since what is gained in one ring is lost in the other; therefore, only twisting, as defined as a reduction in the normal allene dihedral angle of 90°, is available for strain relief. Nakazaki et al., synthesized [8.10]betweenallene **81**, consisting of fused 11 and 13 membered rings, as the first example of a betweenallene (Scheme 18).[61] He suggested that the limiting structure must have two eight-membered rings **82**, and attempted to prepare it by the carbenoid route. However, instead of the desired allene, transannular hydrogen insertion yielded **83**.



Scheme 17.



Scheme 18.

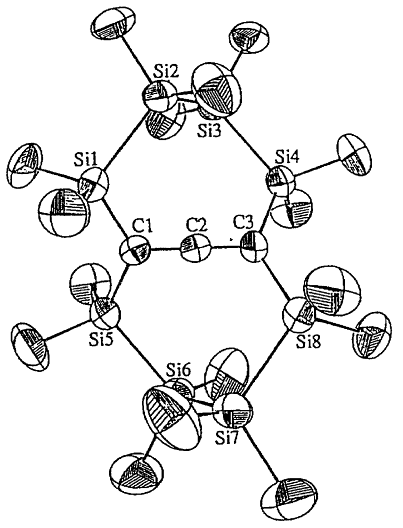
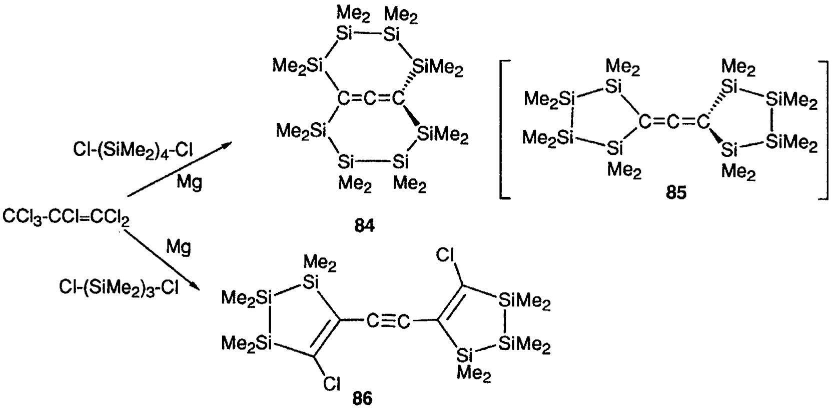


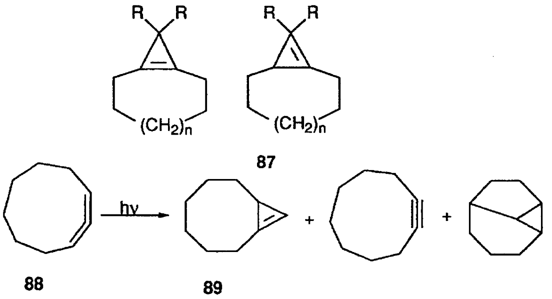
Fig. 7. ORTEP drawing of **84**.

Octasila[4.4]betweenallene **84** was prepared by the reaction of hexachloropropene with 1,4-dichlorooctamethyltetrasilane in the presence of magnesium in 34% yield; another expected isomer **85** could not be obtained. The corresponding [3.3]betweenallene could not be obtained, and an unexpected 2 : 2 adduct **86** was isolated in 16% yield as the volatile product by the reaction of hexachloropropene with 1,3-dichlorohexamethyltrisilane. An X-ray crystallographic analysis of octasila[4.4]betweenallene **84** showed a symmetrical conformation; also, the bond lengths and angles are almost normal (Fig. 7). The torsional angles, (Si1–C1–C3–Si4 and Si5–C1–C3–Si8) are 72.0° and 73.3°, respectively. This deformation from the vertical geometry of the allene is increased compared with that of **76**, which has the same-membered monocyclic system. The allenic sp carbon of **84** is almost liner, though in the case of **76** it is slightly bent. Therefore, the strain, as indicated by the dihedral angles of **84**, can be explained on the basis of the liner geometry of the allenic sp carbon. Barton et al., reported on the synthesis of **84** by another synthetic route (Scheme 19).[62]

Bicyclo[*n*.1.0]alk-1(*n*+3)-enes **87**, as representatives of highly strained olefins, are of considerable interest. Since the photoisomerization of allene to cyclopropene and propyne was first reported by Chapman, allene photochemistry has received much attention.[63] Stierman and Johnson et al., reported several photorearrangements of carbocyclic allenes giving the bicyclo[*n*.1.0]systems. Johnson et al., reported that the hydrocarbon **89** can be isolated as the major product from a singlet photo chemical reaction of 1,2-cyclononadiene **88** (Scheme 20). This singlet photochemistry is accompanied by less efficient 1,3-hydrogen migration and transannular insertion. In a photochemical reaction of hexasilacyclonona-

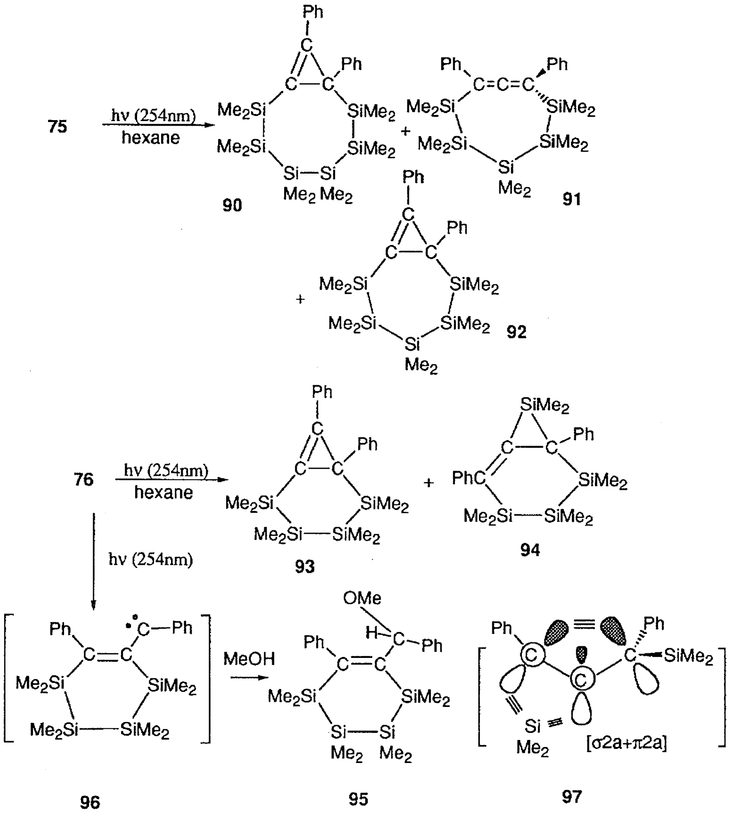


Scheme 19.



Scheme 20.

1,2-diene **75** with a low-pressure mercury lamp, the corresponding hexasilabicyclo[6.1.0]non-1(9)-ene **90** was isolated in 59% yield; additionally, the ring-contracted allene **91** and pentasilabicyclo[5.1.0]oct-1(8)-ene **92** were obtained in 14 and 23% yields (Scheme 21).[64] Irradiation of 1,2,3,4-tetrasilacyclohepta-5,6-diene **76** gave the tetrasilabicyclo[4.1.0]hept-1(7)-ene **93** and the 2,3,4,7-tetrasilabicyclo[4.1.0]hept-5-ene **94** in 45 and 20% yields, probably via the vinylcarbene intermediate or concerted process. The photolysis of a methanol solution of tetrasilacyclohexa-1,2-diene **76** gave a methanol-incorporated product **95** in 54% yield, together with the bicyclo[4.1.0]heptene derivative **93** (8%). The formation of **95** can be explained by a methanol reaction of a vinylcarbene **96** generated by 1,2-silyl shift. However, the photolysis of the bicyclo[4.1.0]heptene derivative **93** in methanol did not give methanol incorporated product **95**.

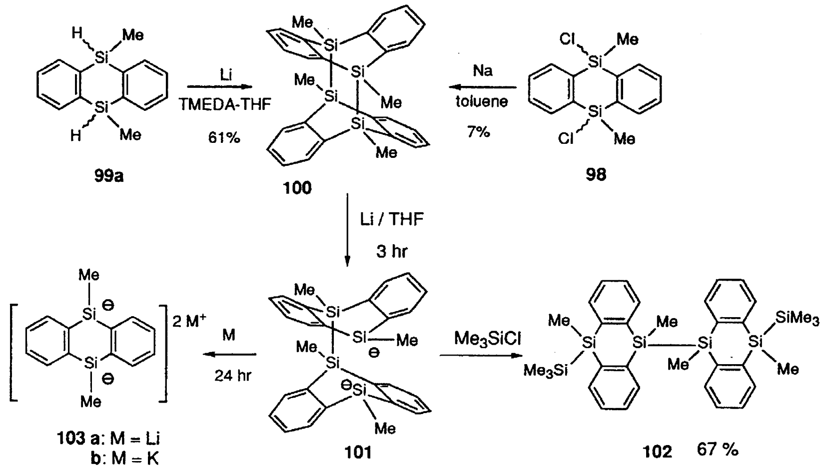


Scheme 21.

No methanol-incorporated products, **90**, **91**, and **92** were obtained in the photolysis of a methanol solution of 1,2,3,4,5,6-hexasilacyclonona-7,8-diene **75**. It is anticipated that there could be two reasons for being unable to trap the vinylcarbene intermediate. One is that the mechanism might be concerted through **97**; another may be due to the very short lifetime of the corresponding vinylcarbene intermediate.

Silaanthracenes: Synthesis and Reactions. The chemistry of 9,10-dihydroanthracenes with silicon in the position 9 and/or 10 position has been considerably developed for some time by Jutzi[65] and Bickelhaupt[66] and modified by Corey.[67]

Although a Wurtz coupling reaction of 9,10-dichloro-9,10-dimethyl-9,10-disilaanthracene (**98**) with sodium in toluene affords a bridged dimer (**100**), the reaction of a cis/trans mixture of 9,10-dihydro-9,10-dimethyl-9,10-disilaanthracene (**99**) with lithium in THF containing *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) produces **100** in moderate yield (Scheme 22), probably via the silicon centered 9,10-disilaanthracene biradical or its equivalent intermediate.[68] A silicon–silicon bond cleavage of the dimer **100** by excess lithium or potassium produced 9,10-disilaanthracene dianion **103a**, or **103b**. The ^{29}Si NMR chemical shifts in THF-d_8 were observed at −45.4 and at −42.8 ppm, respectively, a large upfield shift compared to that of other silyl anions (Ph_3SiM: −9.0 (M = Li), −7.5 (M = K) ppm; Ph_2MeSiM: −20.6 (M = Li), −18.5 (M = K) ppm) (Fig. 8).[69] The formation of these dianions (**103**) is strongly dependent upon the solvent; it increased in THF and was suppressed in diethyl ether and 1,2-dimethoxyethane (DME). In general, the formation of silyl potassium reagents from disilanes has been accomplished by reactions with potassium alkoxide[70] potassium hidride[71] or Na–K alloy,[72] and by a treatment with potassium metal in liquid ammonia.[73] During reactions of **100** with an equivalent amount of lithium or potassium, the reaction mixture became a yellow suspension, which reacted with trimethyl chlorosilane to give the opened dimer (**102**) in 67% yield. Since two methyl groups on the disilaanthracene unit of **102** were of the substituted cis configuration, respectively, the silicon–silicon bond cleavage of **100** with alkali metal proceeded with a retention of the configuration around the silicon atom. The reactions of the dipotassium disilaanthracene (**103b**) with trimethylchlorosilane gave the expected adduct (**99d**) in 73% yield as one isomer (Scheme 23). The compound **103b** reacts with dimethyl dichlorosilane to



Scheme 22.

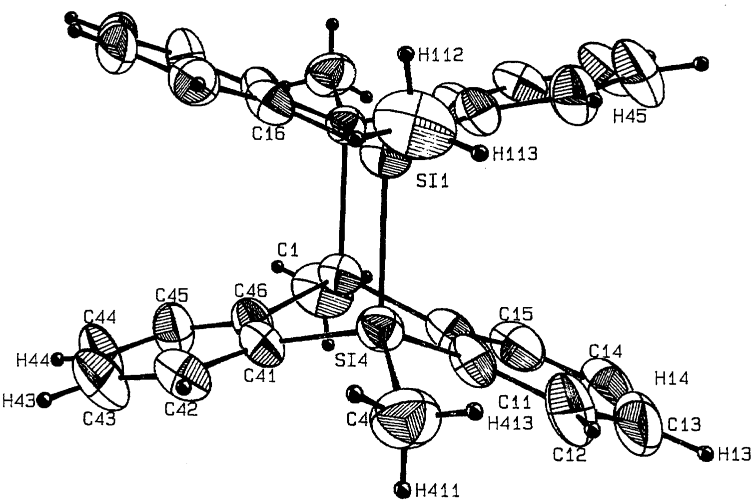
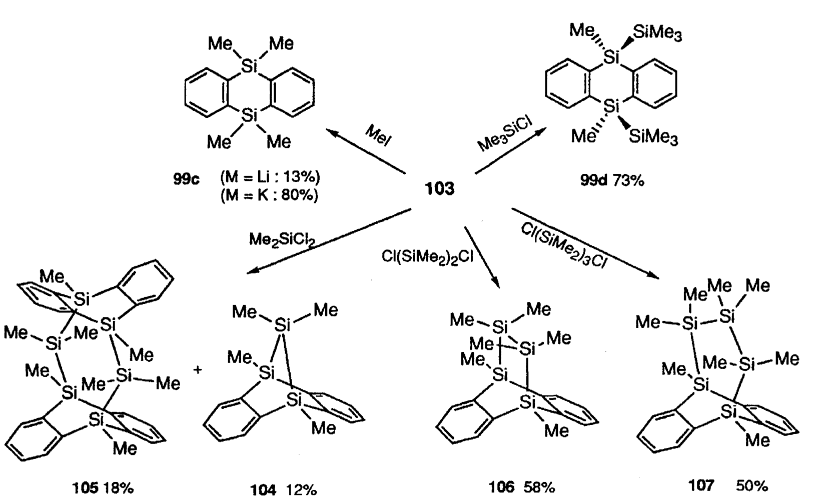


Fig. 8. ORTEP drawing of **100**.



Scheme 23.

give the expected dimethylsilyl adduct (**104**) bonded to the 9 and 10 positions of the disilaanthracene and its dimeric compound (**105**). The corresponding 9 and 10 positions adducts, the compounds **106** and **107** were obtained in good yield when the dipotassium (**103b**) reacted with 1,2-dichlorotetramethyldisilane and 1,3-dichlorohexamethyltrisilane, respectively, without the formation of dimeric products. Dipotassium 9,10-dimethyl-9,10-disilaanthracene (**103b**) can be a valuable intermediate for the synthesis of a great variety of *cis*-9,10-disilaanthracene derivatives.

Silicon Derivatives of Fullerene: Synthesis and Structures. Since the isolation of fullerene (C_{60})[74] in preparatively useful quantities, the chemical functionalization of this new allotropic form of carbon has attracted much interest, and has led to fascinating results.[75—79] Among the attractive targets are fullerene-bonded polysilanes (Fig. 9). One promising approach in this direction is photochemical addition of polysilanes to C_{60}.[80] The successful construction of the silicon derivatives of fullerene aroused intense interest in the addition of reactive silicon species.[81] It might be realized that addition of silylene onto C_{60} actually forms the silirane similar to the case of a carbene-addition.[82,83]

The photolysis of trisilane **108** in a toluene solution of C_{60} showed a color change of the solution from purple to dark brown. Flash chromatography on silica gel furnished thermally stable **110** and **111** in 58 and 27% yields, respectively.[81a] Small amounts of **112** and **113** were also obtained (Scheme 24). These products suggest silylene (**109**) addition to C_{60}. Product **110** displayed a FAB mass peak at 1074—1070 as well as for C_{60} at 723—720, which arose from the loss of silylene **109**. The FAB mass spectra of the

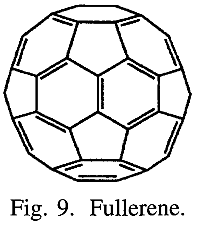
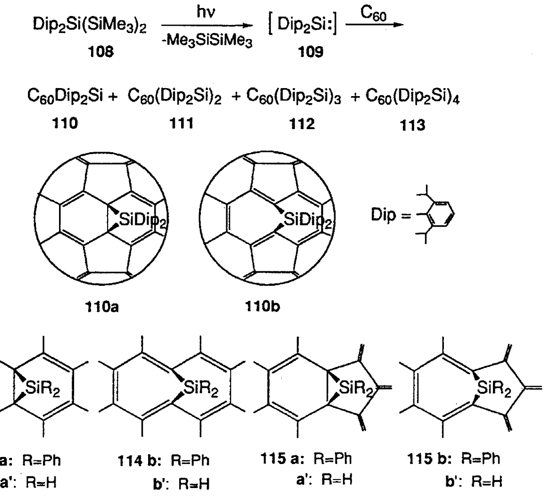
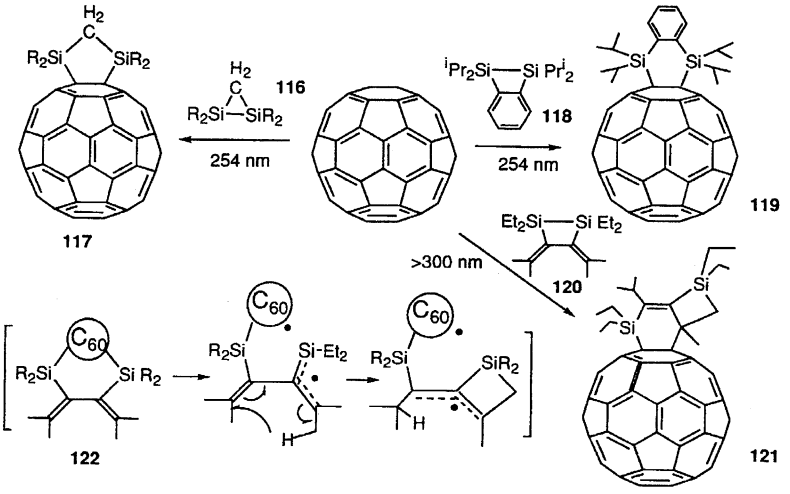


Fig. 9. Fullerene.

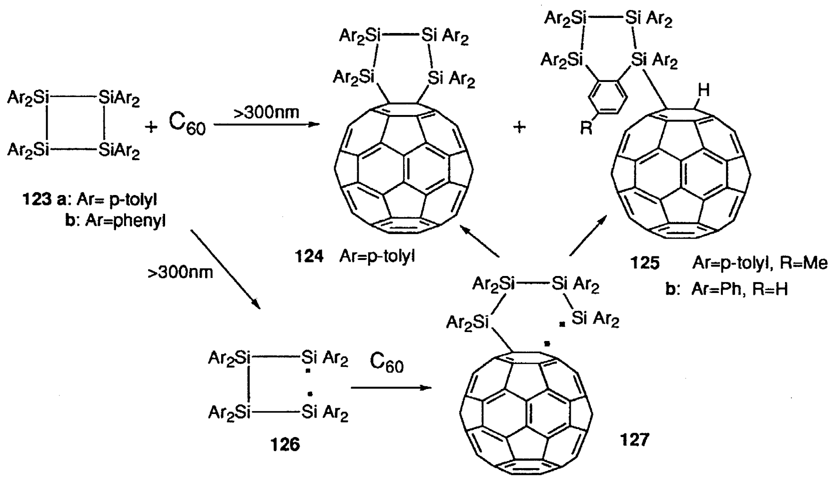


Scheme 24.

$(Dip_2Si)_2$ (**111**), $(Dip_2Si)_3$ (**112**) and $(Dip_2Si)_4$ (**113**) (Dip stand for 2,6-diisopropylphenyl) adducts of C_{60} were reasonably analyzed. The UV-vis absorption spectra of **110** is virtually identical to that of C_{60}, except for subtle differences in the 400—700 nm region. Compound **110** exhibits a new band at 421 nm, but lacks the C_{60} band at 406 nm. Compound **110** shows stronger absorptions at 463 and 508 nm and weaker absorptions at 539 and 599 nm. The FAB mass, UV-vis and FTIR spectra of **110** contain a number of unique features, but also suggest that this new fullerene retains the essential electronic and structural character of C_{60}. Silacyclopropane **110a** of C_{2v} symmetry,[75a,75e,75f,75g,76a] would be derived from the addition of silylene across the reactive 6-6-ring junction. Silano[10]annulene **110b**, analogous to the structure proposed for Ph_2C_{61} could arise via isomerization of **110a**. The proton NMR was consistent with the Dip_2Si adduct of C_{60}. The ^{13}C NMR spectrum shows 17 signals for the C_{60} skeleton, of which four correspond to two carbon atoms and thirteen correspond to four carbon atoms: one at $\delta = 71.12$ and the remainder between $\delta = 140$ and $\delta = 150$. The signal at $\delta = 142.54$ consists of three peaks, each corresponding to four carbon atoms. This is the appropriate number and ratio of the peak intensities for a C_{60} adduct having C_{2v} symmetry. Methyl-substituted silirane carbons typically resonate at $\delta = 15—25$.[84] A downfield shift by 20 ppm may occur when a vinyl group is attached to the ring carbon.[85] The ^{29}Si NMR spectrum of **110** shows a peak at $\delta = -72.74$, which is also assigned to the silicon atom of **110a**. The chemical shift of the silicon atom on silacyclopropane ring typically appears at high field, ranging from $\delta = -50$ to $\delta = -85$.[84] The ^{29}Si chemical shift of diphenyldivinylsilane can be anticipated to appear at $\delta = -20$.[83] Thus, the chemical shifts of the two-carbon and silicon signals are fully consistent with the expectations for the silacyclopropane carbon atoms and



Scheme 25.



Scheme 26.

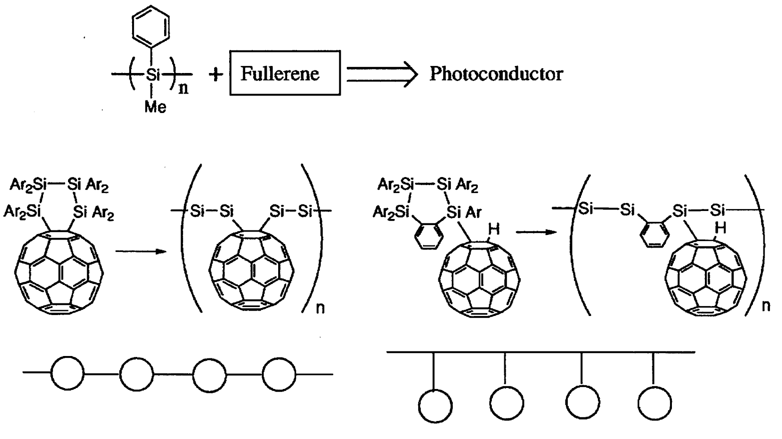


Fig. 10. Application to photoconductive polymer.

silicon atom in **110a**. The experimental finding for **110a** was confirmed by AM1 molecular orbital calculation[86,87] on the reaction of C_{60} and silylenes, $Ph_2Si:$ and $H_2Si:$. They add across the junction of two six-membered rings in C_{60} to give siliranes (a 6-6 adduct), **114a** and **114a′**, with an exothermicity of 61.3 and 78.0 kcal mol^{-1}, respectively. The isomeric **114b** and **114b′** were not located on the potential energy surface. The 6-6 adduct **114a** was 19.4 and 10.7 kcal mol^{-1} more stable than the 5-6 adducts **115a** and **115b**, respectively. Compound **114a′** was 19.0 and 6.2 kcal mol^{-1} more stable than the 5-6 adducts **115a′** and **115b′**, respectively. The less-stable **115a** and **115a′** isomerize to **115b** and **115b′** with small barriers of 2.0 and 1.0 kcal mol^{-1}, respectively. Interestingly, this is in contrast with the addition of diphenylmethylene, for which the 6-6 adduct was calculated to be only 1.2 kcal mol^{-1} more stable than the 5-6 adduct. Although a photoinduced charge-transfer between C_{60} and various electron donors, such as aromatic amines, semiconductor colloids, porphyrins, can occur, there has so far been no example of the formation of a photoadduct. Meanwhile, strained Si–Si σ bonds, such as disilirane, can act as electron donors. The photochemical reaction of C_{60} with a disilirane produces a [2+3] cycloadduct via a charge-transfer interaction. The photolysis of a toluene solution of 1,1,2,2-tetramesityl-1,2-dislacyclopropane (**116**) and C_{60} with a high-pressure mercury arc lamp resulted in the formation of 1,1,3,3-tetramesityl-1,3-disilacyclopentane (**117**) in 82% yield (Scheme 25). On the other hand, the photolysis of 3,4-benzo-1,1,2,2-tetraisopropyl-1,2-disilacyclobutene (**118**) in a toluene solution of C_{60} gave an unidentified complex mixture (complete consumption of C_{60}). However, irradiation of a solution of **118** and C_{60} in a toluene-*t*-BuOH mixed solvent afforded a brown adduct **119** in 14% yield (based on unreacted C_{60}).[88] For an isopropyl group with two diastereotopic methyl groups, two quartets at $d=19.94$ and 20.15 as well as one doublet at 14.74 ppm appear in the ^{13}C NMR spectrum. The corresponding methyl and methine protons resonate at $\delta=1.14$ (d, 12H, $J=7.4$ Hz), 1.40 (d, 12H, $J=7.4$ Hz), and 2.17 (sept, 4H, $J=7.4$ Hz) in the ^{1}H NMR spectrum. One AA′BB′ pattern appears at $\delta=7.58$ (dd, 2H, $J=5.7$, 3.5 Hz) and 8.03 (dd, 2H, $J=5.7$, 3.5 Hz) in the ^{1}H NMR spectrum and two doublets at 128.81 and 136.12 ppm in the ^{13}C NMR spectrum. The ^{13}C NMR spectrum of **119** shows 17 signals for the C_{60} skeleton, of which four correspond to two-carbon atoms and 13 correspond to four-carbon atoms: one at $\delta=63.93$ and the remainder between $\delta=130$ and 160. This is the appropriate number and ratio of peak intensities for a C_{60} adduct of C_{2v} symmetry.[81a)] The ^{13}C NMR signal at $\delta=63.93$ strongly supports 1,2-addition (6-6 closed). The formation of adduct **119** did not occur under the irradiation of a high-pressure mercury lamp (> 300 nm), which indicates that diradical formed by the initial Si–Si bond cleavage might be trapped with C_{60} to afford adduct **119**. Under similar conditions the photolysis of a toluene solution of 21.0 mg (62.4 μmol) of 3,4-dialkylidene-1,2-disilacyclobutanes **120** and C_{60} with a high-pressure mercury lamp (filter: $\lambda<300$ nm) for 24h, followed by purification by means of gel-permeation chromatography, afforded adduct **121** in 61% yields. The mechanistic pathway for the formation of **121** is not clear at present. However, since five equivalents of rubrene, a well-established triplet quencher, completely inhibited the reaction between **120** and C_{60}, and, furthermore, the disilacyclobutanes **120** were stable under the reaction conditions, triplet-excited C_{60} seems to be involved in the course of the reaction. Alternatively, the initially formed **122** might be photolabile and rearrange to **121**. The photolysis of cyclotetrasilanes **123a** in a toluene solution of C_{60} with a high-pressure mercury lamp ($\lambda>300$ nm), followed by purification by means of gel-permeation chromatography, afforded brown adducts **124a** and **125a** in 13 and 46% yields, respectively (Scheme 26). Under identical conditions, only **125b** was obtained from **123b** in 87% yield.[81b)] The ^{13}C NMR spectrum of **124a** displays 38 signals for all quaternary carbon. Of the 38, one fullerene carbon atom resonates at 62.18 ppm. The signals of all other carbons appear in the region between $\delta=125$—165 ppm. The ^{1}H NMR spectrum of **124a** displays 4 methyl signals and 4 pairs of AB quartets, supporting C_s symmetry for the molecule. The ^{29}Si NMR spectrum of **124a** shows two peaks at $\delta=-22.25$ and -11.34 ppm, which are assigned to the silicon atoms of **124a**. Symmetry arguments support that a 6,6-ring junction on the C_{60} with a frozen conformer is most probable for **124a**. The ^{13}C NMR spectrum of **125a** displays 64 signals for all quaternary carbon, which indicates the absence of any symmetry element in this molecule. Of the 64, one fullerene carbon atom resonates at $\delta=60.35$ ppm. The signals of all other carbons appear in the region between 125—160 ppm. The partial structure of the fragment annulated to the C_{60} moiety derives from the NMR spectroscopic properties for **125a**. Regarding the addition pattern of the fullerene moiety, a 6,6-ring junction of the tetrasilacyclohexane fragment is most probable. In the case of a 5,6-junction, the formation of two diastereomeric adducts would have to be expected. The possibility of 1,4-addition can be eliminated by ^{13}C–^{1}H COLOC (correlation spectroscopy via long-range coupling). It was shown that the proton resonance at 6.91 ppm correlates to a quaternary carbon on the C_{60}. In order to obtain information concerning the mechanistic pathway we carried out the photochemical reaction ($\lambda>300$ nm) of **123b** in the presence of CCl_4 to give 1,4-dichloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane and 1,3-dichloro-1,1,2,2,3,3-hexaphenyltrisilane in 37 and 31% yields, respectively. Under identical photolytic conditions, adduct **124a** did not convert to **125a** in a control experiment. These findings indicate that biradical **127** via **126** might be involved in the course of the reaction. Among the attractive targets are the fullerene-bonded polysilanes, Wang and West reported that fullerene-doped polysilane displays enhanced photoconductivity (Fig. 10).[89] Fullerene-bonded polysilane derivatives are now expected to be obtained by a ring-opening polymerization of **124** and **125**.

I wish to thank with great pleasure many collaborators who are listed in the references. They have contributed experimentally as well as conceptually to the development of the organosilicon chemistry in the ring system summarized in this account. The work quoted here has been supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture as well as the Shin-Etsu Chemical Co., Dow Corning Asia, and Toshiba Silicone Co.

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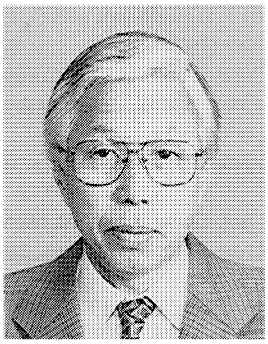

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