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Study of additions of disilanes to acetylenes and their applications in organic and polymer synthesis

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Study of additions of disilanes to acetylenes and their applications in organic and polymer synthesis

by

Zhongxin Ma

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirement for the degree of
DOCTOR OF PHILOSOPHY

Co-Majors: Organic Chemistry; Physical Chemistry
Major Professors: Tom J. Barton and Mark S. Gordon

Iowa State University
Ames, Iowa
1998

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For the Graduate College

DEDICATION

TO THE MEMORY OF MY FATHER

TO MY MOTHER

TO YU AND KATE

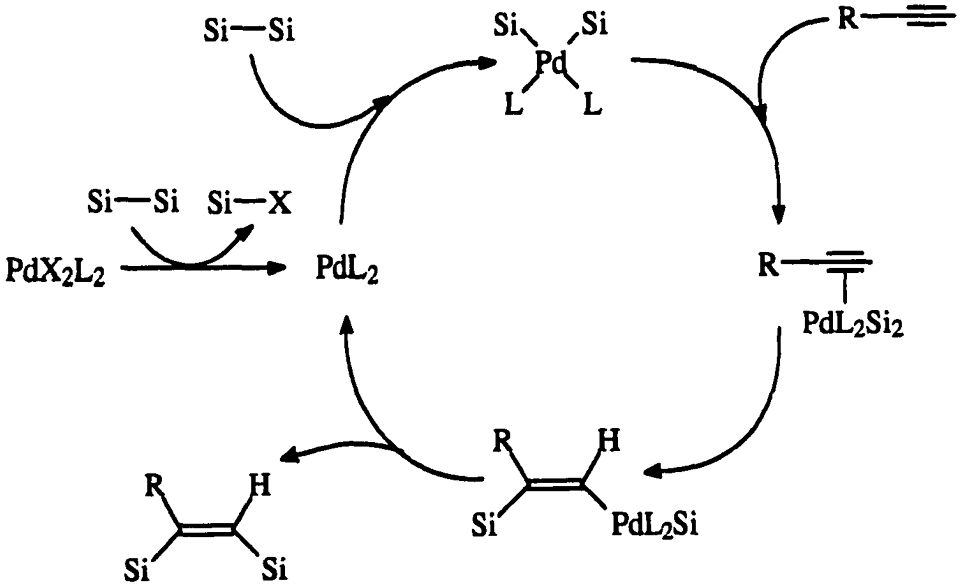
TABLE OF CONTENTS

GENERAL INTRODUCTION

Since the first example of addition of disilanes to acetylenes with a palladium catalyst was reported in 1975, significant efforts have been made to study these reactions.[1,2] In last few years great progress has been made. Now these reactions can be carried out even at room temperature. The studies have demonstrated that these catalytic reactions usually afford the *cis*-addition products with high yields. These bissilylations have been used for organic and polymer synthesis.[1,2]

The process of addition of disilanes to acetylenes releases about 40 kcal/mol of heat.[3] Even though this is an energy-favored process, thermal and photochemical additions of disilanes to acetylenes have not been reported so far. The addition has been restricted to transition-metal catalyzed reactions. Kumada et al. found that the cis-addition of disilanes to acetylenes twenty three years ago and proved that the reaction gave a *Z* stereochemistry of the double silylation product.[4] The catalysts are mainly soluble palladium-based complexes. The Pd(0) complexes gave higher yields than did the Pd(II) catalysts. Seyferth *et al.* revealed some mechanistic details by reacting the strained 1,2-disilacyclobutane with acetylenes. When 1 equivalent of $PdCl_2(PPh_3)_2$ was used, the disilylpalladium complex was formed.[5] This palladium species was shown to react stoichiometrically with phenylacetylene to give the addition of disilane and acetylene, which was the same as obtained from the catalytic reaction. The disilylpalladium compound is a probable intermediate in the catalytic reaction. With this mechanistic information, the mechanism for the addition of disilanes to acetylenes was proposed as follows (Scheme 1).[1] First a Pd(0) catalyst was formed. Then oxidative addition of the disilane to this species proceeded. Third, a π complex with the acetylene was formed. Fourth, the acetylene was inserted into one of the palladium-silicon bonds. And last, the disilylethylene product was reductively eliminated. An X-ray crystal structure of (dcpe)Pd($SiHMe_2$)$_2$ was determined.[6] This complex reacted cleanly with dimethyl acetylenedicarboxylate at 25°C to give cis-bis(dimethylsilyl)maleate. This reaction strongly supported the mechanism Seyferth suggested.

Scheme 1[1]

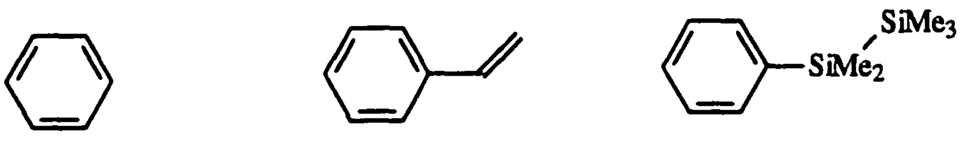


The reactivity of organodisilanes in such addition chemistry is enhanced by electronegative substituents fluorine, chlorine, and alkoxide.[7-10] The order of reactivity increases with the substituents: p-$CH_3C_6H_4 < C_6H_5 < p$-$CF_3C_6H_4 < CH_3 < Cl < OCH_3 < F$. The strain in the disila-cyclic systems also enhances the reactivity.

Intramolecular addition of disilanes to acetylenes also has been extensively studied. Because this reaction can control the stereo and regional chemistry effectively, and the silyl group can been transformed into other functional groups, these have been used for organic natural product synthesis.[11]

The silicon-silicon single bond has many characteristics of π bond in the carbon-carbon double bond. First, like the double bond, the silicon-silicon single bond can be electronically conjugated to other aromatic systems (Scheme 2).[12,13] Second, it can donate one electron or accept an electron to form a disilanyl radical cation or anion as a carbon-carbon double bond does (Scheme 3).[14,15] Third, like the π bond, the silicon-silicon single bond can also be electrophilically cleaved by bromine and peroxide compounds (Scheme 4).[14] A π bond can be thermally and photochemically added to a double or triple bond, but thermal or photochemical addition of silicon-silicon bond to double and triple bond has not been reported yet. In this dissertation, we start to address this issue.

Scheme 2[12,13]



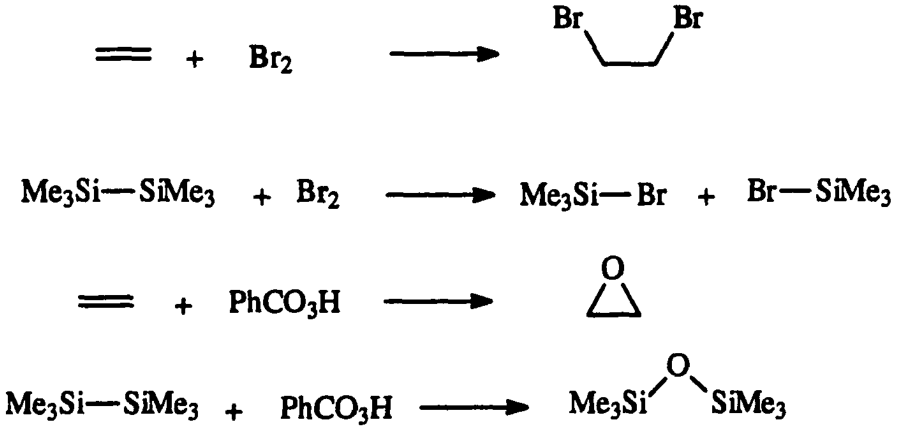
202 nm (^{1}La band) 244 nm 230 nm

Scheme 3[14,15]

$$Me_3Si\text{—}SiMe_3 \xrightarrow{(CN)_2C{=}C(CN)_2} [Me_3Si\text{—}SiMe_3]^{\dot{+}}$$

$$Me_3Si\text{—}SiMe_3 \xrightarrow{K} [Me_3Si\text{—}SiMe_3]^{\dot{-}}$$

Scheme 4[14]



Dissertation Organization

This dissertation is comprised of three papers prepared for submission to journals and general conclusions.

In the first part of the dissertation, a variety of systems were designed to examine the disilane's chemical properties. The *suprafacial-antarafacial* [2+2] addition is a thermally-allowed process, which has been observed in some double bond reactions.[16,17] Can disilane resemble the property of double bond in this kind of reaction? Considering only energetics, the reaction is favorable, and can gain about 40 kcal/mol. However, the activation entropy is a major barrier for this reaction. To overcome this problem, intramolecular processes offer an approach.

The *suprafacial-suprafacial* [2+2] addition is a photo-allowed process. This reaction is commonly seen in the organic photochemistry.[18] The proper systems also were designed to examine the similarity of disilane with ethylene in photoadditions.

In the second part of the dissertation, unique luminenscent materials were designed and synthesized by using the addition of disilanes to acetylenes. The silyl group is a unique group for tailoring the molecular properties. For example, it can decrease the energy of the LUMO of a conjugated system significantly. By addition of disilanes to acetylenes, two silyl groups are introduced to a conjugated system simultaneously in a certain way to change the properties of the molecule. Light-emitting diodes (LED) were fabricated with the new material. The materials also have been incorporated into polymers to improve the mechanical properties and their morphology.

In the third part of dissertation, the catalytic addition of disilanes to acetylenes will be used to synthesize a highly strained four-membered ring, a 2-silaoxetane, which was desired by us to study the mechanism of reactions of silenes with carbonyl compounds. The thermal and photochemical stabilities of the molecule were studied.

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I. DISCOVERY OF TRANS-ADDITION OF DISILANES TO ACETYLENES THERMOCHEMICALLY AND PHOTOCHEMICALLY

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Abstract

An apparent $[2_s+2_a]$ intramolecular addition was discovered between disilanes and acetylenes. The reaction was performed with the 5,5,6,6-tetramethyl-3,3,8,8-tetraphenyl-4,7-dioxa-5,6-disila-cyclooctyne (3) under argon flow at 600°C to give 1,1,4,4-tetramethyl-3,3,6,6-tetraphenyl-2,5-dioxa-1,4-disila-dicyclo[3,3,0]octa-7-ene (4). *Ab initio* calculations with MP4/6-31G** were carried out to find the transition state structure of the $H_3SiSiH_3 + HC{\equiv}CH$ reaction. The activation energy was determined to be 34 kcal/mol. It was found that the intramolecular *trans*-bissilylation of acetylene also photochemically occurred when the acetylene is conjugated with an aromatic group.

1. Introduction

Since Woodward and Hoffmann established the concerted reaction theory based on molecular orbital theory and orbital symmetry principles in 1965,[1] it has been extensively used for understanding and predicting chemical reactions.[2,3] Thus, the thermal cycloaddition of two ethylenes is a symmetry-allowed reaction as a concerted $[2_s+2_a]$ addition process (Figure 1). However, because of the inefficient orbital overlap and steric hindrance, the ***suprafacial, antarafacial*** addition process is unfavorable. Experimental[4-6] and theoretical[7-9] studies have shown that the [2+2] addition in two ethylenes usually proceeds in a stepwise manner. Recently, Pedersen, Herek and Zewail for the first time directly observed the existence of the diradical intermediate of the cycloaddition of two ethylene molecules, using femtosecond laser technique.[6] Only a few cases of the concerted process are known, such as the reaction of ketenes with olefins[10] and ketene dimerizations.[11] A concerted process is possible in these cases because ketenes have smaller steric hindrance and larger reactivity than olefins do. In the reaction of ketenes with olefins, the olefin is always found as the 2_s component and the ketene as the 2_a component, which are shown in Figure 2. Huisgen investigated the cycloadditions of olefins to ketenes and concluded that the reaction was concerted but bond formation in the transition state was unequal.[12] He also found these reactions to have a very low ΔH^* (~9-10 kcal/mol) and large negative ΔS^* (~-40 e.u.).[12] This large negative activation entropy is the major impediment for this reaction, explained with the following equation:

$$\Delta G^* = \Delta H^* - T\,\Delta S^* \tag{1}$$

Fortunately, this low activation enthalpy enables the reactions to take place. In order to make the reactions proceed in non-ketene systems, a reduction of the large negative $\Delta S^{\neq}$ is necessary. Intramolecular reaction is an obvious strategy.

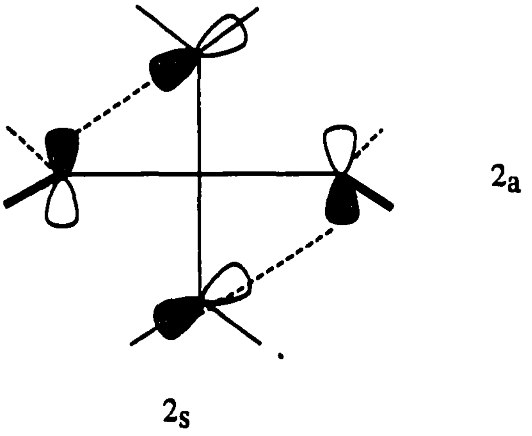
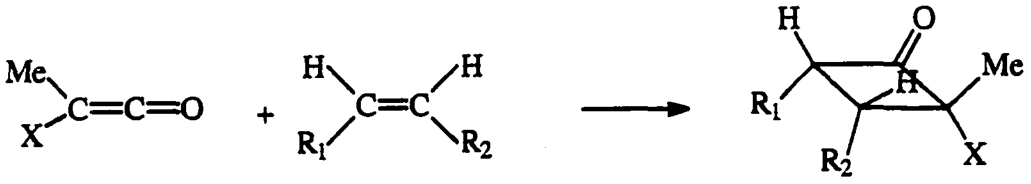


Figure 1. The orbital interaction in the concerted $[2_s+2_a]$ cycloaddition

Scheme 1



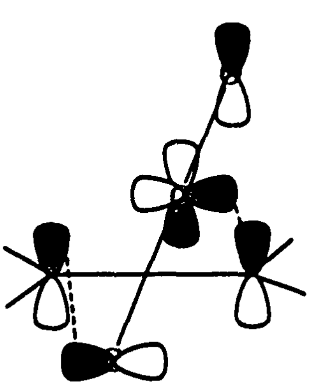
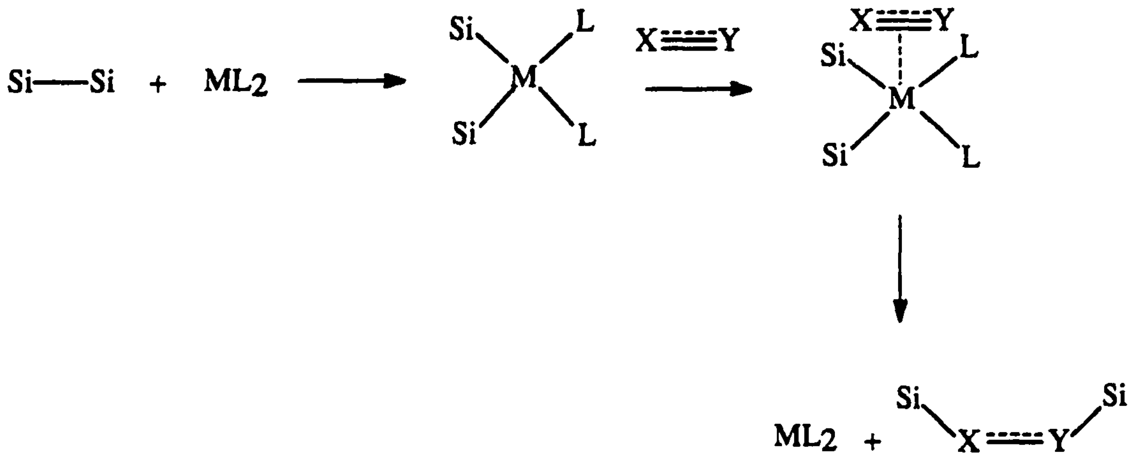


Figure 2. The orbital interaction in concerted $[2_s+2_a]$ reaction of an olefin and a ketene

The catalytic addition of disilanes to olefins or acetylenes has been well known for decades, and plays a very important role in organic and polymer syntheses.[13,14] Oxidative addition of Si-Si bonds to a transition metal forms a complex which inserts in an acetylene or an olefin. Reductive elimination to give a *cis* disilated product completes the catalytic cycle (Scheme 2). The transition metal usually is palladium. Sharma and Pannell have extensively reviewed the addition reactions in which disilanes and acetylenes and olefins are involved.[13]

According to Woodward-Hoffmann molecular orbital symmetry theory, the addition reaction of disilanes to acetylenes or ethylenes should be a thermally-allowed concerted $[2_s+2_a]$ process. The addition would thus be a *trans*-addition, in contrast to the catalytic process. Disilanes normally extrude a silylene photochemically.[15,16] Silyl-migration also occurs when a disilane is directly attached to an aromatic or an acetylene group.[15] To our knowledge, no thermal or photochemical additions of disilanes to acetylenes or ethylenes have ever been reported. Herein, we report for the first examples of apparent concerted $[2_s+2_a]$ additions of disilanes to acetylenes, and *ab initio* calculations carried out to investigate this process.

Scheme 2.



2. Results and Discussions

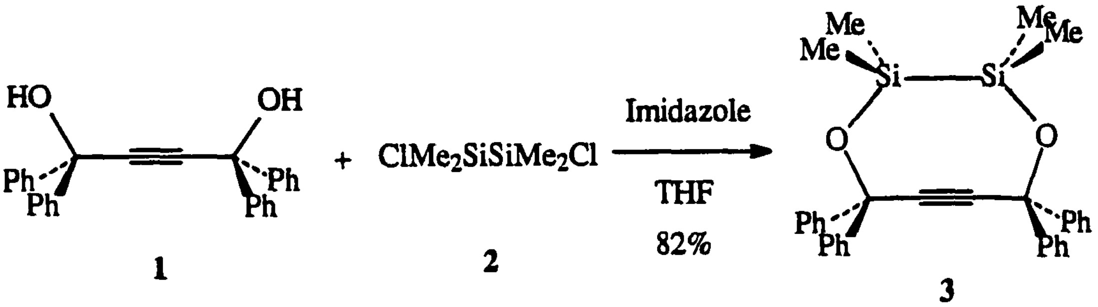
2.1. Thermochemical *trans*-addition of disilanes to acetylenes

Five different systems were synthesized to study thermochemical properties compounds contain acetylene and disilane groups. Three cyclic, an acyclic and a bi-molecular system were investigated respectively.

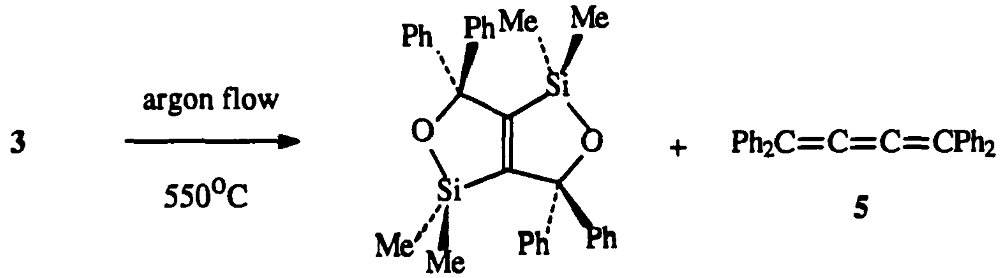
2.1.1 4,7-Dioxa-5,6-disila-cyclooctyne (3 and 10).

The first system, 5,5,6,6-tetramethyl-3,3,8,8-tetraphenyl-4,7-dioxa-5,6-disila-cyclooctyne (**3**), was synthesized by condensation of 1,1,4,4-tetraphenyl-2-butyn-1,4-diol (**1**)[17] with 1,2-dichloro-1,1,2,2-tetramethyldisilane (**2**)[18] in THF (Scheme 3). Flow pyrolysis under argon was carried out at different temperatures from 400 to 600°C. An isomerization took place (Scheme 4) at 550°C in 70% yield. The isomer, 1,1,4,4-tetramethyl-3,3,6,6-tetraphenyl-2,5-dioxa-1,4-disila-dicyclo[3,3,0]octa-7-ene (**4**), was characterized by NMR and X-ray diffraction. At the same time, 10% of tetraphenylbutatriene was also obtained. For the first time the addition of a disilane to an acetylene gave a *trans* product. Although the X-ray diffraction gave a clear structure of compound **4**, a publishable structure could not be obtained because of the high thermal factor for the structure refinement. Thus, an analog, 3,8-bis(4-trimethylsilylphenyl)-3,8-diphenyl-5,5,6,6-tetramethyl-4,7-dioxa-5,6-disila-cyclooctyne (**10**) was synthesized in order to unequivically establish the structure (Scheme 5).[19] This analog went through the same isomerization reaction and gave a similar product, giving a crystal structure (Figure 3 and Appendix I).

Scheme 3



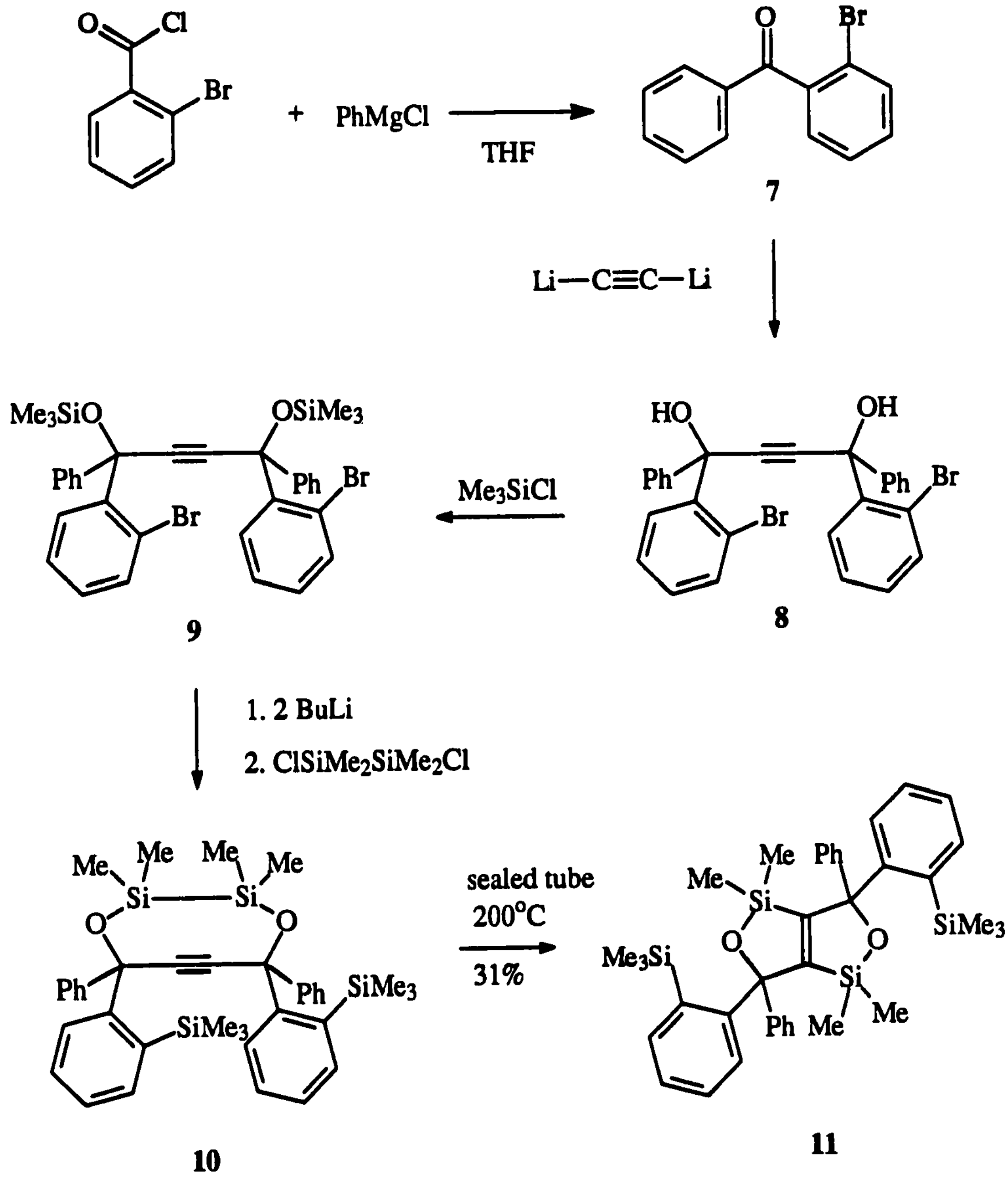
Scheme 4



4

As these reactions appear to be examples of suprafacial, antarafacial [2+2] *trans*-addition, AM1 calculations were carried out to understand the process.[20] The calculations showed that in **3** the Si-Si bond crosses the C≡C bond with a 40° angle in the compound **1** (Figure **4**), which is half way to perfect $[2_s+2_a]$ addition geometry (90°). This process has a lower barrier than the $[2_s+2_s]$ process (Figure **5**). An *ab initio* calculation was carried out for the simplest model, hexahydridodisilane reacting with acetylene. A transition state (Figure **6** and Table **1**) found with the Restricted-Hartree-Fock (RHF) method with 6-31G* basis set is very late and thus close to the product.

Scheme 5


PhMgCl
THF
7
Li—C≡C—Li
8
Me3SiCl
9
1. 2 BuLi
2. ClSiMe2SiMe2Cl
10
sealed tube
200°C
31%
11

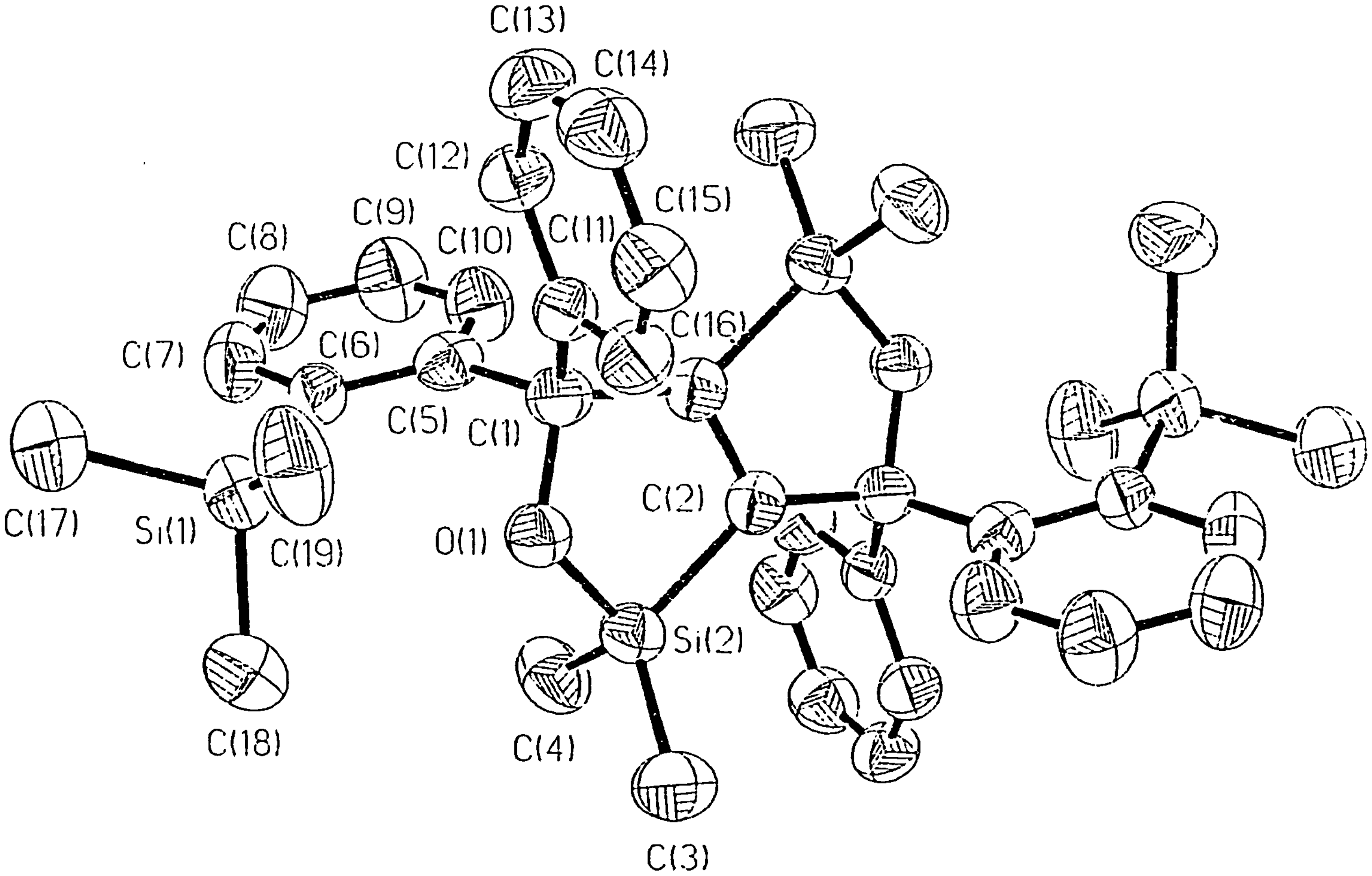


Figure 3. X-ray structure of molecule **11**.

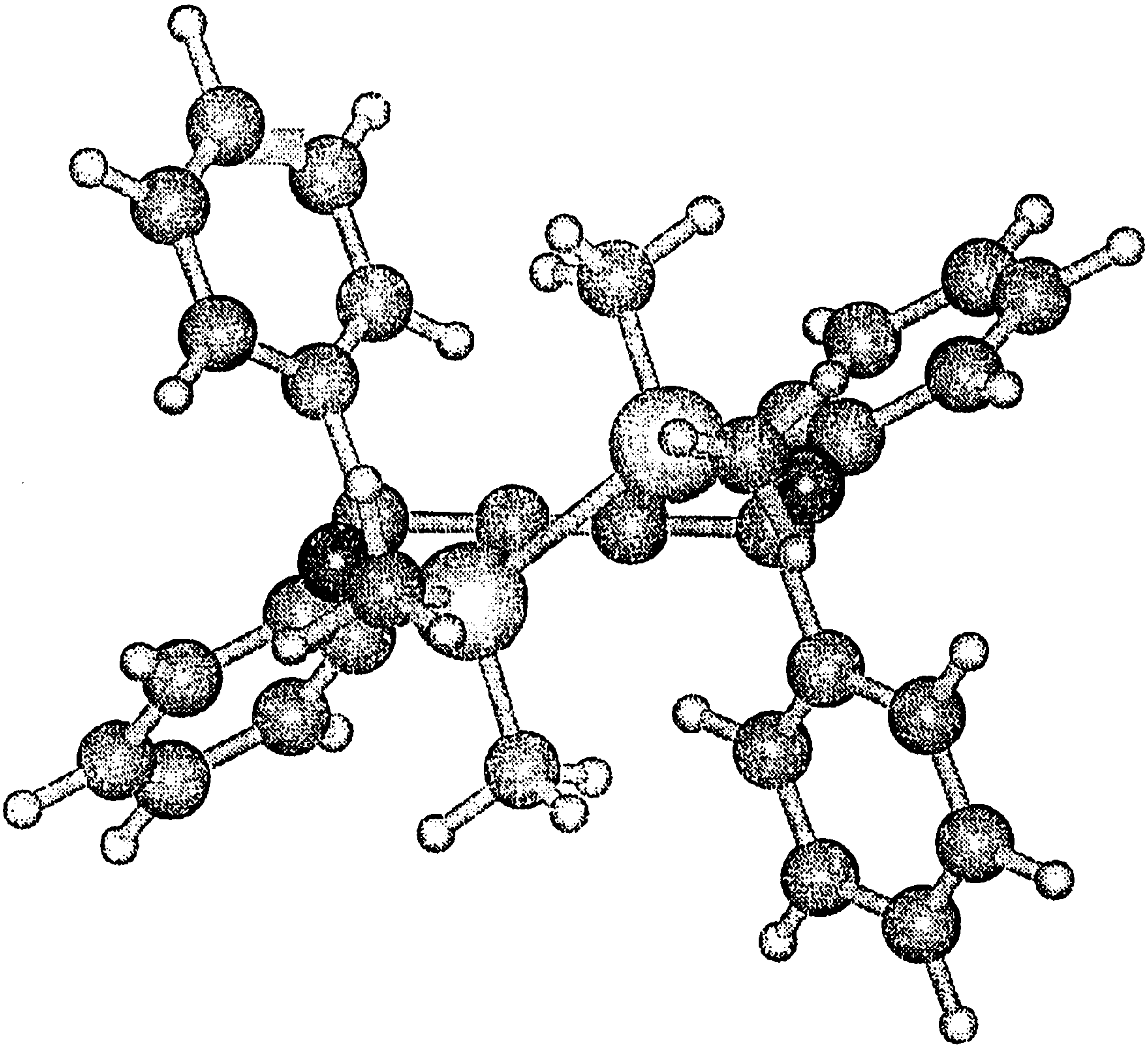


Figure 4. The geometry of 3 calculated by AM1 method.

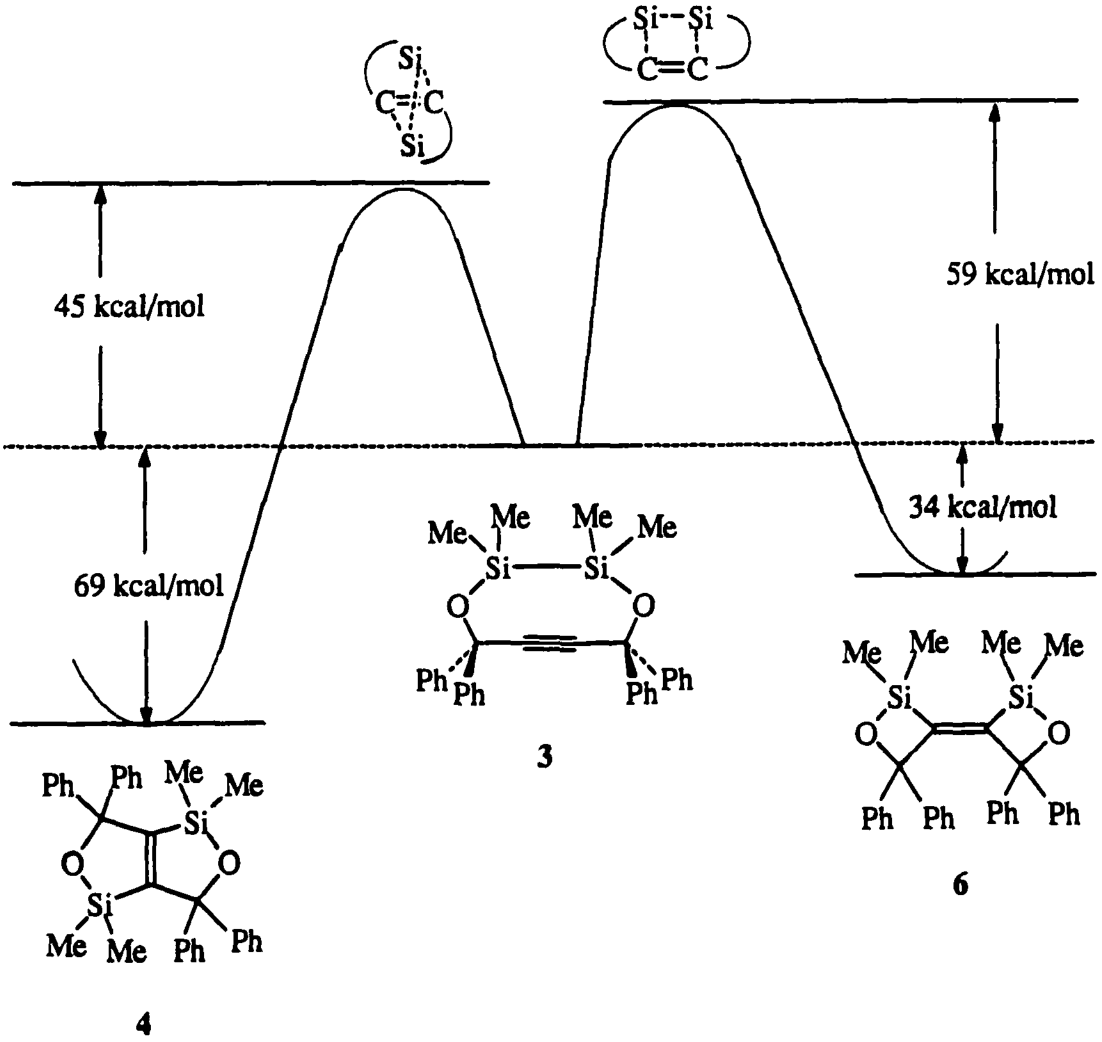


Figure 5. Potential energies of **3** calculated with AM1 method.

The activation energy at the MP4 level with 6-31G** basis set based on the geometries optimized with RHF/6-31* was found to be 34 kcal/mole. For a unimolecular reaction, this value is moderate, and an isomerization would be expected to proceed easily. The activation entropy was found to be –35.16 cal/mol·K for the reaction of disilane and acetylene. This could be the main barrier for this intermolecular reaction according to the equation (1). In order to confirm the conclusion, a bi-molecular reaction of hexamethyldisilane with phenylacetylene was attempted out in an argon flow at 550°C. No reaction between these two reactants was observed.

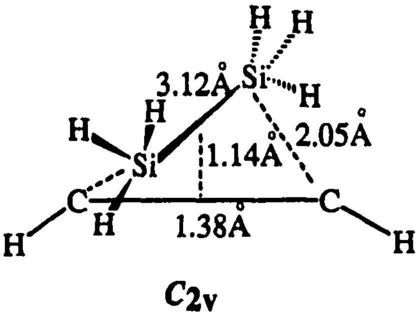
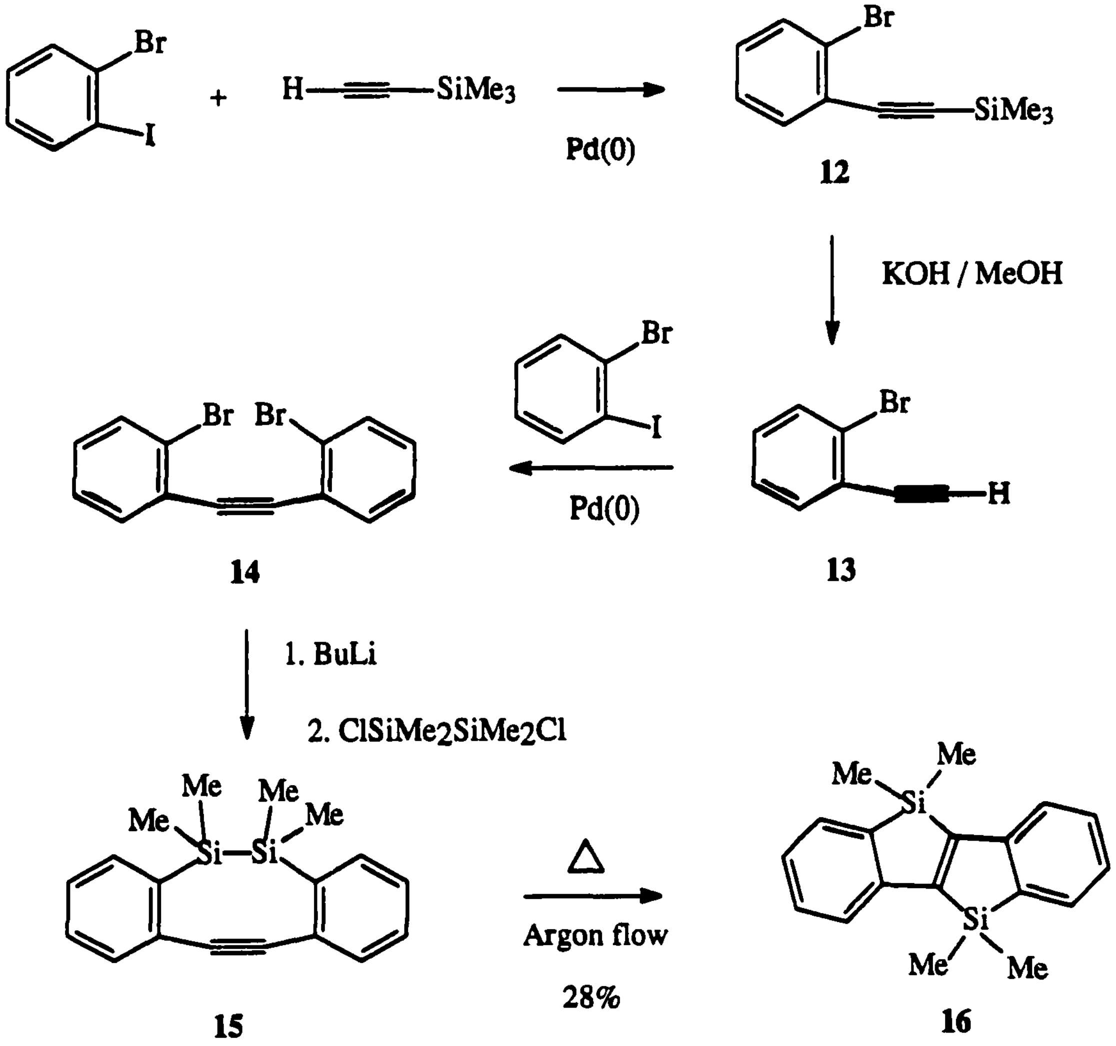


Figure 6. The geometry of the transition state of addition of disilane to acetylene

2.1.2. 5,5,6,6-tetramethyl-5,6-disila-dibenzo[*c;g*]cyclooctyne (15)

A quite different eight-membered ring system, 5,5,6,6-tetramethyl-5,6-disila-dibenzo[*c;g*]cyclooctyne (**15**) was synthesized to test the generality of our observation (Scheme **6**). The thermal isomerization of **15** was carried out at 550°C under argon-flow to produce **16** in 28% yield. Thus we have another apparent example of intramolecular $[2_s+2_a]$ *trans*-addition. The product **16** was characterized by NMR, mass spectroscopy and X-ray structure (Figure 7 and Appendix II). This unique molecule, a silicon-bridged trans-stilbene, has many potential applications in electro-optic and organic light-emitting diode devices.[20-24]

Scheme 6



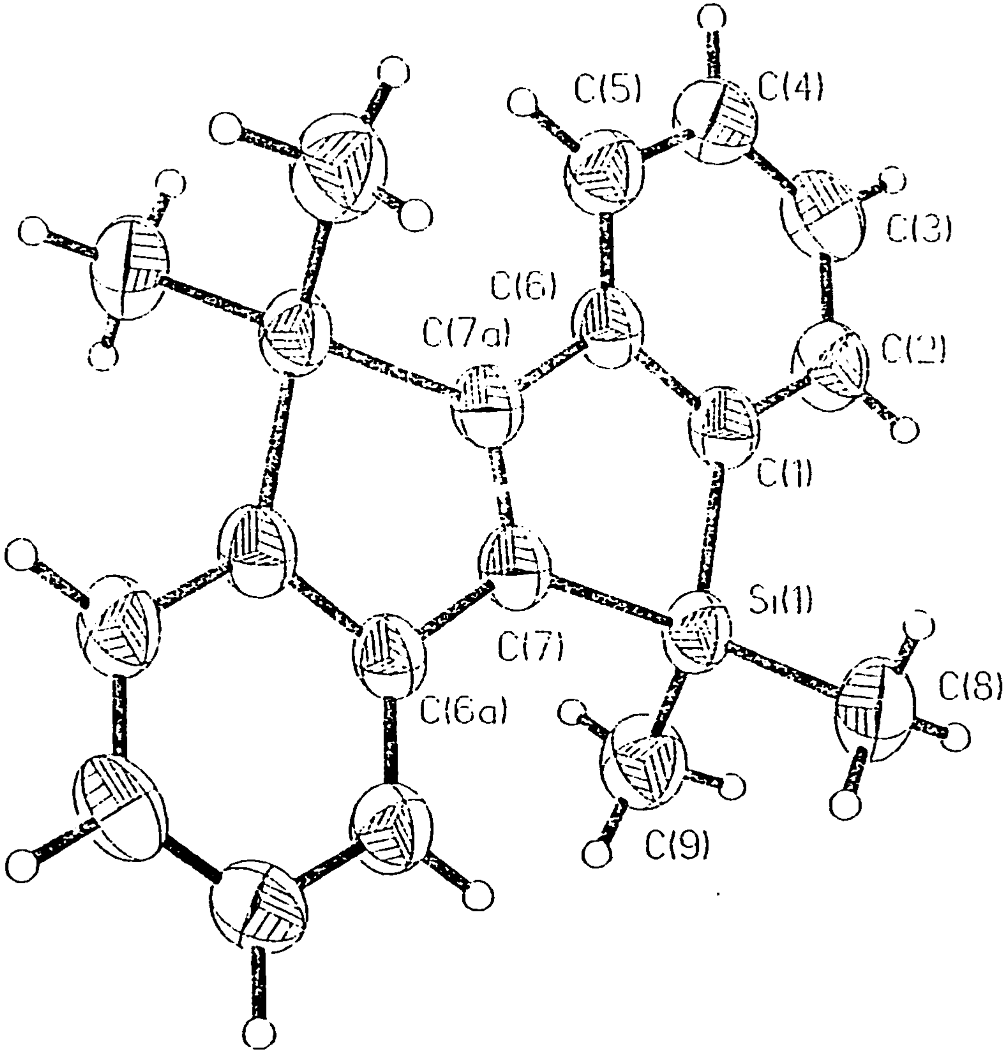
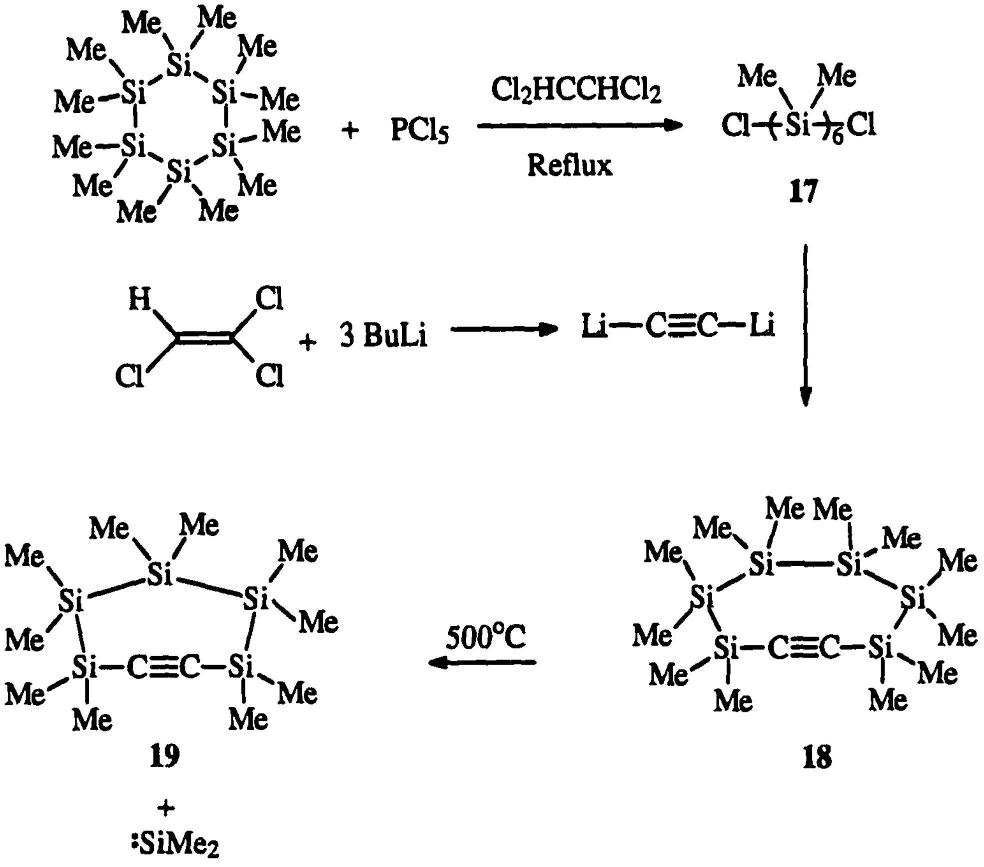


Figure 7. X-ray structure of molecule 16

2.1.3. Hexasilacyclooctyne 18

For comparison, 3,3,4,4,5,5,6,6,7,7,8,8-dodecamethyl-3,4,5,6,7,8-hexasilacyclooctyne **18** was synthesized by reacting 1,6-dichlorododecamethylhexasilane (**17**) with dilithioacetylene (Scheme 7), which was similar to Ando's procedure.[16] Thermolysis under argon flow also only gave silylene extrusion, which was consistent with previous reports (Scheme 7).[15,16] That is, the silylene extrusion process overwhelmingly dominates the possible addition reaction in this system.

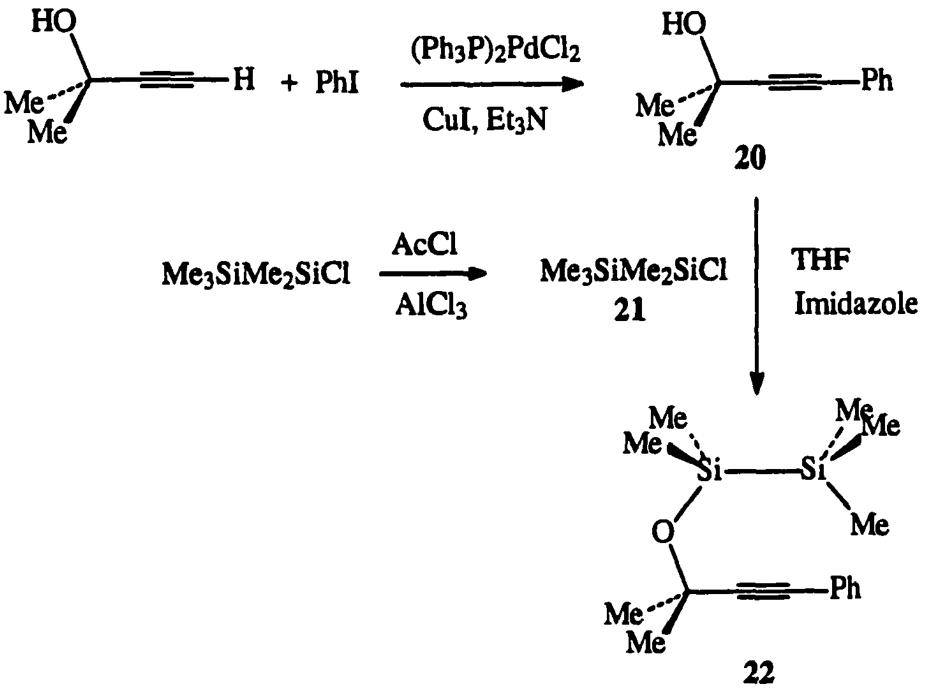
Scheme 7



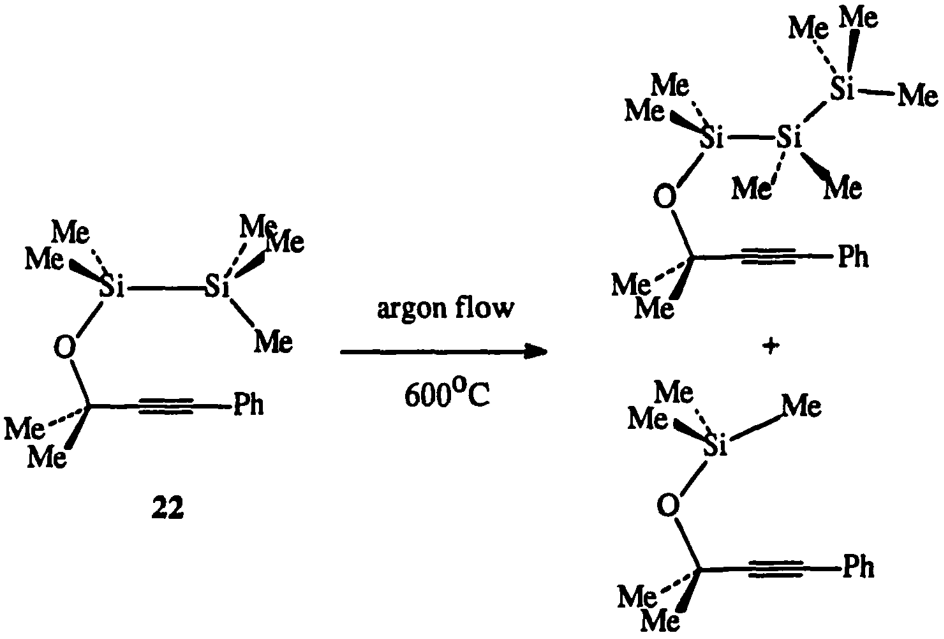
2.1.4 Acyclic analog of 3

In order to determine whether or not a cyclic system was necessary for the thermal trans-addition of disilane to acetylene, compound **22**, an acyclic analog of **3**, was synthesized (Scheme **9**). However, this system did not undergo the concerted $[2_s+2_a]$ addition process. The possible reason is that the molecule **22** is not easily aligned up to form a $[2_s+2_a]$ transition state. At 600°C, an extrusion of silylene and insertion into the Si-Si bond was observed (Scheme **10**). The monosilyl product **24** was produced by the extrusion of silylene and the trisilyl product **23** was produced by the silylene insertion to the Si-Si bond of **22**.

Scheme 9



Scheme 10



22

23

24

2.1.5. Conclusion for thermochemical additions of disilanes to acetylenes

A novel disilane *trans*-addition to acetylenes was discovered. This reaction only occurs in cyclic disilane systems. These systems do not have large negative activation entropy and undergo the concerted $[2_s+2_a]$ addition process. However, silylene extrusion is the competing reaction for polysilane and acyclic systems.

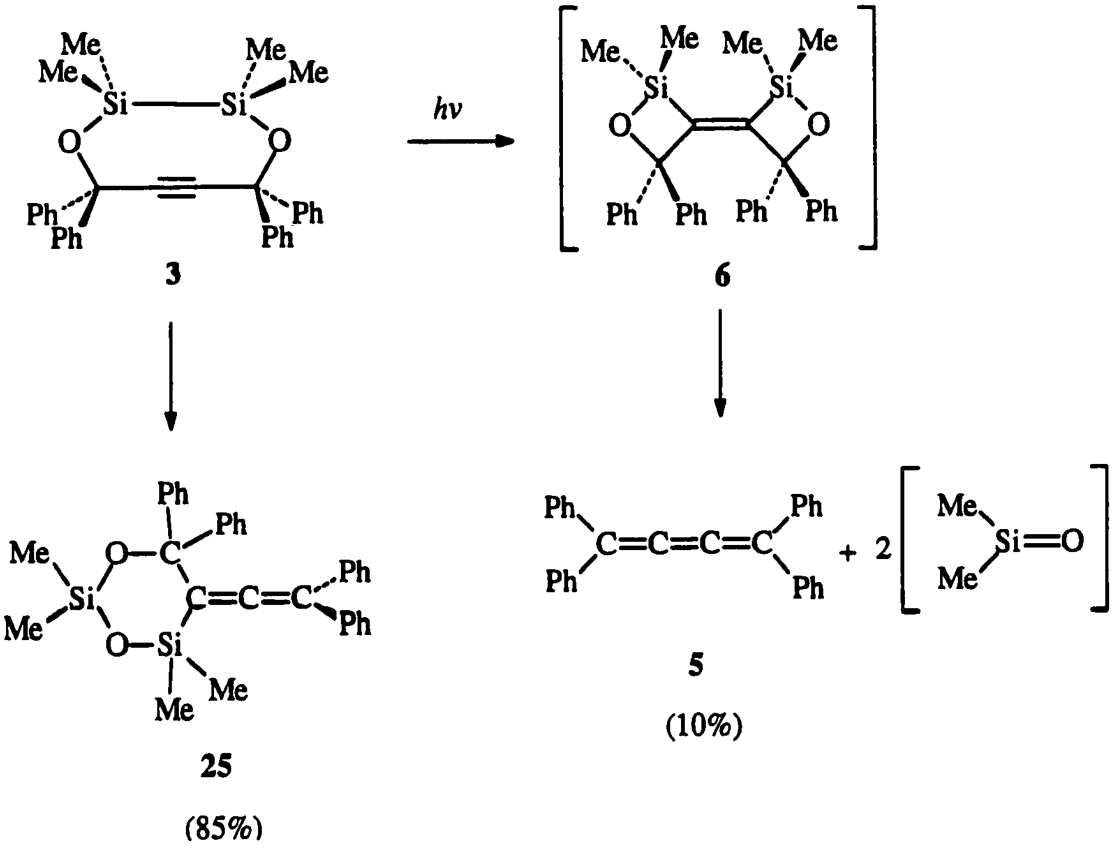
2.2. Photochemical reactions of disilane and ethynyl compounds

Photochemical properties of the cyclic, acyclic and bi-molecular systems which contain disilane and acetylene groups were studied.

2.2.1. Photolysis of 3

The compound 5,5,6,6-tetramethyl-3,3,8,8-tetraphenyl-4,7-dioxa-5,6-disilacyclooctyne (**3**), would appear to be a likely candidate for an intramolecular $[2_s+2_s]$ photochemical addition. However, the product of the photochemical reaction at 254 nm was not the expected four-membered ring system (**6**), but, instead, an isomeric *exo*-allylcyclic system (**25**) obtained in 85% yield (Scheme **11**, Figure **8** and Appendix III) along with 10% of tetraphenylbutatriene (**5**). A possible diradical mechanism for formation of **25** is shown in Scheme **12**. In this mechanism a phenyl group absorbs a photon, and the energy is than transferred to the disilane portion to produce a diradical. One of the silyl radicals attacks the oxygen atom in an S_H2 process to form a more stable conjugated radical, followed by radical coupling to form **25** (Scheme **12**). The minor product **5** may arise from the extrusion of dimethylsilanone, Me_2SiO, from intermediate **6**, itself formed from intramolecular $[2_s+2_s]$ photochemical addition. Catalytic addition of disilanes to acetylenes usually gave *cis* products. We expected that the catalytic reaction of compound **3** would give isomer **6**. However, the only isolated product was tetraphenylbutatriene (**5**) with 100% yield (Scheme **13**). This reaction further supports the assumption that the compound **5** came from the compound **6** in the photochemical reaction.

Scheme 11



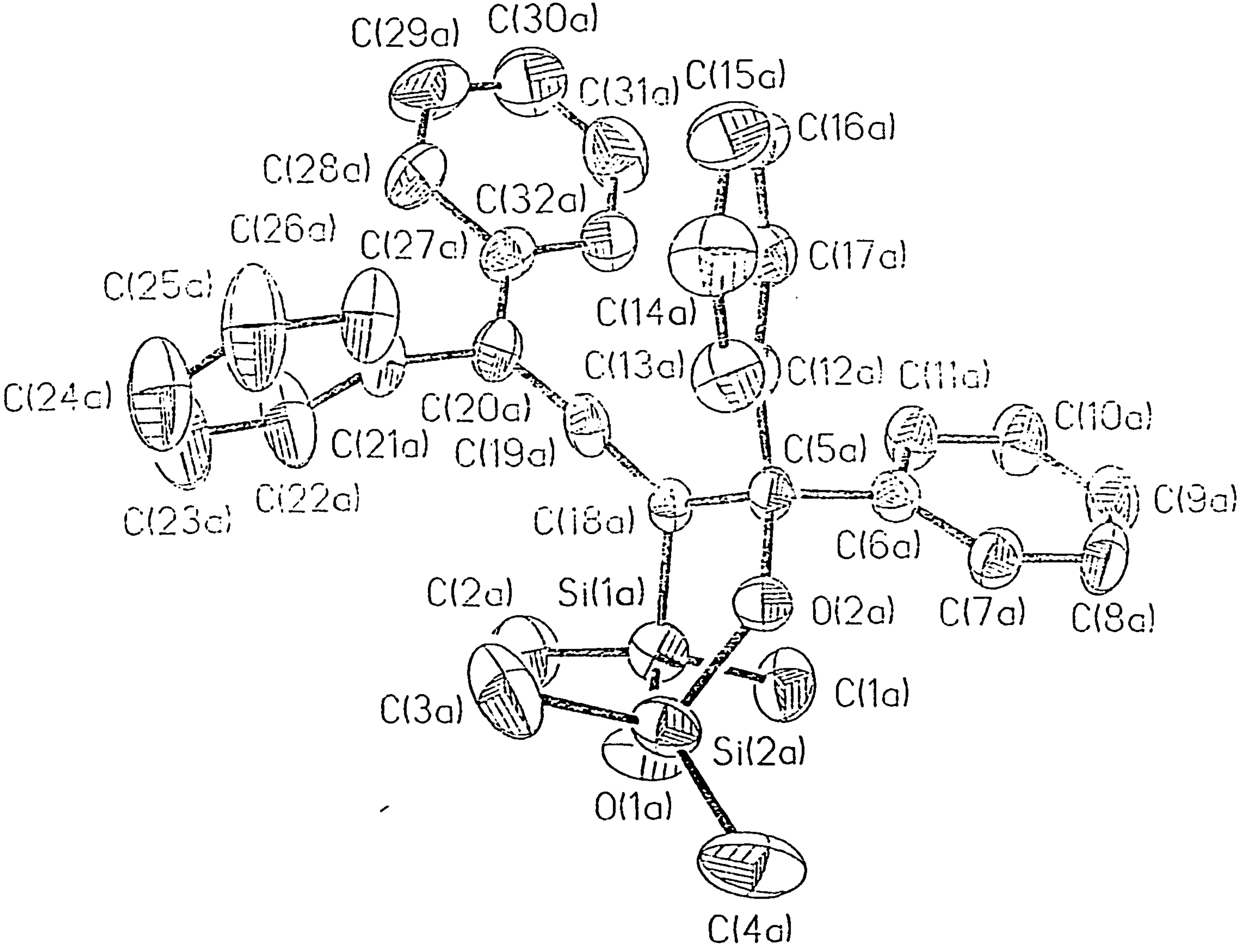
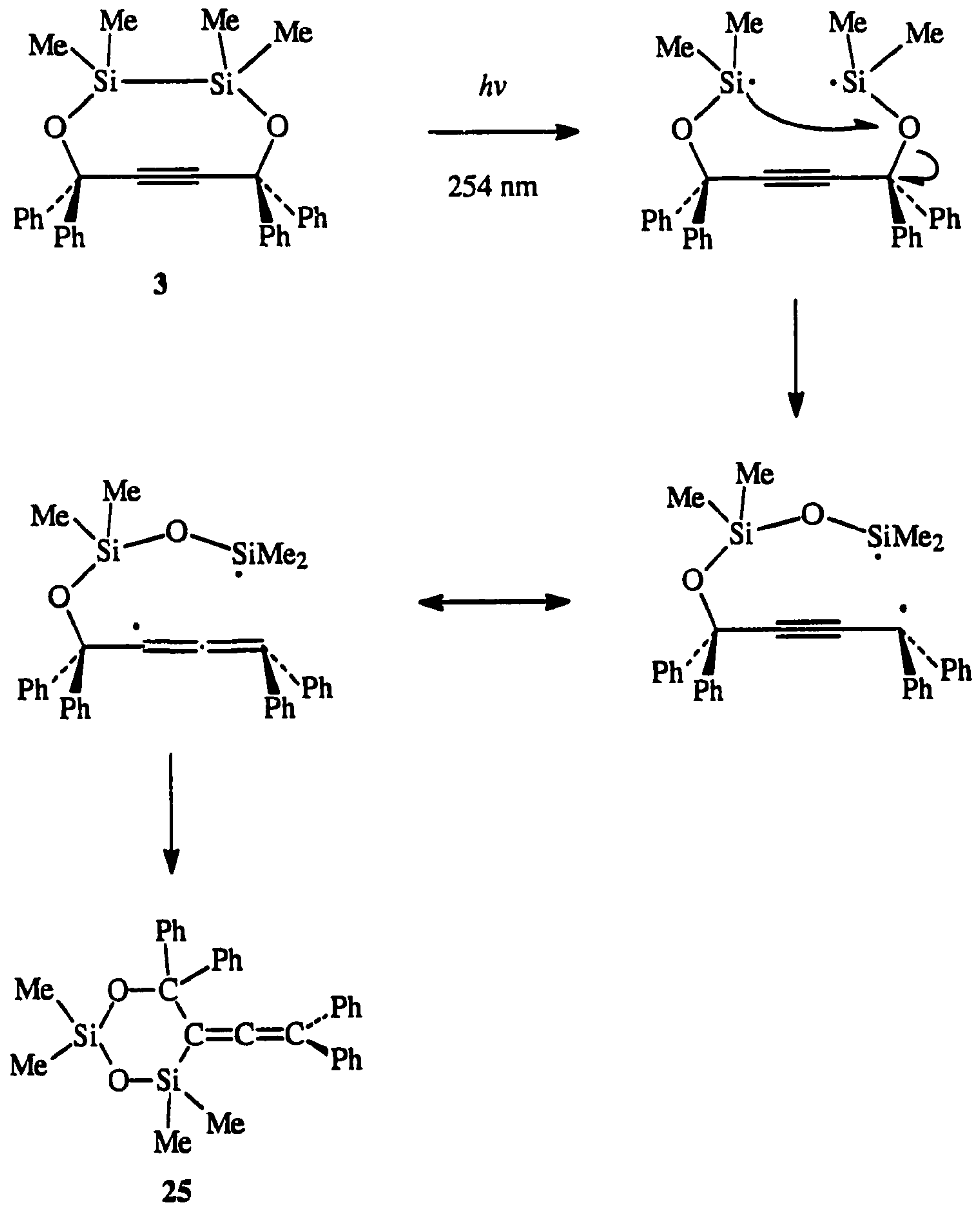
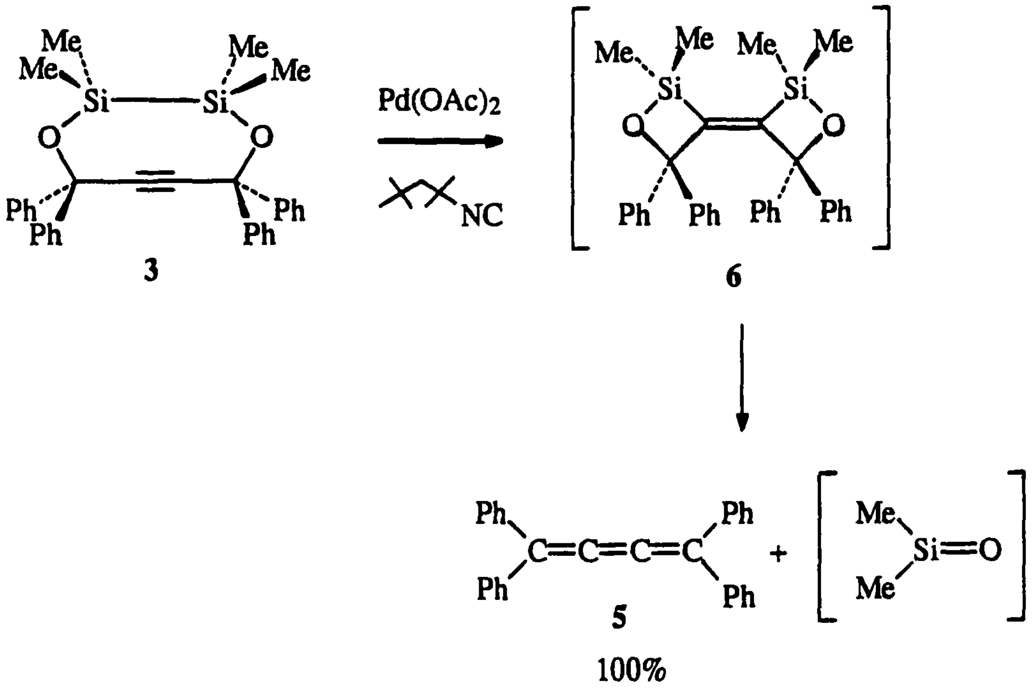


Figure 8. X-ray structure of molecule **20**.

Scheme 12



Scheme 13

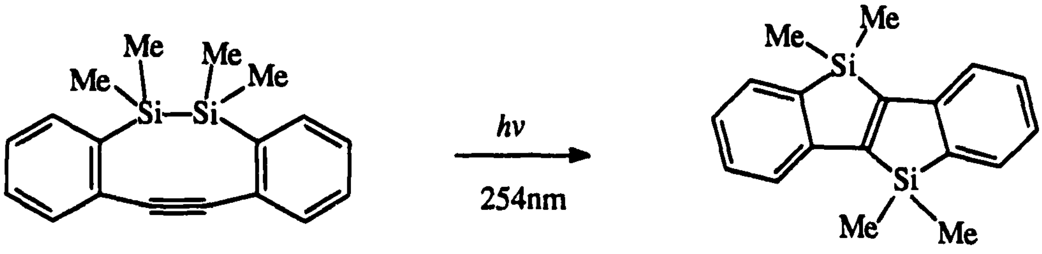


2.2.2 Photolysis of 15

Compound **15**, 5,5,6,6-tetramethyl-5,6-disila-dibenzo[*c*;*g*]cyclooctyne was also irradiated under UV with 254 nm wavelength in hexanes. The product (92%) was the same as in the thermolysis of **15**, 3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,1-*a*]indene(**16**) (Scheme **14**). This process provided us a more practical way to make the novel molecule **16** in high yield.

There are three likely mechanisms for this photochemical isomerization, diradical, 1,3-silyl migration, and electron transfer mechanisms. To check if this reaction is a diradical process, isopentyl chloride was used as solvent. No chlorosilyl product was found (Scheme **15**). Only **16** was formed. If a radical process is occurring, we are unable to intercept it with isopentyl chloride.

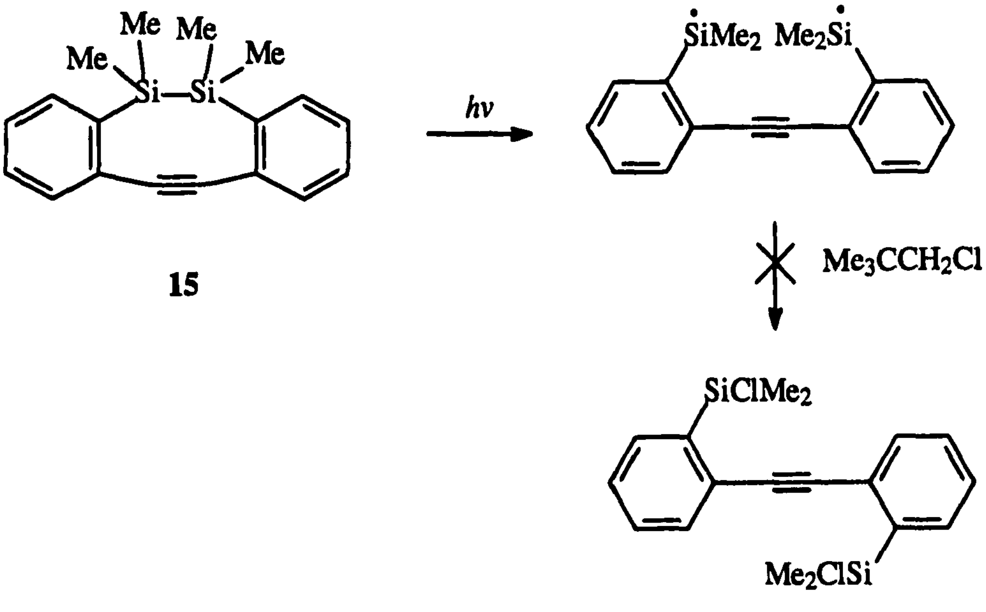
Scheme 14



15

16

Scheme 15

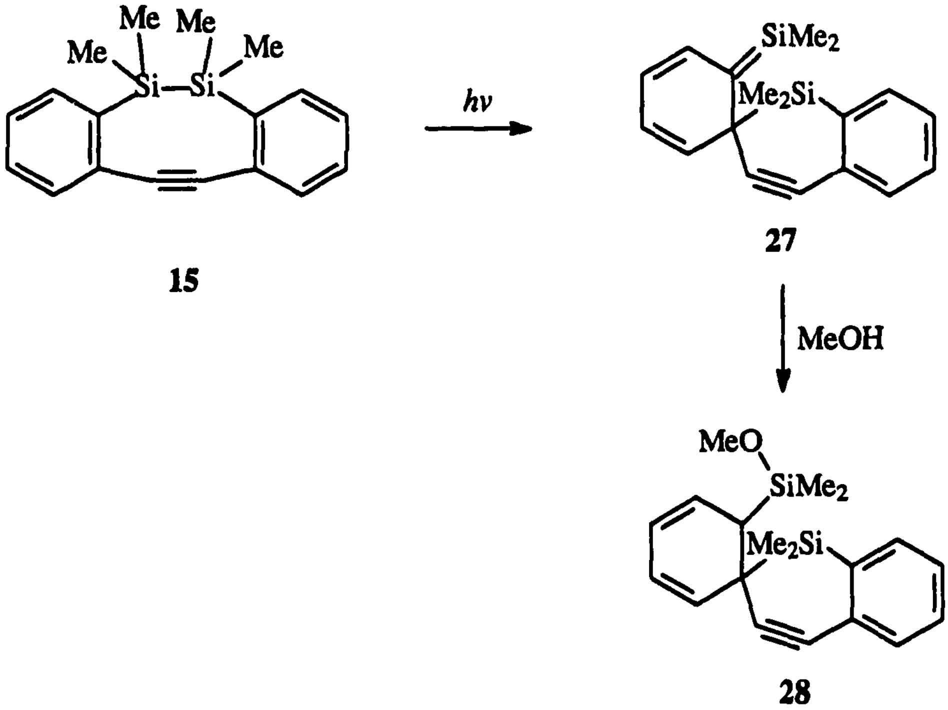


15

25

In the phenyl disilanes, a 1,3-silyl migration mechanism is a well recognized photochemical reaction for many years and the intermediate can also be trapped by methanol.[15, 26-28] With this mechanism, the intermediate **27** could be trapped (Scheme **16**). However, when methanol was used as solvent, we did not observe the adduct **28**.

Scheme 16



The photochemical electron transfer process also has been observed for many years, in which an electron is excited from π to π^* orbital and an electron transferred from σ orbital of Si-Si to half occupied π orbital (Figure 9).[29,30] The methanol adduct (**29**) is consistent with an electron transfer mechanism (Scheme **17**). So, based on the analysis and experiments mentioned above, we proposed an electron transfer mechanism (Scheme **18**). When **15** absorbs a photon, an electron in the conjugated portion is excited to an unoccupied orbital, and then an electron from the disilyl group transferred to the "hole" in the conjugated portion. By attacking silyl cation with the acetylene group, the product **16** was formed.

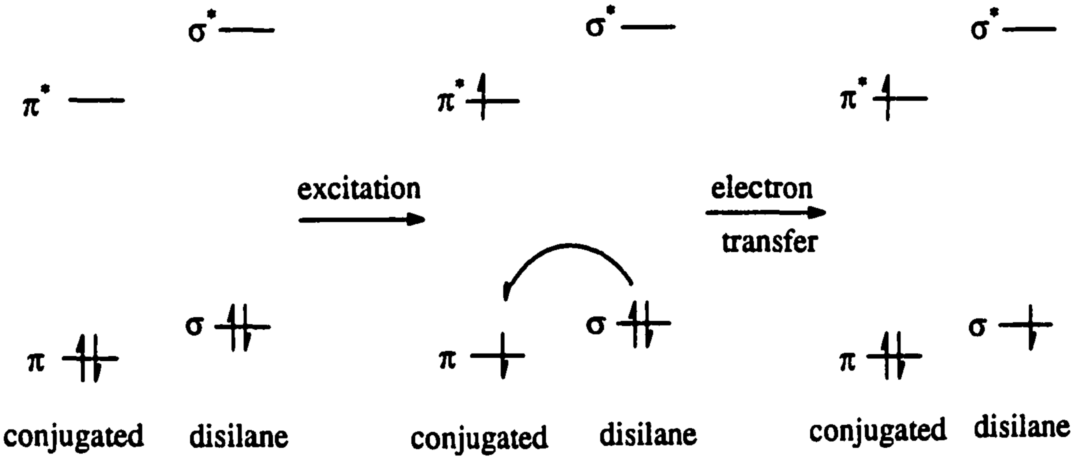
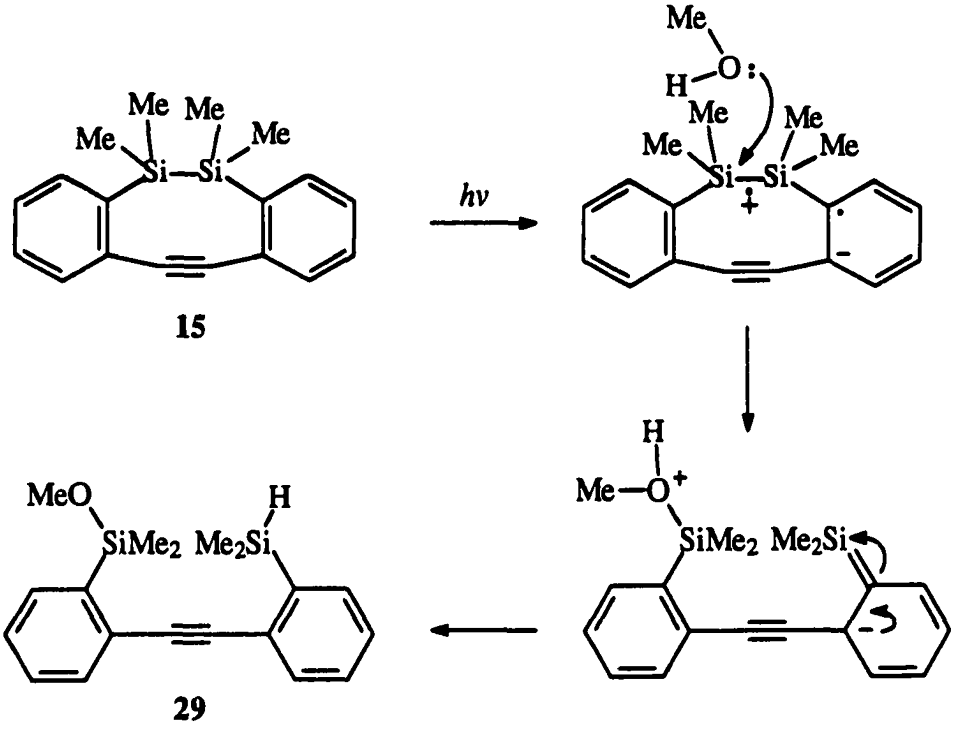
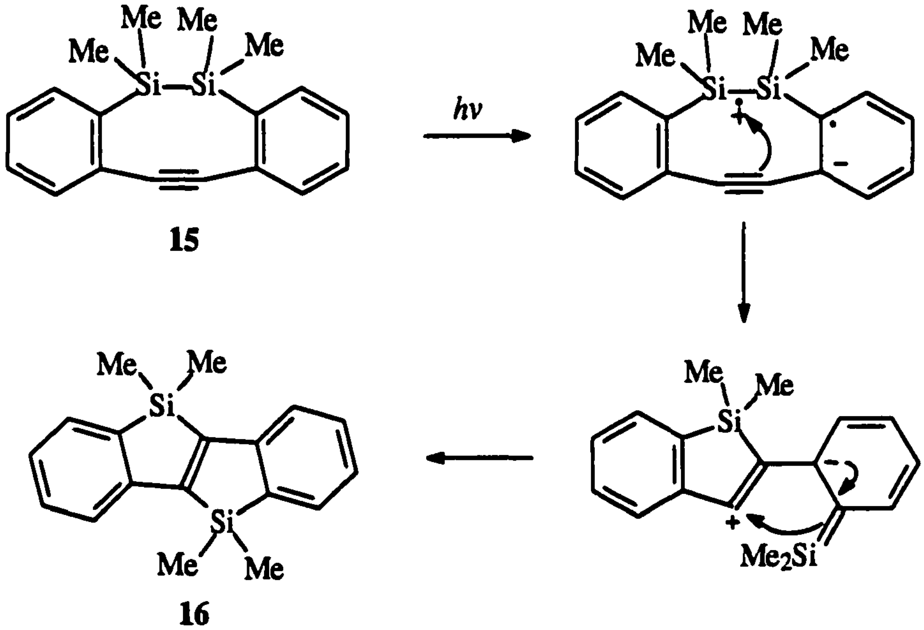


Figure 9. The photochemical electron transfer process between conjugated part with disilane part.

Scheme 17



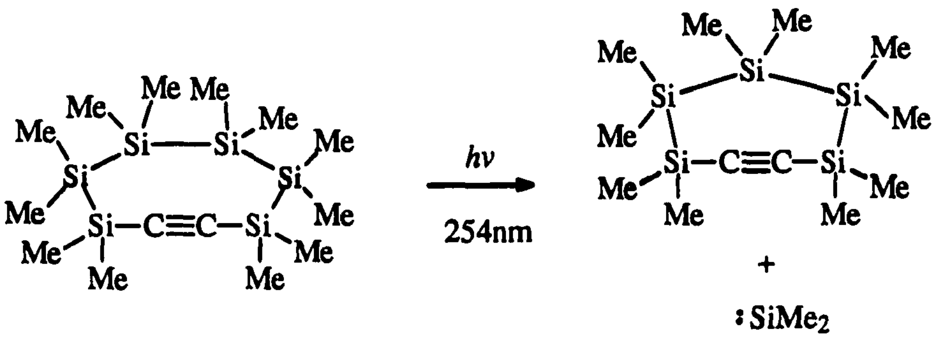
Scheme 18



2.2.3. Photolysis of Hexasilacyclooctyne 18

Irradiation of 3,3,4,4,5,5,6,6,7,7,8,8-dodecamethyl-3,4,5,6,7,8-hexasilacyclooctyne (**18**) with the UV light at 254 nm wavelength gave the same product as did the thermochemical reaction (Scheme **19**). The result was consistant with previous reports that photochemically polysilanes usually extrude a silylene.[15,16]

Scheme 19



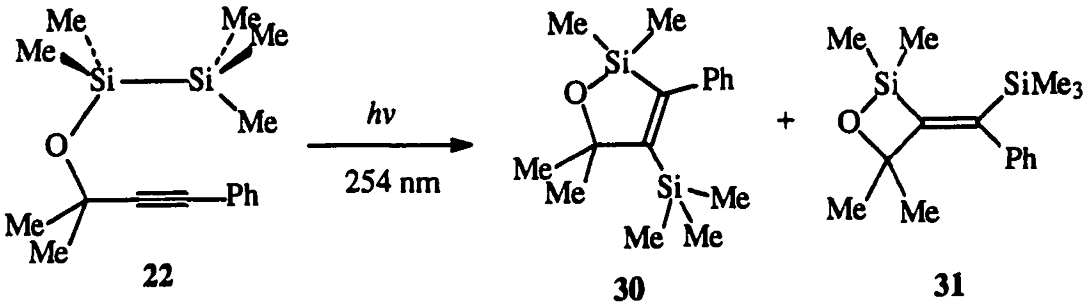
18

19

2.2.4. Photolysis of the propargyloxy disilane 22

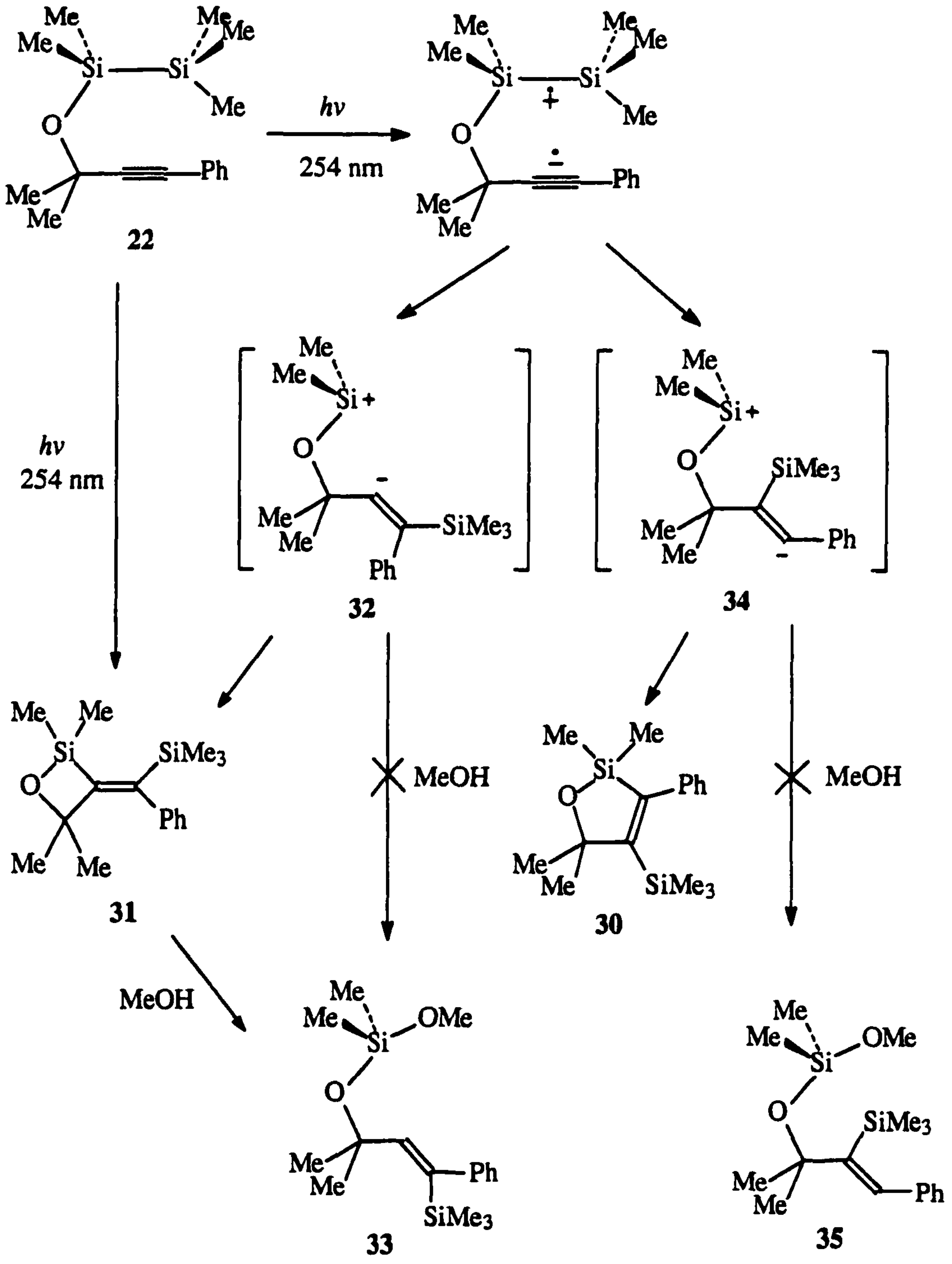
The acyclic system **22** was irradiated with 254 nm UV light. *Trans*-addition of the disilane to acetylene occurred to give isomers **30** (84-90%) and **31** (10-16%) in hexanes (Scheme **20**). Isomer **31** could be formed via $[2_s+2_s]$ photochemical addition or a photo-induced electron transfer process (Scheme **21**). When the reaction was carried out in methanol, the photochemical reaction was relatively slower than that in hexane and adduct **33** was obtained. Comparing with the reaction of methanol with **31** which was synthesized from catalytic reaction, **33** was from the reaction of product **31** with methanol instead of **32**. A possible mechanism of forming **20** is via a photo-induced electron transfer process (Scheme **21**). The zwitterion (**34**) could not be trapped by methanol. Intramolecular ring formation from **34** could be faster than intermolecular reaction of the zwitterion with methanol. For comparison, another propargyloxy disilane **36** was synthesized and irradiated under the same condition (Scheme **22**). No products were observed after 2 hours. Therefore, a conjugated system is needed to connect directly to the acetylene group to absorb a photon.

Scheme 20

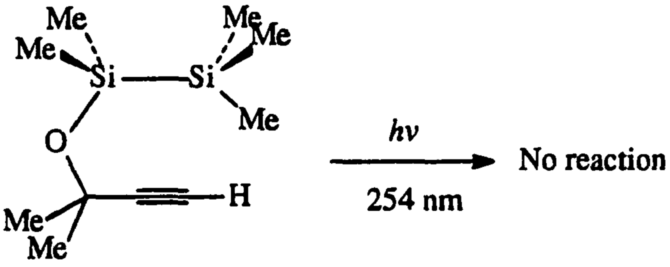


22 **30** 84% **31** 16%

Scheme 21



Scheme 22



36

2.2.5. Intermolecular systems

No reaction occurred between hexamethyldisilane and phenylacetylene under the UV light irradiation.

2.2.6. Conclusion for photochemical reaction in ethynyl disilanes

From above photochemcal reaction, an interesting conclusion can be drawn. Either in cyclic or acyclic systems, if the acetylene group conjugates with an aromatic group like phenyl, this new intramolecular *trans*-addition of disilane to acetylene would occur. The possible mechanism involves charge transfer process. The aromatic group is required not only to absorb a photon as chromaphore but also to stabilize the zwitterion.

3. Conclusion

This is the first evidence that concerted $[2_s+2_a]$ addition can occur between disilanes and acetylenes. The MP4/6-31** calculations found that the activation energy and activation entropy were about 34 kcal/mol and –35 cal/mol·K, respectively. The major barrier of the addition is the entropy and can be overcome via intramolecular reaction. The photochemical intramolecular *trans*-addition of disilanes to acetylenes was also discovered if an aromatic group conjugated with the acetylene group. The catalytic product further supported the possible mechanism of the photochemical $[2_s+2_s]$ addition of disilanes to acetylenes.

4. Calculations

***Ab initio* Calculations.** All *ab initio* geometry optimizations, and transition state searches calculations were executed by the program GAUSSIAN 92[31] at restricted Hartree-Fock level using the 6-31G* basis set. The optimized geometry is shown in the Figure 5. The effect of electron correlation was included by carrying out single-point energy calculations at the 6-31G*-optimized geometries, with the Moller-Plesset perturbation theory up to fourth order, including all single, double, triple, and quadrupole excitations at 6-31G** basis set (denoted as MP4SDTQ/6-31G**//RHF/6-31G*). This effect decreased the activation energy by almost 10 kcal/mol as shown in table 1.

Table 1. Calculated Total Energies of Molecules (in a.u.) and Activation Energies (in kcal/mol) and entropy (in cal/mol·K) of the Reaction

Molecule	RHF/6-31G*	RHF/6-31G** //RHF/6-31G*	MP4SDTQ/6-31G** //RHF/6-31*
Acetylene	-76.8178	-76.8218	-77.1067
Hexahydrodisilane	-581.3049	-581.3130	-581.5618
TS	-658.0523	-658.0639	-658.6141
trans-1,2-Disilylethylene	-658.1855	-658.1971	-658.7336
Activation energy	44.17	44.49	34.14
Activation entropy	-35.16		

A semi-empirical calculation was also carried out to optimize the geometry of the actual molecular **3**.[20] The result shows that the dihedral angle of Si-Si bond and C≡C bond is already 40 degree (Figure 4).

5. Experimental

General Procedures. ^1H and ^{13}C NMR spectra were acquired on a Varian VXR-300 spectrometer. In order to assure the quantitative feature of the ^{13}C NMR spectra, the relaxation agent chromium (III) acetylacetonate was added in $CDCl_3$ with a relaxation delay of 5 seconds.

Exact masses were obtained from a Kratos MS 50 mass spectrometer with 10,000 resolution. Infrared spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer from neat sample. UV/Vis spectra were obtained on a Hewlett Packard 8452A diode array UV/Vis spectrometer. Reactions were monitored by Hewlett Packard 5890 series II GC and Hewlett Packard tendem GC-IR-MS (5890A GC-5965A IR-5970 Series MS) parallel connected.

THF was distilled over sodium-benzophenone and ether was distilled over CaH_2 right before use. Other reagents were used as received from Aldrich or Fisher Chemical Co. without further purification unless specified otherwise.

Flow pyrolysis experiments were performed by dripping the starting material (ca. 20 drops/min) into a vertical quartz tube (400mm in length and 15mm in diameter) packed with quartz chips under argon flow (15 ml/min). The tube was maintained at a certain temperature in an oven. The pyrolysate was collected in a trap at –78°C.

Photolysis experiments were carried out in a Rayonet photochemical reactor equipped with sixteen 5W low pressure Hg lamp. A solution (ca. $2x10^{-3}M$) of starting material dissolved in 50 ml solvent (HPLC grade) was prepared in a quartz tube capped with a septum. The air in the solution was removed by bubbling argon through it for half an hour. The tube was then connected to an argon balloon and exposed to 254nm UV. The reaction was monitored by frequent sampling and analyzed by a capillary GC.

Synthesis of 1,1,4,4-Tetraphenyl-2-butyn-1,4-diol (1).[17] 1,1,4,4-Tetraphenyl-2-butyn-1,4-diol was synthesized by reacting acetylene dilithium with benzophenone, which was similar to Kazarian's the procedure by reaction calcium carbide with benzophenone. To a solution of 14.3 ml (30mmol, 2.1M) of BuLi in a 100 ml flask at -78° C, 0.90 ml (10 mmol) of trichloroethylene was added added dropwise and the mixture was stirred 2 hr at room temperature. The solution was cooled to -78°C and 3.64g (20 mmol) of benzophenone was added, and was stirred at room temperature overnight. As a yellowish solid 1,1,4,4-tetraphenyl-2-butyn-1,4-diol was obtained in quantitative yield (3.85g): m.p. 189-191°C (lit.[17] 191-192°C).

Synthesis of 1,2-dichlorotetramethyldisilane (2) and chloropentamethyldisilane (21).[18] 1,2-Dichlorotetramethyldisilane (2) and chloropentamethyldisilane (21) were prepared according to Sakurai's procedure[18] in 95% and 93% yields, respectively.

Synthesis of 1,6-dichlorododecamethylhexasilane (17).[32] 1,6-Dichlorododecamethylhexasilane (17) was prepared according to Gilman's procedure.[32] To 50 ml of 1,1,2,2-tetrachloroethane in a 250 ml round bottom flask with a magnetic stirrer, 6.98 g (20 mmol) of dodecamethylcyclohexasilane was added. Under argon atmosphere, 6.25 g (30 mmol) of phosphorus pentachloride was added. The solution was refluxed for 10 minutes and the product, 1,6-dichlorododecamethylhexasilane, was distilled out in 60% yield (5.02 g) (b. p. 158-161°C and lit. 160°-162°C at 0.8 mm[32]).

Synthesis of 1-bromo-2-ethynylbenzene (13).[33] To a 250 ml round bottom flask equipped with magnetic stirrer, 3.32 ml (24 mmoL) of trimethylsilylacetylene and 2.55 ml (20 mmoL) of 1-bromo-2-iodobenzene were added. Under argon atmosphere, 140 mg (2%) of $PdCl_2(PPh_3)_2$ and 151 mg (4%) of copper (I) chloride were added. Then 50 ml of triethylamine was injected into the solution. After being stirred at room temperature for 5 hours, the solution was poured into 200 ml of aqueous ammonium chloride solution. The product was extracted with hexanes (2x100 ml), and then washed with distilled water twice and dried over sodium sulfate. After removing the solvent, 1-bromo-2-(trimethylsilylethynyl)-benzene (12) was obtained. Under argon atmosphere, 4.8 g of the 1-bromo-2-(trimethylsilylethynyl)-benzene was added to 20 ml of methanol in 125 ml of round bottom flask with a magnetic stirrer. Then, 2 drops of saturated aqueous potassium hydroxide were added. After one and half an hours of stirring, the reaction solution was poured into 100 ml of saturated aqueous sodium chloride. The product was extracted with hexanes (2x50 ml). The combined organic layer was washed twice with distilled water. The solvent was removed by rotary evaporation. After flash column chromatography on silica, 3.57 g (93% total yield) of 1-bromo-2-ethynylbenzene (13) was obtained.

Synthesis of 5,5,6,6-tetramethyl-3,3,8,8-tetraphenyl-4,7-dioxa-5,6-disila-cyclooctyne (3). The 1,1,4,4-tetraphenyl-2-butyn-1,4-diol (**1**) (0.39 g, 1 mmol) and imidazole (0.272 g, 4 mmol) were added into a 50 ml round bottom flask with 25 ml THF, and then 0.187 g (1 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane (**2**) was injected into the solution, which then was stirred at room temperature overnight. Compound **3** was obtained in 82% yield after purification by flash chromatography over silica: ^{1}H NMR (300MHz, Acetone-d_6), δ 0.102(s, 12H, methyl), δ 7.645 (d, J=7.5Hz, 8H, aromatic), δ 7.324 (t, J=7.7Hz, 8H, aromatic), δ 7.227 (t, J=7.2Hz, 4H, aromatic); ^{13}C NMR (75MHz, acetone-d_6), δ 0.124 (4C), δ 77.676 (2C), δ 95.124 (2C), δ 126.242 (8C), δ 128.294 (4C), δ 128.999 (8C), δ 146.401 (4C); solid mass spectrum *m/z* 504(5, M$^+$), 427(21), 356(38), 323(21), 322(74), 307(25), 248(54), 178(100), 133(49), 105(22), 75(41), 73(28), 45(17); exact mass *m/z* 504.19397 (calc. for $C_{32}H_{32}O_2Si_2$ 504.19408); m. p. 169-170°C.

Thermochemical isomerization of 3 to 1,1,4,4-tetramethyl-3,3,6,6-tetraphenyl-2,5-dioxa-1,4-disila-dicyclo[3,3,0]octa-7-ene (4). Pyrolysis of 0.01M solution in hexanes of compound **3** at 550°C with argon-flow gave **4** in 70% yield. The product **4** was identified by X-ray diffraction. Even though the X-ray structure was not qualified for publication, it gave the basic structural information. ^{1}H NMR (300MHz, methylene chloride-d_2), δ -0.024(s, 12H, methyl), δ 7.257-7.318 (m, 20H, aromatic); ^{13}C NMR (75MHz, methylene chloride-d_2), δ 0.076 (4C), δ 90.643 (2C), δ 126.693 (8C), δ 126.785 (4C), δ 127.583 (8C), δ 145.612 (4C), δ 166.911 (2C); mass spectrum, *m/z* 504(M$^+$, 35), 430(28), 427(50), 337(21), 322(100), 279(34), 252(19), 202(16), 178(23), 165(20), 140(51), 133(89), 125(28), 105(32), 77(40), 75(50), 73(41), 43(21); exact mass *m/z* 504.19401 (calc. for $C_{32}H_{32}O_2Si_2$ 504.19408); m.p. 286-288°C

Synthesis of 5,5,6,6-tetramethyl-5,6-disila-dibenzo[*c;g*]cyclooctyne (15). To a 250 ml of round bottom flask with a magnetic stirrer, 3.57 g (19 mmol) of 1-bromo-2-ethynylbenzene (13) and 2.3 ml (18 mmol) of 1-bromo-2-iodobenzene were added. Under argon atmosphere, 140 mg (2%) of $PdCl_2(PPh_3)_2$ and 151 mg (4%) of copper (I) chloride were added. Then, 50 ml of triethylamine was injected into the solution. After stirring overnight, it was worked up with saturated aqueous ammonium chloride solution. After flash chromatographic purification on silica, 5.86 g (97%) of bis(2-bromophenyl)acetylene was obtained. To 50 ml of tetrahydrofuran (THF) in a 125 ml round bottom flask, 1.58 g (5 mmol) of bis(2-bromophenyl) acetylene was added under argon atmosphere. After it was cooled down to –78°C, 4 ml (2.5M, 10 mmol) of butyl lithium was injected into the solution over 10 minutes. After being stirred for one hour at the temperature, 0.76 ml (5 mmol) of 1,2-dichlorotetramethyldisilane (2) was injected into the solution over 5 minutes. The reaction mixture was gradually warmed to room temperature, and then stirred overnight. It was worked up with saturated aqueous ammonium chloride and purified with flash column chromatography. 5,5,6,6-Tetramethyl-5,6-disila-dibenzo[*c;g*]cyclooctyne (15), a white crystalline solid, was obtained with a yield of 0.67 g (46%): ^{1}H NMR (300Hz, $CDCl_3$) δ 0.255 (s, 6H) 7.331-7.607 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -3.738, 98.762, 127.284, 128.195, 128.594, 133.78, and 149.124; FTIR ν(cm^{-1}) 3052 (s), 2951 (s), 1584 (s), 1244 (vs), and 1119 (s); mass spectrum *m/z* 292 (59,

M^+), 277 (100), 131 (44); exact mass *m/z* 292.10965 (calc. for $C_{18}H_{20}Si_2$ 292.11036); m.p. 98-99°C.

Synthesis of 3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,1-*a*]indene(16) by thermolysis of 15. Pyrolysis of 292 mg of **15** in 200 ml of hexanes was conducted by flow pyrolysis at ca. 550°C. The pyrolysate was collected in a trap cooled to –78°C. After removing the solvent with a rotatory evaporator, the major product was purified by flash column chromatography on silica gel and crystallized from hexanes in 28% yield. The product was identified with NMR, mass spectroscopy, and single crystal X-ray diffraction (Appendix II) to be 3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,1-*a*]indene(**16**) as yellowish crystals: ^{1}H NMR (300Hz, $CDCl_3$) δ: 0.463 (s, 6H) 7.186-7.582 (m, 8H); ^{13}C NMR (75.429 MHz, $CDCl_3$) δ -3.783, 124.534, 126,129, 129.830, 131.957, 140.383, 149.343, and 163.624; FTIR ν(cm^{-1}): 3055 (s), 2955 (s), 1586 (m), 1248 (vs), 1123 (s), 1058 (w), 902 (m), and 841 (s); mass spectrum *m/z* 292 (96, M^+), 277 (100), 131 (53); exact mass *m/z* 292.11012 (calc. for $C_{18}H_{20}Si_2$ 292.11036); m.p. 182-183°C.

Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8-dodecamethyl-3,4,5,6,7,8-hexasilacyclooctyne (18).[16] The procedure used here was similar to Ando's synthesis in which 1,6-dichlorododecamethylhexasilane was reacted with acetylene di-Grinard.[16] After the 100 ml of THF and 0.90 ml (10 mmol) of trichloroethene in a 250 ml round bottom flask with magnetic stirrer was cooled down to –78°C, 12 ml (30 mmol) of 2.5M butyl lithium was injected over 10 minutes. After removing the ice-bath, the solution was stirred for other two hours. The solution was cooled down to –78°C again, and 4.18g (10 mmol) of 1,6-dichlorododecamethylhexasilane (**17**) was added over 30 minutes. After stirred overnight, the reaction was worked up the saturated aqueous ammonium chloride. After purification with flash column chromatography, product, 3,3,4,4,5,5,6,6,7,7,8,8-dodecamethyl-3,4,5,6,7,8-hexasilacyclooctyne (**18**), was obtained at 38% yield (1.42 g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.214 (s, 12H), 0.200 (s, 12H), 0.191 (s, 12H); ^{12}C NMR (75 MHz, $CDCl_3$) δ 118.428, -2.810, -4.641, -5.873; mass spectrum, *m/z* 372 (74, M^+), 357 (61), 299 (100, base), 241 (36), 73 (58), which were consistent with literature: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.20 (s, 12H), 0.17 (s, 12H), 0.15 (s, 12H); ^{12}C NMR (125 MHz, $CDCl_3$) δ 117.89, -2.84, -4.88, -5.97.[16]

Flow pyrolysis of 18.[16] Flow pyrolysis of **18** (200 mg) in 50 ml of hexanes was carried out at 500°C to afford product 3,3,4,4,5,5,6,6,7,7-decamethyl-3,4,5,6,7-pentasilacycloheptyne (**19**) in 21% yield (42 mg): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.194 (s, 6H), 0.206 (s, 12H), 0.213 (s, 12H); ^{12}C NMR (75 MHz, $CDCl_3$) δ 124.182, -3.250, -4.893, -5.764; mass spectrum *m/z* 314 (40, M+), 299 (100, base), 241 (57), 73 (21), which was consistent with the report by Ando.[16]

Flow pyrolysis of 3,3,5,5,6,6-hexamethyl-1-phenyl-5,6-disila-4-oxa-1-heptyne (22). Synthesis of **22** will be described in Part III in this thesis. Flow pyrolysis of **22** (200 mg in 100 ml of hexanes) was carried out at 600°C to afford two products 3,3,5,5,6,6,7,7-octamethyl-1-phenyl-5,6,7-trisila-4-oxa-1-octyne (**23**) (26 mg, 13% yield) and 3,3,5,5-tetramethyl-1-phenyl-5-sila-4-oxa-1-hexyne (**24**) (36 mg, 18% yield). Spectral data of **23**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.014 (9H, s), 0.113 (6H, s), 0.328 (6H, s), 1.532 (6H, s), 7.322-7.487 (5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -2.031 (3C), -1.018 (2C), 1.349 (2C), 34.013 (2C), 67.028 (1C), 82.727 (1C), 94.732(1C), 123.002 (1C), 127.905 (1C), 128.119 (2C), 131.367 (2C); mass spectrum: *m/z* 349 (2), 348 (7, M^+), 276 (31), 275 (100, M^+-73), 260 (28), 205 (87, $Me_3SiMe_2SiMe_2SiO^+$), 147 (30), 133 (43), 73 (38); exact mass 348.17597 (calc. for $C_{18}H_{32}OSi_3$ 348.17610). Spectral data of **24**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.301 (9H, s), 1.539 (6H, s), 7.324-7.473 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.319 (3C), 34.198 (2C), 67.103 (1C), 82.721 (1C), 94.729 (1C), 123.017 (1C), 127.911 (1C), 128.124 (2C), 131.371 (2C); mass spectrum: *m/z* 232 (4, M^+), 218 (18), 217 (100, M^+-15), 159 (23, M^+-75), 73 (13); exact mass 232.12628 (calc. for $C_{14}H_{20}OSi$ 232.12634).

Flow pyrolysis of mixture of hexamethyldisilane and phenylacetylene. To 50 ml of hexanes, 1.46 g (10 mmol) of hexamethyldisilane and 1.02 g (10 mmol) of phenylacetylene were added. Flow pyrolysis of the mixture was carried out at 550°C. No adduct of hexamethyldisilane and phenylacetylene was observed with GC-MS.

Photo-isomerization of 3. A solution of 5,5,6,6-tetramethyl-3,3,8,8-tetraphenyl-4,7-dioxa-5,6-disila-cyclooctyne (**3**) (50 mg) in 50 ml hexanes (HPLC grade) was irradiated for about 6 hours before the starting material was gone. From the GC analysis, two products were formed. After removing the solvent with rotatory evaporator, the two products were separated by flash column chromatography with hexane as eluent. The product 1-(3′,3′-diphenyl-allylic)-2,2-diphenyl-4,4,6,6-tetramethyl-3,5-dioxa-4,6-disilacyclohexane (**25**) (42 mg, 85%) was identified by NMR and X-ray diffraction (Figure 6 and Appendix III): ^{1}H NMR (300MHz, Acetone-d_6), δ 0.127(s, 6H, methyl), 0.228 (s, 6H, methyl) 6.912-7.396 (m, 20H, aromatic); ^{13}C NMR (75MHz, CD_2Cl_2), δ 0.503 (6C), 1.387 (6C), 84.993 (1C), 106.413 (1C), 107.859 (1C), 126.664 (4C), 127.220, 127.505, 128.018, 136.103, 146.317, 205.940 (1C); mass spectrum *m/z* 506 (5), 505 (15), 504(34, M^+), 356(10), 323(21), 322(73), 308 (28), 307(100), 232(50), 178(34), 133(31), 73(21); FTIR ν (cm^{-1}) 3053 (m), 2961 (s), 1919 (s), 1491 (m), 1256 (s), 1057 (vs), 1023 (s), 887(s), 801 (vs); exact mass *m/z* 504.19401 (calc. for $C_{32}H_{32}O_2Si_2$ 504.19408). The product 1,1,4,4-tetraphenylbutatriene (**5**) was identified by the NMR: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.316-7.571 (m, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.027 (2C), 127.397 (4C), 127.832 (8C), 128.801 (8C), 138.061 (4C), and 151.253 (2C); EI MS *m/z* 356 (12,M^+), 219 (25), 69 (43), and 44 (100); exact mass *m/z* 356.15658 (calc. for $C_{28}H_{20}$ 356.15650) m. p. 236-237°C (lit.[34] 237°C).

Photolysis of 15 in hexanes. A solution of 60 mg of **15** in 80 ml of hexanes was irradiated for 40 minutes before the reaction was complete. After removing the solvent with rotatory evaporator, the product was purified by flash column chromatography on silica gel. 3,3,3′,3′-Tetramethyl-3,3′-disila-indeno[2,1-*a*]indene (**16**) (56 mg, 92% yield) was obtained as light blue crystals. The product was identical to that obtained by thermolysis of **15**.

Photolysis of 15 in neopentyl chloride. A solution of 30 mg of **15** in 40 ml of neopentyl chloride was prepared in a quartz tube. The procedure was the same as photolysis of **15** in hexanes. After the starting material was completely gone (ca. 2 hour), the only product observed by GCMS was 3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,1-*a*]indene(**16**).

Photolysis of 15 in methanol. A solution of 30 mg of **15** in 40 ml of methanol with 5 drops of ethyl acetate (to increase the solubility of 3 in methanol) was prepared in a quartz tube. The procedure was the same as photolysis of **15** in hexanes. After the starting material was completely gone (ca. 70 minutes), the solvent was removed by a rotatory evaporator. The products were separated by flash chromatography over silica gel with hexane as eluent and identified by GC-MS, ^1H NMR and FTIR to be 1-(2′-dimethylsilylphenyl)-2-(2′-dimethylmethoxysilylphenyl)-acetylene (**29**) (76%) and 3,3,3′,3′-tetramethyl-3,3'-disila-indeno[2,1-*a*]indene(**16**) (24%). Spectral data of **29**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.283 (s, 6H), 0.340 (s, 6H), 3.473 (s, 3H, H_3C-O), 3.592 (s, 1H, H-Si), 7.190-7.606 (m, 8H, aromatic); GCMS *m/z* 326 (3), 325 (9), 324 (28, M^+), 310 (31), 309 (100, M^+-15), 280 (23), 279 (84), 233 (22), 207 (23), 193 (32), 132 (27), 89 (28, $MeOMe_2Si^+$), 59 (54, Me_2HSi^+); FTIR ν (cm^{-1}): 3054 (m), 2956 (s), 2832 (m), 2248 (s, H-Si), 2125 (w, C≡C), 1584 (s), 1459 (m), 1249 (s), 1080 (vs, Si-O), 909 (s), 840 (s), 783 (s); exact mass *m/z* 324.13703 (calc. for $C_{19}H_{24}OSi_2$ 324.13717).

Photolysis of hexasilacyclooctyne 18. A solution of 40 mg of **18** in 50 ml of hexanes was irradiated as described in photolysis of **3**. The product identified by GC-MS was 3,3,4,4,5,5,6,6,7,7-decamethyl-3,4,5,6,7,-pentasilacycloheptyne (**19**), which was the same as the of pyrolysis of **18**.

Photolysis of 3,3,5,5,6,6-hexamethyl-1-phenyl-5,6-disila-4-oxa-1-heptyne (22) in hexane. A solution of 30 mg of **22** in 50 ml of hexanes was irradiated for 40 minutes before the starting material was gone. Two products were identified as 3,3,5,5-tetramethyl-2-phenyl-1-trimethylsilyl-4-oxa-3-sila-cyclopentene (**30**) and 2,2,4,4-tetramethyl-3-((Z)-phenyltrimethylsilyl)methylene-2-silaoxetane (**31**). The minor product **31** was the same compound obtained by the catalytic intramolecular addition of **22**, which will be discussed in part III of this thesis. The compound **30** was the major product and its yield (84-90%) was changed from reaction to reaction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.042 (s, 9H); 0.199 (s, 6H), 1.474 (s, 6H), 7.190-7.606 (5H, aromatic); ^{13}C NMR (75 Mz, $CDCl_3$) δ 0.879 (2C), 0.816 (3C), 29.658 (2C), 88.276 (1C), 124.605 (1C), 125.702 (2C), 126.963 (2C), 140.376 (1C), 154.060 (1C), and 163.933 (1C); GCMS *m/z* 290 (9, M^+), 275 (76), 217 (100), 159 (45), 143 (43), 73 (56); GCIR ν (cm^{-1}): 3054 (m), 2975 (s), 1255 (s), and 885 (s); exact mass *m/z* 290.15201 (calc. for $C_{16}H_{26}OSi_2$ 290.15209).

Photolysis of 3,3,5,5,6,6-hexamethyl-1-phenyl-5,6-disila-4-oxa-1-heptyne (22) in methanol. A solution of 30 mg of **22** in 50 ml of methanol was irradiated as the same as in hexanes. Major product 3,3,5,5-tetramethyl-2-phenyl-1-trimethylsilyl-4-oxa-3-sila-cyclopentene (**30**) and minor product 3-(dimethylmethoxysiloxy)-3-methyl-1-phenyl-1-trimethylsilyl-1-butene (**33**), an adduct of **22** with methanol, were found. The reaction of methanol and deuterated methanol (*d*$_4$) with **31**, which was synthesized from **22** by catalytic reaction, afforded **33** at room temperature. Spectral data of **33**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.016 (s, 9H); 0.049 (s, 6H), 1.160 (s, 6H), 3.437 (s, 3H), 6.083 (s, 1H), 6.885-7.260 (5H, aromatic); GCMS *m/z* 307 (4, M^+-15), 249 (27), 218 (44), 203 (15), 163 (58), 147 (42), 129 (39), 89 (100, $MeOMe_2Si^+$), 73 (72, Me_3Si^+), and 59 (31); GCIR ν (cm^{-1}) 3054 (m), 2967 (s), 1263 (s), 1026 (s), and 845 (vs).

Synthesis of 3,3,5,5,6,6-hexamethyl-5,6-disila-4-oxa-1-heptyne (36). The 2-methyl-3-butyn-2-ol (0.84 g, 10 mmol) and imidazole (1.36 g, 20 mmol) were added into a 100 ml round bottom flask with 50 ml THF, and then 1.66 g (10 mmol) of chloro-pentamethyldisilane (**21**) was injected into the solution, which then was stirred at room temperature overnight. Compound **36** was obtained in 92% yield after purification by flash chromatography over silica: ^{1}H NMR (300MHz, $CDCl_3$), δ 0.017 (s, 9H), δ 0.369 (s, 8H), δ 1.590 (s, 6H), 2.405 (s, 1H); ^{13}C NMR (75MHz, $CDCl_3$), δ -2.102 (3C), 1.382 (2C), 33.041 (2C), 66.963 (1C), 81.463 (1C), 91.052 (1C); mass spectrum *m/z* 156 (9, M^+), 141 (100), 83 (21), 67 (54); exact mass *m/z* 156.09692 (calc. for $C_8H_{16}OSi$ 156.09704).

Photolysis of 36 in hexane and in benzene. A solution of 30 mg of **36** in 50 ml of hexanes was irradiated for 2 hours and no reaction was observed by GC-MS. A solution of 30 mg of **36** in 50 ml of benzene was irradiated for 2 hour minutes and no reaction was observed also.

Photolysis of the mixture of hexamethyldisilane and phenylacetylene. A 1:1 mixture of 7.3 g (50 mmol) of hexamethyldisilane and 5.1g (50 mmol) of phenylacetylene was irradiated for 2 hours and no reaction of hexamethyldisilane and phenylacetylene was observed with GC-MS.

Catalytic decomposition of 3 in toluene at 80°C. Into 3.5 ml of distilled toluene in a 25 ml round bottom flask equipped with magnetic stirrer, 50 mg of **3** was dissolved. Under argon, 2.5 mg of $Pd(OAc)_2$ and 5 mg of 1,1,3,3-tetramethylbutyl isocyanide were added respectively. The solution was stirred at 80°C for six hours. After removing the catalysts with silica gel column chromatography, product 1,1,4,4-tetraphenylbuta-1,2,3-triene (**5**) was obtained as yellow crystals (35mg, 99% yield) (see photolysis of **3** for spectral data).

Catalytic decomposition of 3 in hexane at room temperature. The procedure was the same as in toluene except the reaction in hexanes at room temperature. An attempt to obtain **6** by recrystallization in hexanes failed. Purification by column chromatography over silica gel afforded 1,1,4,4-tetraphenylbuta-1,2,3-triene (**5**).

Catalytic reaction of 15. In 10 ml of hexanes, 60 mg of **15** was stirred under the catalytic condition described in the catalytic reaction of **3** in hexanes at room temperature. After stirring overnight, no reaction was observed by GC-MS.

Catalytic reaction of 18. In 10 ml of hexanes, 40 mg of **18** was stirred under the catalytic condition described in the catalytic reaction of **3** in hexanes at room temperature. After stirring overnight, no reaction was observed by GC-MS.

Catalytic reaction of 22. In 10 ml of hexanes, 40 mg of **22** was stirred under the catalytic condition described in the catalytic reaction of **3** in hexanes at room temperature. After stirring overnight, cis-3-(2′-trimethylsilyl-2′-phenylvinylene)-2,2,4,4-tetramethyl-2-silaoxetane (**31**) was obtained by crystallization from hexanes. The detail will be reported in part III of this thesis.

Catalytic reaction of hexamethyldisilane and phenylacetylene. A solution of 0.73 g (5 mmol) of hexamethyldisilane and 0.51g (5 mmol) of phenylacetylene in 10 ml of hexanes was stirred under the catalytic condition described in the catalytic reaction of **3** in hexanes at room temperature. After stirring overnight, no reaction was observed by GC-MS.

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APPENDIX I

CRYSTAL STRUCTURE DATA OF 1,1,4,4-TETRAMETHYL-3,6-DIPHENYL-3,6-(2′-TRIMETHYLSILYLPHENYL)-2,5-DIOXA-1,4-DISILA-DICYCLO[3,3,0]OCTA-7-ENE (**11**)

A crystal of **11** was mounted on a glass fiber on the Enraf-Nonius CAD4 for a data collection at 293 (2) ± 1K. The cell constants for the data collection were determined from reflections found from an incremental search of reciprical space. 23 reflections in the range of 2.24-17.66° θ were used to determine precise cell constants.

The space group $P2_1/n$ was chosen based on systematic absences and intensity statistics. This assumption proved to correct as determined by a successful direct-methods solution and subsequent refinement. All non-hydrogen atoms were refined with anisotropic displacement parameters. Final refinements were done with SHELXL-93.

Table I.1. Crystal Data

Empirical Formula	$C_{38}H_{48}O_2Si_4$
Color, Habit	Clear, triangular
Crystal Size (mm)	0.4 x 0.2 x 0.15
Crystal System	Monoclinic
Space Group	$P2_1/n$
Unit Cell Dimension	a = 12.323(2) Å, b = 11.538(2) Å, c = 13.304(3) Å
	$\alpha = 90°$, $\beta = 97.62(3)°$, $\gamma = 90°$
Volume	1874.9(6) $Å^3$
Z	2
Formula Weight	649.12
Density (calc.)	1.150 Mg/m^3
Absorption Coefficient	0.189 mm^{-1}
F(000)	696

Table I.2. Data Collection

Diffractometer Used	Enrof-Nonius CAD4
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	293(2)
Monochromator	Graphite
θ Range	2.12 to 27.67°
Scan Type	$\omega - 2\theta$
Standard Reflections	3 measured every 60 minutes
Index Range	$-1 \leq h \leq 16$, $-1 \leq k \leq 14$, $-17 \leq l \leq 17$
Reflections Collected	5391
Independent Reflections	4295 (R_{int} = 0.0542)
Observed Reflections	1691 ($I \geq 2\sigma(I)$)
Min./Max. Transmission	0.613 / 0.577
Absorption Correction	Semi-empirical

Table I.3. Solution and Refinement

System Used	SHELXL-93 (Sheldrick, 1993)
Solution	Direct
Refinement Method	Full-matrix least-squares on F^2
Extinction Correction	0.0011(13)
Extinction expression	$Fc^* = kFc[1+0.001 \times Fc^2\lambda^3/sin(2\theta)]^{-1/4}$
Hydrogen Atoms	Riding
Weighting Scheme	$W = 1 / [\sigma(Fo^2) + (0.0800P)^2 + 0.0000P]$
Parameters	200
Final R Indices [$I \geq 2\sigma(I)$]	R1 = 0.0697, wR2 = 0.1505
R Indices (all data)	R1 = 0.2320, wR2 = 0.2211
GooF, Observed and All Data	1.039, 0.934
Largest and Mean Δ / σ	0.000, 0.000
Largest Difference Peak	0.209 e/Å^{-3}
Largest Difference Hole	-0.226 e/Å^{-3}

Where $P = (Fo^2 + 2\,Fc^2)/3$

$R1 = \Sigma|\,|Fo| - |Fc|\,| / \Sigma|Fo|$

$WR2 = [\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]]^{0.5}$

where $w = 1/[\sigma^2(Fo^2) + (a * P)^2 + b * P + d + e * sin\,\theta$

$GooF = [\Sigma[w(Fo^2 - Fc^2)^2] / (n - p)]^{0.5}$

Table I.4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3)

Atom	x	y	y	U (eq)
Si(2)	6213(1)	538(1)	9074(1)	47(1)
Si(1)	8668(1)	-2151(1)	10030(1)	58(1)
O(1)	6895(3)	-300(3)	9951(2)	48(1)
C(1)	6176(4)	-1051(4)	10437(3)	44(1)
C(2)	4947(4)	466(4)	9700(3)	41(1)
C(3)	6967(5)	1911(5)	9006(4)	70(2)
C(4)	6024(5)	-148(5)	7821(4)	67(2)
C(5)	6217(4)	-2237(4)	9928(3)	45(1)
C(6)	7232(4)	-2739(4)	9768(3)	47(1)
C(7)	7159(5)	-3805(5)	9259(4)	64(2)
C(8)	6188(5)	-4353(5)	8918(4)	73(2)
C(9)	5227(5)	-3847(5)	9090(4)	72(2)
C(10)	5245(4)	-2800(5)	9594(4)	60(2)
C(11)	6542(4)	-1068(4)	11576(3)	43(1)
C(12)	6423(4)	-2047(4)	12140(4)	51(1)
C(13)	6671(4)	-2022(5)	13185(4)	60(2)
C(14)	7033(4)	-1020(5)	13660(4)	64(2)
C(15)	7157(4)	-41(5)	13107(4)	59(2)
C(16)	6900(4)	-53(5)	12059(4)	54(1)
C(17)	9627(5)	-3419(5)	10115(5)	82(2)
C(18)	8963(5)	-1287(6)	8934(5)	98(2)
C(19)	9056(4)	-1358(6)	11212(5)	90(2)

Equivalent isotropic U defined as one third of the trace of the orthogonalized Uij tensor.

Table I.5. Bond lengths (Å).

Si(2) – O(1)	1.657(3)
Si(2) – C(3)	1.845(6)
Si(2) – C(4)	1.832(5)
Si(2) – C(2)	1.867(5)
Si(1) – C(18)	1.841(6)
Si(1) – C(19)	1.827(6)
Si(1) – C(17)	1.875(6)
Si(1) – C(6)	1.884(5)
O(1) – C(1)	1.450(5)
C(1) – C(11)	1.523(6)
C(1) – C(2)	1.528(6)
C(1) – C(5)	1.531(6)
C(2) – C(2)A	1.335(9)
C(2) – C(1)A	1.528(6)
C(5) – C(10)	1.382(7)
C(5) – C(6)	1.420(6)
C(6) – C(7)	1.401(7)
C(7) – C(8)	1.376(7)
C(8) – C(9)	1.366(7)
C(9) – C(10)	1.381(7)
C(11) – C(12)	1.374(6)

Table I.5. (Continued).

C(11) – C(16)	1.379(7)
C(12) – C(13)	1.384(7)
C(13) – C(14)	1.364(7)
C(14) – C(15)	1.367(7)
C(15) – C(16)	1.388(7)

Table I.6. Bond angle (°).

O(1) – Si(2) – C(3)	108.9(2)
O(1) – Si(2) – C(4)	112.4(2)
C(3) – Si(2) – C(4)	109.4(3)
O(1) – Si(2) – C(2)	92.0(2)
C(3) – Si(2) – C(2)	121.1(2)
C(4) – Si(2) – C(2)	112.0(2)
C(18) – Si(1) – C(19)	110.8(3)
C(18) – Si(1) – C(17)	106.3(3)
C(19) – Si(1) – C(17)	104.4(3)
C(18) – Si(1) – C(6)	109.1(3)
C(19) – Si(1) – C(6)	118.1(2)
C(17) – Si(1) – C(6)	107.4(3)
C(1) – O(1) – Si(2)	112.3(3)
O(1) – C(1) – C(11)	109.5(4)

Table I.6. (Continued)

O(1) – C(1) – C(2)A	106.3(4)
C(11) – C(1) – C(2)A	105.6(4)
O(1) – C(1) – C(5)	106.2(4)
C(11) – C(1) – C(5)	113.9(4)
C(2)A – C(1) – C(5)	115.1(4)
C(2)A – C(2) – C(1)A	116.3(5)
C(2)A – C(2) – Si(2)	106.3(4)
C(1)A – C(2) – Si(2)	136.4(3)
C(10) – C(5) – C(6)	120.2(4)
C(10) – C(5) – C(1)	118.9(5)
C(6) – C(5) – C(1)	120.8(4)
C(7) – C(6) – C(5)	115.4(5)
C(7) – C(6) – Si(1)	113.9(4)
C(5) – C(6) – Si(1)	130.5(4)
C(8) – C(7) – C(6)	124.1(5)
C(9) – C(8) – C(7)	118.9(5)
C(8) – C(9) – C(10)	119.8(6)
C(5) – C(10) – C(9)	121.6(5)
C(12) – C(11) – C(16)	119.6(4)
C(12) – C(11) – C(1)	121.0(5)
C(16) – C(11) – C(1)	119.1(4)

Table I.6. (Continued)

C(11) – C(12) – C(13)	120.4(5)
C(14) – C(13) – C(12)	119.8(5)
C(15) – C(14) – C(13)	120.3(5)
C(14) – C(15) – C(16)	120.3(5)
C(11) – C(16) – C(15)	119.5(5)

APPENDIX II

CRYSTAL STRUCTURE DATA OF 3,3,3′,3′-TETRAMETHYL-3,3′-DISILA-INDENO[2,1-*a*]INDENE (16)

A crystal of **16** was mounted on a glass fiber on the Siemens P4 for a data collection at 293 (2) ± 1K. The cell constants for the data collection were determined from reflections found from a 360° rotation photograph. 25 reflections in the range of 20-30° θ were used to determine precise cell constants.

The space group $P2_1/n$ was chosen basen on systematic absences and intensity statistics. This assumption proved to correct as determined by a successful direct-methods solution and subsequent refinement. All non-hydrogen atoms were placed directly from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. Final refinements were done with SHELXL-93.

Table II.1. Crystal Data

Empirical Formula	$C_{18}H_{20}O_2Si_2$
Color, Habit	Pale yellow, rectangular plate
Crystal Size (mm)	0.5 x 0.3 x 0.2
Crystal System	Monoclinic
Space Group	$P2_1/n$
Unit Cell Dimension	a = 10.441(4) Å, b = 6.700(2) Å, c = 12.399(3) Å
	$\alpha = 90°$, $\beta = 100.83(3)°$, $\gamma = 90°$
Volume	851.9(5) $Å^3$
Z	2
Formula Weight	292.52
Density	1.140 Mg/m^3
Absorption Coefficient	1.777 mm^{-1}
F(000)	312

Table II.2. Data Collection

Diffractometer Used	Siemens P4
Radiation	CuKα (λ = 1.54178 Å)
Temperature (K)	293(2)
Monochromator	Graphite
θ Range	5.09 to 56.71°
Scan Type	$2\theta - \theta$
Standard Reflections	3 measured every 97 reflections
Index Range	$-1 \leq h \leq 11$, $-1 \leq k \leq 17$, $-13 \leq l \leq 13$
Reflections Collected	1607
Independent Reflections	1139 (R_{int} = 0.0667)
Observed Reflections	958 ($I \geq 2\sigma(I)$)
Min./Max. Transmission	0.810 / 0.313
Absorption Correction	Semi-empirical from psi-scans

Table II.3. Solution and Refinement

System Used	SHELXL-93 (Sheldrick, 1993)
Solution	Direct
Refinement Method	Full-matrix least-squares on F^2
Extinction Correction	0.0035(22)
Extinction expression	$Fc^* = kFc[1+0.001 \times Fc^2\lambda^3/sin(2\theta)]^{-1/4}$
Hydrogen Atoms	riding
Weighting Scheme	$w = 1 / [\sigma(Fo^2) + (0.0800P)^2 + 0.0000P]$
Parameters	92
Final R Indices $[I \geq 2\sigma(I)]$	R1 = 0.0611, wR2 = 0.1765
R Indices (all data)	R1 = 0.0668, wR2 = 0.1837
GooF, Observed and All Data	1.191, 1.130
Largest and Mean Δ / σ	0.000, 0.000
Largest Difference Peak	0.425 e/Å^{-3}
Largest Difference Hole	-0.517 e/Å^{-3}

Where $P = (Fo^2 + 2\,Fc^2)/3$

$R1 = \Sigma \big|\, |Fo| - |Fc| \,\big| / \Sigma |Fo|$

$WR2 = [\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]]^{0.5}$

where $w = 1/[\sigma^2(Fo^2) + (a * P)^2 + b * P + d + e * sin\ \theta$

$GooF = [\Sigma[w(Fo^2 - Fc^2)^2] / (n - p)]^{0.5}$

Table II.4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3)

Atom	x	y	z	U(eq)
Si(1)	1358(1)	1668(1)	4172(1)	45(1)
C(1)	231(3)	303(5)	3066(2)	45(1)
C(2)	130(3)	238(5)	1927(3)	54(1)
C(3)	-834(3)	-925(6)	1285(3)	59(1)
C(4)	-1697(4)	-1992(6)	1759(3)	58(1)
C(5)	-1635(3)	-1928(5)	2894(3)	52(1)
C(6)	-671(3)	-801(5)	3541(2)	42(1)
C(7)	491(3)	618(5)	5240(2)	43(1)
C(8)	1230(4)	4411(6)	4002(3)	66(1)
C(9)	3073(3)	809(6)	4334(3)	68(1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized Uij tensor.

Table II.5. Bond lenghts (Å)

Si(1) – C(8)	1.852(4)
Si(1) – C(8)	1.856(3)
Si(1) – C(8)	1.869(3)
Si(1) – C(8)	1.876(3)
C(1) – C(2)	1.398(4)
C(1) – C(6)	1.410(4)

Table II.5. (Continued).

C(2) – C(3)	1.397(5)
C(3) – C(4)	1.367(5)
C(4) – C(5)	1.397(5)
C(5) – C(6)	1.387(4)
C(6) – C(7A)	1.493(4)
C(7) – C(7A)	1.365(6)
C(7) – C(6A)	1.493(4)

Table II.6. Bond angles (°)

C(8) – Si(1) – C(9)	111.6(2)
C(8) – Si(1) – C(1)	112.3(2)
C(9) – Si(1) – C(1)	112.9(2)
C(8) – Si(1) – C(7)	114.8(2)
C(9) – Si(1) – C(7)	113.0(2)
C(1) – Si(1) – C(7)	90.78(13)
C(2) – C(1) – C(6)	118.4(3)
C(2) – C(1) – Si(1)	132.4(2)
C(6) – C(1) – Si(1)	109.2(2)
C(3) – C(2) – C(1)	120.2(3)
C(4) – C(3) – C(2)	120.6(3)
C(3) – C(4) – C(5)	120.6(3)

Table II.6. (Continued).

C(6) – C(5) – C(4)	119.3(3)
C(5) – C(6) – C(1)	120.9(3)
C(5) – C(6) – C(7A)	124.7(3)
C(1) – C(6) – C(7A)	114.3(3)
C(7A) – C(7) – C(6A)	115.7(3)
C(7A) – C(7) – Si(1)	110.0(3)
C(6A) – C(7) – Si(1)	134.3(2)

APPENDIX III

CRYSTAL STRUCTURE DATA OF 2,2,4,4-TETRAMETHYL-6,6-DIPHENYL-1-(*exo*-2′,2′-DIPHENYL-ALLYL)-3,5-DIOXA-2,4-DISILA-CYCLOHEXANE (25)

A crystal of **25** was mounted on a glass fiber on the Siemens P4RA for a data collection at 293 (2) ± 1K. The cell constants for the data collection were determined from reflections found from a 360° rotation photograph. 25 reflections in the range of 17.5-25.0 θ were used to determine precise cell constants.

The space group P1 was chosen based on the lack of systematic absences and intensity statistics. This assumption proved to correct as determined by a successful direct-methods solution and subsequent refinement. All non-hydrogen atoms were placed directly from the E-Map. All non-hydrogen atoms were refined with anisotropic displacement parameters. Final refinements were done with SHELXL-93.

Table III.1 Crystal Data

Empirical Formula	$C_{32}H_{32}O_2Si_2$
Color, Habit	Light yellow, block
Crystal Size (mm)	0.50 x 0.30 x 0.25
Crystal System	Triclinic
Space Group	P1
Unit Cell Dimension	a = 9.399(1) Å, b = 9.526(2) Å, c = 27.267(4) Å
	α = 81.01(1) °, β = 85.10(1) °, γ = 61.42(1) °
Volume	2117.4(6) Å^3
Z	3
Formula Weight	1514.27
Density	1.188 Mg/m^3
Absorption Coefficient	1.338 mm^{-1}
F(000)	804

Table III.2. Data Collection

Diffractometer Used	Siemens P4RA
Radiation	CuKα (λ = 1.54178 Å)
Temperature (K)	293(1)
Monochromator	Graphite
θ Range	3.28 to 56.56°
Scan Type	$2\theta - \theta$
Standard Reflections	3 measured every 97 reflections
Index Range	$-10 \leq h \leq 0$, $-10 \leq k \leq 9$, $-29 \leq l \leq 29$
Reflections Collected	6047
Independent Reflections	6047 (R_{int} = 0.0000)
Observed Reflections	4869 ($I \geq 2\sigma(I)$)
Min./Max. Transmission	0.924 / 0.815
Absorption Correction	Semi-empirical

Table III.3. Solution and Refinement

System Used	SHELXL-93 (Sheldrick, 1993)
Solution	Direct
Refinement Method	Full-matrix least-squares on F^2
Absolute Structure	0.00(3)
Hydrogen Atoms	Riding, isotropic
Weighting Scheme	$W = 1 / [\sigma^2(Fo^2) + (0.0664P)^2 + 0.0000P]$
Parameters Refined	1047
Final R Indices [$I \geq 2\sigma(I)$]	R1 = 0.0434, wR2 = 0.1004
R Indices (all data)	**R1 = 0.0545, wR2 = 0.1055**
GooF, Observed and All Data	1.036, 0.953
Largest and Mean Δ / σ	0.005, 0.000
Largest Difference Peak	0.183 e/Å^{-3}
Largest Difference Hole	-0.254 e/Å^{-3}

Where $P = (Fo^2 + 2\,Fc^2)/3$

$R1 = \Sigma \| Fo| - |Fc\| / \Sigma |Fo|$

$wR2 = [\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]]^{0.5}$

where $w = 1/[\sigma^2(Fo^2) + (a * P)^2 + b * P + d + e * \sin\theta]$

$GooF = [\Sigma[w(Fo^2 - Fc^2)^2] / (n - p)]^{0.5}$

Table III.4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3).

Atom	x	y	z	U(eq)
Si(1)	7010(2)	798(2)	526(1)	45(1)
Si(2)	7733(2)	-2006(2)	1258(1)	46(1)
O(1)	8251(5)	-1017(5)	799(2)	58(1)
O(2)	6227(4)	-695(4)	1558(1)	38(1)
C(1)	7617(9)	2268(9)	673(3)	65(2)
C(2)	7054(10)	760(10)	-152(3)	77(2)
C(3)	7148(10)	-3356(9)	1024(3)	76(3)
C(4)	9373(9)	-3094(9)	1708(3)	88(3)
C(5)	4856(7)	811(6)	1382(2)	33(3)
C(6)	4952(7)	2135(6)	1615(2)	33(1)
C(7)	5794(7)	1766(7)	2045(2)	41(1)
C(8)	5865(9)	2964(8)	2249(3)	55(2)
C(9)	5138(8)	4525(8)	2029(3)	55(2)
C(10)	4275(9)	4914(8)	1606(3)	53(2)
C(11)	4191(8)	3737(7)	1393(2)	44(2)
C(12)	3320(7)	714(7)	1559(2)	36(1)
C(13)	3379(9)	-698(7)	1813(2)	49(2)
C(14)	1977(10)	-765(9)	1973(3)	64(2)
C(15)	511(9)	551(9)	1891(3)	62(2)

Table III.4. (Continued).

C(16)	406(9)	1967(9)	1633(3)	57(2)
C(17)	1789(8)	2045(8)	1473(2)	47(2)
C(18)	4984(7)	1106(6)	804(2)	32(1)
C(19)	3868((7))	1285(6)	518(2)	37(2)
C(20)	2806(8)	1369(7)	215(2)	40(2)
C(21)	2964(8)	-168(7)	95(2)	46(2)
C(22)	3673(11)	-745(10)	-343(3)	83(3)
C(23)	3824(13)	-2183(12)	-453(4)	108(4)
C(24)	3311(13)	-3051(11)	-118(4)	100(3)
C(25)	2564(14)	-2497(10)	312(3)	98(3)
C(26)	2418(10)	-1061(9)	428(3)	68(2)
C(27)	1425(7)	2915(7)	10(2)	41(2)
C(28)	299(8)	2940(9)	-296(2)	55(2)
C(29)	-1018(10)	4392(11)	-474(3)	78(2)
C(30)	-1218(10)	5819(10)	-344(3)	76(2)
C(31)	-98(10)	5797(10)	-56(3)	74(2)
C(32)	1213(8)	4380(7)	121(2)	52(2)

Equivalent isotropic U defined as one third of the trace of the orthogonalized Uij tensor.

Table III.5. Bond lengths (Å).

Si(1) – O(1)	1.649(4)
Si(1) – C(1)	1.852(7)
Si(1) – C(2)	1.852(7)
Si(1) – C(18)	1.891(6)
Si(2) – O(1)	1.631(5)
Si(2) – O(2)	1.631(4)
Si(2) – C(4)	1.831(8)
Si(2) – C(3)	1.832(7)
O(2) – C(5)	1.439(6)
C(5) – C(12)	1.523(8)
C(5) – C(6)	1.541(7)
C(5) – C(18)	1.560(8)
C(6) – C(7)	1.373(8)
C(6) – C(11)	1.396(8)
C(7) – C(8)	1.376(8)
C(8) – C(9)	1.363(9)
C(9) – C(10)	1.365(9)
C(10) – C(11)	1.379(8)
C(12) – C(13)	1.392(8)
C(12) – C(17)	1.397(8)
C(13) – C(14)	1.380(1)

Table III.5. (Continued)

C(14) – C(15)	1.353(10)
C(15) – C(16)	1.384(10)
C(16) – C(17)	1.367(9)
C(18) – C(19)	1.291(8)
C(19) – C(20)	1.315(8)
C(20) – C(27)	1.484(8)
C(20) – C(21)	1.485(8)
C(21) – C(22)	1.375(9)
C(21) – C(26)	1.381(9)
C(22) – C(23)	1.386(11)
C(23) – C(24)	1.350(12)
C(24) – C(25)	1.358(12)
C(25) – C(26)	1.392(10)
C(27) – C(32)	1.391(8)
C(27) – C(28)	1.392(8)
C(28) – C(29)	1.392(10)
C(29) – C(30)	1.380(11)
C(30) – C(31)	1.356(10)
C(31) – C(32)	1.371(9)

Table III.6. Bond angles (°)

O(1) – Si(1) – C(1)	109.4(3)
O(1) – Si(1) – C(2)	109.2(3)
C(1) – Si(1) – C(2)	111.3(4)
O(1) – Si(1) – C(18)	101.9(2)
C(1) – Si(1) – C(18)	113.7(3)
C(2) – Si(1) – C(18)	110.8(3)
O(1) – Si(2) – O(2)	108.0(2)
O(1) – Si(2) – C(4)	110.4(3)
O(2) – Si(2) – C(4)	105.3(3)
O(1) – Si(2) – C(3)	110.3(3)
O(2) – Si(2) – C(3)	110.7(3)
C(4) – Si(2) – C(3)	112.0(4)
Si(2) – O(1) – Si(1)	124.3(3)
C(5) – O(2) – Si(2)	131.0(3)
O(2) – C(5) – C(12)	108.1(4)
O(2) – C(5) – C(6)	106.9(4)
C(12) – C(5) – C(6)	110.0(5)
O(2) – C(5) – C(18)	108.4(4)
C(12) – C(5) – C(18)	112.7(4)
C(6) – C(5) – C(18)	110.5(4)
C(7) – C(6) – C(11)	118.5(5)

Table III.6. (Continued).

C(7) – C(6) – C(5)	120.9(5)
C(11) – C(6) – C(5)	120.6(5)
C(6) – C(7) – C(8)	120.1(6)
C(9) – C(8) – C(7)	121.4(6)
C(8) – C(9) – C(10)	119.1(6)
C(9) – C(10) – C(11)	120.6(6)
C(10) – C(11) – C(6)	120.2(6)
C(13) – C(12) – C(17)	117.2(6)
C(13) – C(12) – C(5)	121.6(6)
C(17) – C(12) – C(5)	121.2(5)
C(14) – C(13) – C(12)	120.9(7)
C(15) – C(14) – C(13)	120.6(7)
C(14) – C(15) – C(16)	120.0(7)
C(17) – C(16) – C(15)	119.8(7)
C(16) – C(17) – C(12)	121.5(7)
C(19) – C(18) – C(5)	122.3(5)
C(19) – C(18) – Si(1)	119.3(4)
C(5) – C(18) – Si(1)	117.4(4)
C(18) – C(19) – C(20)	175.9(6)
C(19) – C(20) – C(27)	123.1(5)
C(19) – C(20) – C(21)	117.8(5)

Table III.6. (Continued).

C(27) – C(20) – C(21)	119.1(5)
C(22) – C(21) – C(26)	118.6(6)
C(22) – C(21) – C(20)	121.1(6)
C(26) – C(21) – C(20)	120.3(6)
C(21) – C(22) – C(23)	121.0(8)
C(24) – C(23) – C(22)	119.3(9)
C(23) – C(24) – C(25)	121.2(8)
C(24) – C(25) – C(26)	119.8(8)
C(21) – C(26) – C(25)	120.0(8)
C(32) – C(27) – C(28)	118.1(6)
C(32) – C(27) – C(20)	120.9(5)
C(28) – C(27) – C(20)	121.0(6)
C(29) – C(28) – C(27)	120.6(7)
C(30) – C(29) – C(28)	119.8(8)
C(31) – C(30) – C(29)	119.6(8)
C(30) – C(31) – C(32)	121.4(8)
C(31) – C(32) – C(27)	120.5(7)

II. DESIGN AND SYNTHESIS OF NOVEL BLUE-LIGHT-EMITTING PHOTOLUMINESCENT AND ELECTROLUMINESCENT MATERIALS

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Abstract

Novel, blue-light-emitting molecules containing the 3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,1-*a*]indene unit were synthesized with the recently discovered intramolecular addition of disilanes to acetylenes. Light-emitting diodes (LEDs) were fabricated by chemical vapor deposition. The chromophore was also incorporated into polysiloxanes and polymethacrylate as pendent groups. Due to their highly chemical stabilities and photoluminescent quantum yields, these polymers are excellent candidates for fabrication of polymer-based blue-light LEDs.

1. Introduction

After the first commercial GaAsP light-emitting diodes (LEDs) were introduced in 1962, people soon started to explore the possibility of making organic LEDs,[1] because organic materials have many potential advantages over inorganic materials in construction of large, flat, flexible, and inexpensive screens. Since Tang's report of LEDs composed of vapor-deposited fluorescent dyes in 1982,[2] great efforts and achievements have been made.[3-12] Recently, Kodak announced a device with a brightness as high as 1400 candelas per square meter of surface (cd/m^2) and a lifetime as long as 6000 hours, while Pioneer Electronic Corporation unveiled a prototype bright-green organic display with over 16,000 individual LED picture elements and a lifetime of 5000 hours and plans to sell as 64-by-256-pixel green flat-panel displays.[11,12] Though these companies are pushing ahead with commercialization, there still are many hurdles, like lifetime, efficiency, reproducibility, and reliability, to be overcome before organic materials achieve widespread use.

While the progress in small-molecule organic LEDs is very impressive, polymer-based organic LEDs have had less success even though Gang Yu of Uniax Co. made a polymer-based device showing a lifetime of over 10,000 hours at a brightness of 100 cd/m^2.[11] For small-molecule-based LEDs, high vacuum deposition technology is used to produce high quality crystalline films with few defects. For the polymers, it is hard to make a film with very few defects with the usual spin-coating technique. However, a serious disadvantage of devices consisting of organic materials of rather low molecular weight is the tendency of the materials to recrystallize (initiated by the heat produced in the device), which leads to a drastic decrease in quantum efficiency.[13] Another drawback is the cost of making crystalline films that must be painstakingly grown in a vacuum. Therefore, research in polymer-based organic LEDs remains very active.

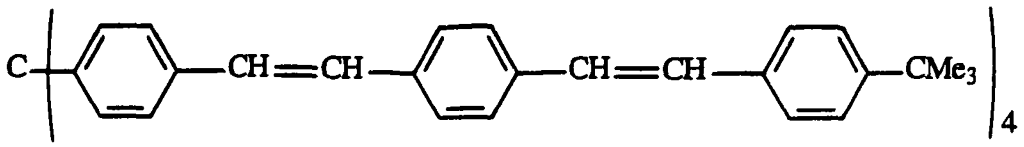
For polymer-based LEDs, the light-emitting materials are classified into three categories, main-chain conjugated polymers, rigid-flexible main-chain block copolymers, and pendant polymers. Main-chain conjugated polymers have the disadvantages that they are somewhat difficult to synthesize; they exhibit poor solubility which makes them difficult to process into optical quality thin films; and they inevitably contain randomly distributed defects, i.e., nonconjugated segments, which lead to a statistical distribution of fluorophores and lower quantum efficiency.

As discussed by Tsutsui and Saito,[14] zero-dimensional π-conjugated systems of small molecules have inherently superior fluorescence properties than those of one-dimensional structures, and much better than those of two-dimensional structures. Thus, the shorter the conjugation length of a compound, the higher the photoluminescent quantum yield.[15] So, rigid-flexible main-chain alternating di-block copolymers were designed to fix the conjugation length in these polymers.[17] In these materials, the electroluminescent group, or its precursor, was first synthesized as a co-monomer. The rigid, conjugated co-monomer was condensed with a second co-monomer containing a saturated, flexible segment which prevents extended conjugation and aids solubility. The resulting strictly alternating rigid-flexible copolymers exhibit electroluminescence which closely coincides with the fluorescence spectrum of the monomer. The major drawback of these materials is the multistep synthesis required for difunctionalization and the stringent process requirements of condensation polymerization.

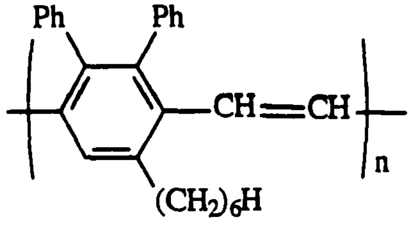
Side-chain electroluminescent polymers are another approach to fixed conjugation length. In these polymers, the fluorophores are attached to a random-coil polymer as pendant groups. These polymers should have some advantages over the other two kinds of polymers. The synthetic routes are simpler than those used for main-chain polymers, the solubility is relatively good, and the emission wavelength is predetermined. An electroluminescent group can be placed on every repeat unit, or nearly every one, and a high concentration of the active species in a film can be made.

It is possible to convert blue light into green and red light in LEDs by a "color conversion layer" interposed between the emitter and the metallic layer.[16] For instance, a green color conversion layer absorbs blue light and emits green light that has less energy. Blue-light-emitting organic materials that usually have shorter conjugation lengths should have higher quantum efficiency as mentioned earlier. (photoluminescent quantum efficiency is the ratio of number of emission photons to number of absorption photons, and electroluminescent quantum efficiency is the ratio of number of emission photons to number of electrons injected). Therefore, blue electroluminescent devices are particularly desirable.[13,15,17]

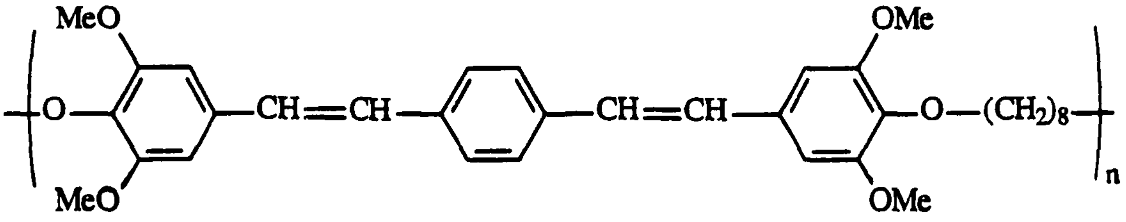
Poly(*p*-phenylene) (PPP) was first used to make polymer-based blue-light-emitting LEDs by Grem and co-workers.[18] Its band gap is about 2.7 eV.[19] PPP itself was prepared by a precursor-polymer route created by Ballard et al.[20] The film (0.5 μm thick) was prepared from the soluble phase of the prepolymer by spin-coating onto an indium-tin oxide (ITO) glass and was converted to PPP by an annealing process in vacuum at 340°C. The quantum efficiency for the PPP device was found to be 0.01-0.05%.



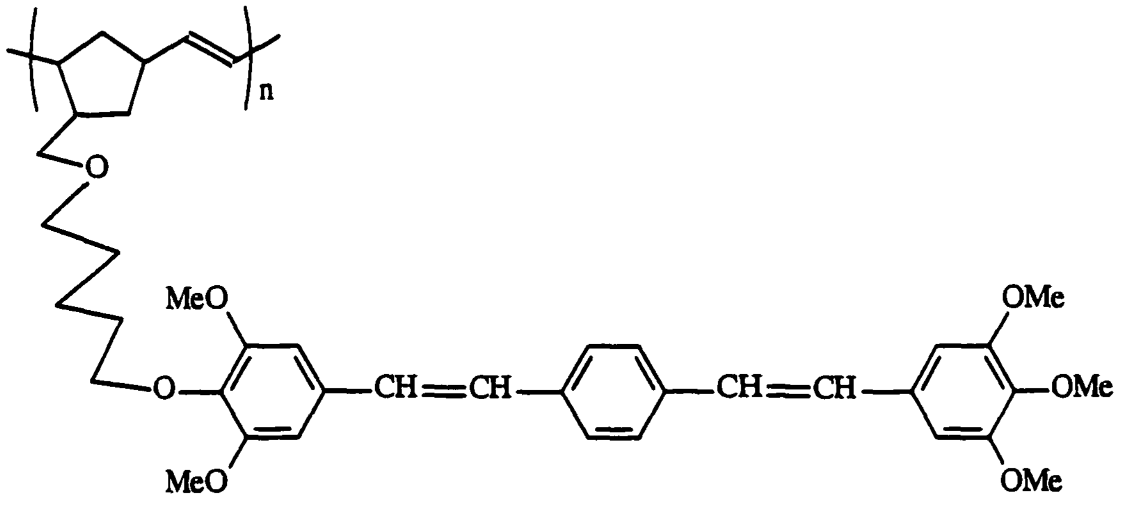
Oldham (1998)[22]



Hsieh (1998)[21]



Sokolik and Karasz (1994)[17]



Schrock (1995)[15]

Figure 1. Stilbene-type compounds for LEDs.

Recently, Hsieh and co-workers reported remarkable progress in the synthesis of full conjugated blue-emitting poly(p-phenylene vinylenes).[21] The polymer, poly(2,3-diphenyl-5-hexyl-*p*-phenylene vinylene) (DP6-PPV), was made via monomer synthesis by the Diels-Alder reaction and then polymerization of the monomers by a modified Gilch route. The polymer was soluble and showed an incredibly high photoluminescence (PL) quantum efficiency of 65% in the solid state. Even though it was not a pure blue emission, the PL emission peak of 490nm (bluish green) was the closest to a blue emission reported for a fully conjugated PPV. LEDs made with these materials have not been reported yet.

In order to obtain a pure blue-light emission with the PPV structure, Yang, Sokolik and Karasz tried to fix the length of conjugation by synthesizing a rigid-flexible diblock polymer.[17] A substituted bi-stilbene as a flourophore was co-polymerized with a long flexable chain. The polymer was soluble in THF and $CHCl_3$. The films made with the polmer had UV absorption at $\lambda_{ab} = 370$ nm and electroluminescent emission at $\lambda_{em} = 465$ nm. The efficiency was not reported.

Schrock and co-workers synthesized side-chain polymers to obtain a pure blue-light emission with the PPV structure.[15] They made a substituted bi-stilbene, and then attached it to a norbornene, finally polymerized the monomer via the ring-opening metathesis polymerizatio (ROMP) method. The polymer containing phenylenevinylene oligomer units as side chains was soluble in THF and was used to make films with absorption at $\lambda_{ab} = 362$ nm and emission at $\lambda_{em} = 475$ nm. The electroluminescent efficiency was 0.3% in single layer LEDs.

Recently, Oldham et al. developed a tetrakis(4-tert-butylstyrylstilbenyl)methane system to fix the wavelength and improve the morphology.[22] Even though the system was still in the small molecular range, morphology was significantly improved. In $CHCl_3$ solution, the wavelengths of absorption and emission maximum of the compound were 368 nm and 427 nm, respectively. The photoluminenscent quantum yield and fabrication of an LED device have not been reported yet.

Bisberg and Kolb of Polaroid Co. developed side-chain polymers by attaching pyrene to polysiloxanes.[23,24] They found that the pyrene excimer was responsible for the light (λ_{em} = 500 nm) from devices made with the polymers. The brightness of 168 cd/m^2 and quantum efficiency of 0.20% were obtained by adding another charge transport layer of a polymer with pendent triarylamine in their two-layer LED devices.

We can see that in the construction of photoluminescent polymers, PPV segments are commonly used either in main-chain conjugated polymers,[26] rigid-flexible bi-block copolymers,[17] or side-chain polymers.[15] The small molecule stilbene is an obvious model for the phenylenevinylene repeat unit except for the fact that stilbene has a very low quantum efficiency at room temperature (Φ_f=0.05). This low quantum efficiency is due to the fact that after absorbing a photon trans-stilbene isomerizes into the cis isomer via a twisted 1,2-diradical intermediate.[27] This energized diradical readily reacts with impurities, such as residual solvents, oxygen, and species on the interfaces, so that the lifetime and efficiency of the devices are gradually reduced. Herein, we report the synthesis of a locked trans-stilbene and its use in blue-light emitting LEDs. Polymers were also synthesized bearing the locked trans-stilbene as a pendant group that eliminates isomerization and improves the electroluminescenct quantum efficiency.

2. Synthesis of a highly photoluminescent molecule and fabrication of LEDs with it

Once a molecule absorbs a photon, it actually becomes a different species chemically and physically. Especially, it has very different chemical properties. After *trans*-stilbene absorbs a photon at room temperature in solution, it becomes a very reactive molecule. Because of the very low barrier ($\Delta H^{\neq}$=3 kcal/mol) for isomerization by twisting, this new species lasts only about 70 picoseconds and the fluorescence quantum yield is only about 0.05.[28] If we modify the trans-stilbene by locking the double bond to avoid twisting, we would have a molecule indeno[2,1-*a*]indene. Now, this new molecule is "perfect". It no longer twists when it absorbs a photon. The lifetime of singlet excited molecule is much longer (1.99 ns, about 30 times of that of trans-stilbene), and the fluorescence quantum yield is 1. However, because this species is long-lived and very reactive, it dimerizes or reacts with other olefins to form [2+2] cyclo-adducts besides emitting light.[29] If we lock the stilbene to avoid twisting and have some bulky groups around the double bond to reduce its reactivity, we would have a better chromophore. The molecule 3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,1-*a*]indene (**2**) is an excellent candidate. Two silicon atoms lock the stilbene to avoid twisting and four methyl groups sterically protect the central double bond.

Recently, we have discovered that intramolecular, thermal and photochemical *trans*-addition of disilanes to acetylenes can occur in appropriate systems in high yield.[30] This discovery has allowed us to synthesize the novel silyl-bridged stilbene derivative, 3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,1-*a*]indene (**2**) from the photolysis of disila-cycloacetylene **1** at high yield (Scheme 1). Because of the silyl bridges, the molecule has higher photochemical and thermal stability than stilbene, as well as a much higher photoluminescent quantum yield ($\Phi_f = 0.68$). No dimers were found under irradiation with UV for 24 hours. Thus systems containing this molecular unit should be excellent candidates for optoelectronic applications.

Introduction of the silyl group significantly reduces the energy of the π^* orbital in the molecule. From the UV spectrum of **2**, the bandgap reduction is estimated as 0.4 eV from stilbene or 0.3 eV from indeno[2,1-*a*]indene. Thus, only one stilbene unit is needed to emit blue light otherwise two stilbene units are normally needed as Oldham et al.[22] in did in their tetrakis(4-tert-butylstyrylstilbenyl)methane, Yang et al.[17] did in their rigid-flexible block polymer, and Schrock et al.[15] did in their side-chain polymer. Silyl groups usually lower the LUMO in the conjugated system by interaction of σ^* of Si-Me with π^* orbitals.[31] This shift should provide systems containing **2** with better electron-transport properties in addition to the well-established hole-transporting properties of phenylene-vinylene-containing polymers. Balancing of injection of electrons by the cathode and injection of holes by the anode should improve electroluminescent efficiency. Otherwise, the combination of holes and electrons predominantly occurs at the cathodic interface for single-layer phenylenevinylene devices, and the resulting excitons can be easily quenched by defects on the polymer/cathode interface.

The emission spectrum of **2** (Figure **2**) shows strong emission of blue light with λ_{max}=425 nm. Two-layer LEDs were fabricated by vacuum vapor deposition of **2**. The devices emitted strong blue light. The lifetime of the devices was only a few minutes in air before they burned out.

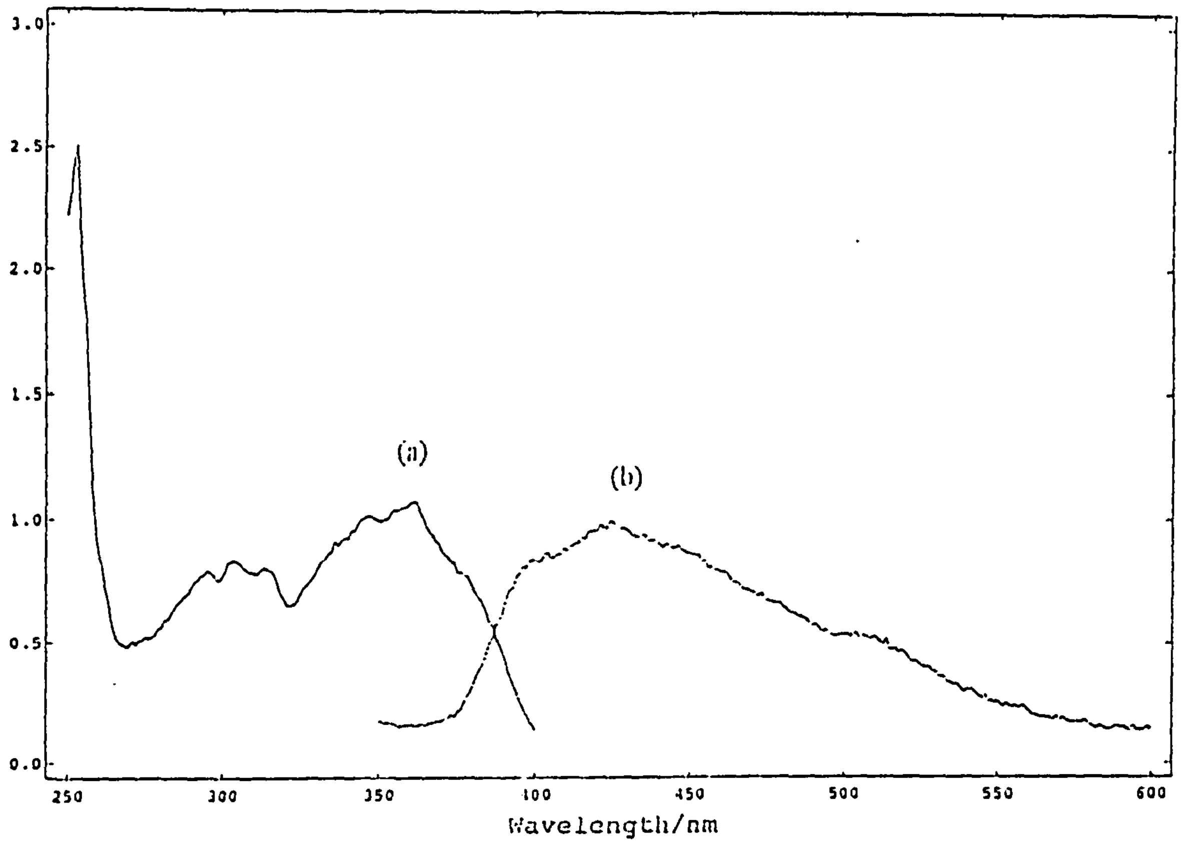
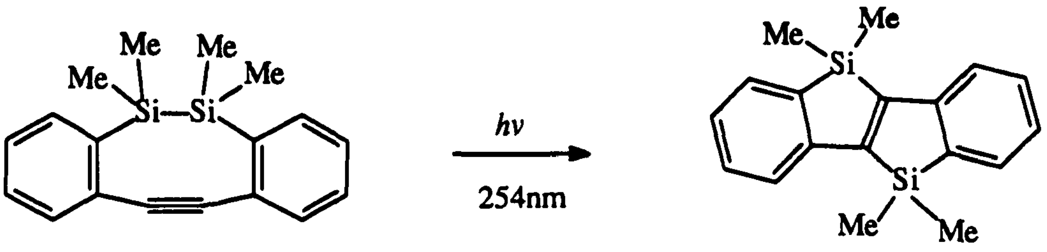


Figure 2. Absorption (a) and photoluminescence (b) of 2.

Scheme 1



1

2

3. Synthesis of polymethacrylate side chain polymers

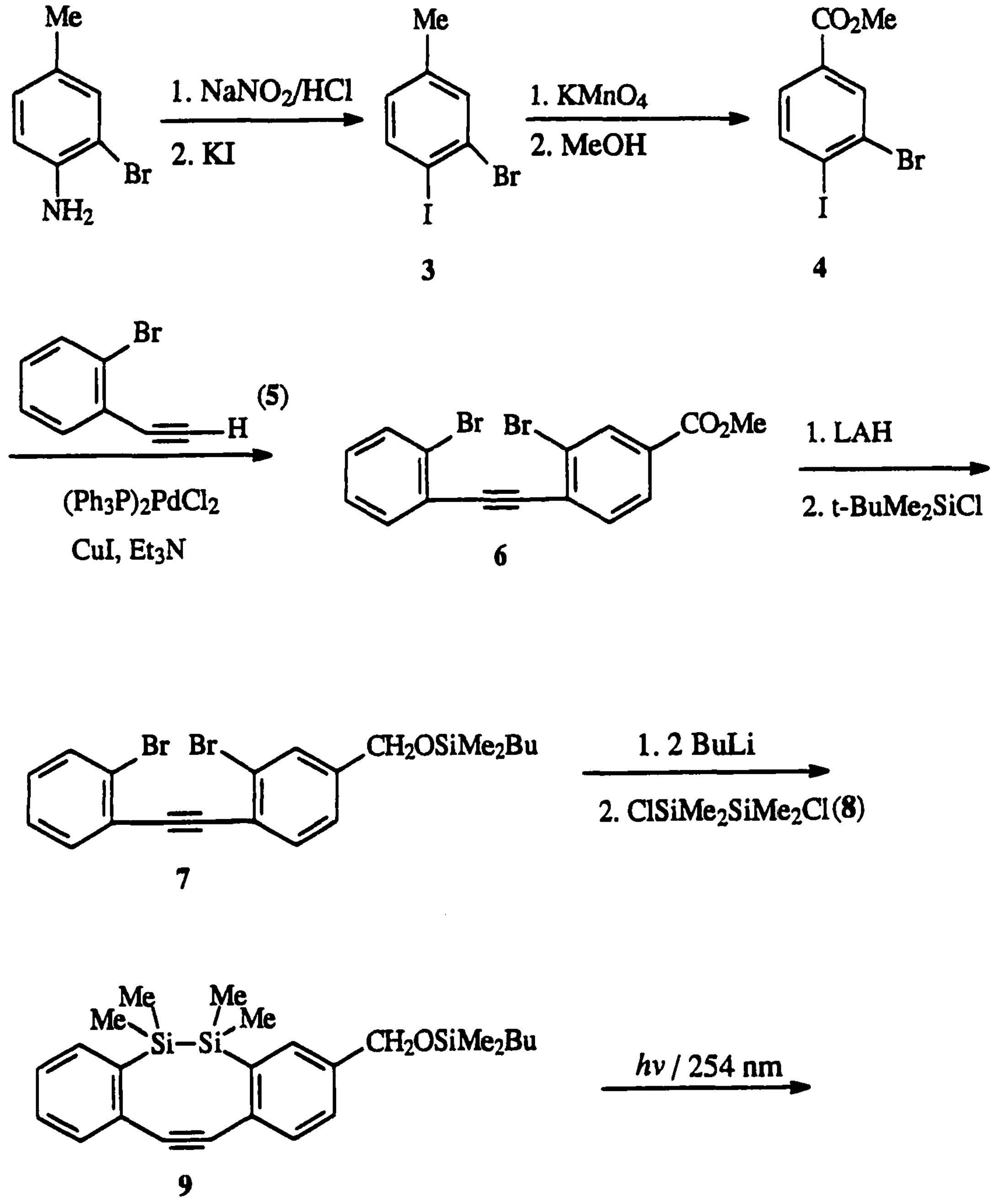
A polymethacrylate with disila-indeno[2,1-*a*]indene pendant groups was synthesized as shown in Scheme **2**. 2-Bromotoluidine was diazotized and reacted with iodide to form 3-bromo-4-iodotoluene (**3**). Methyl oxidation with potassium permanganate in acetic acid afforded carboxylic acid, which was protected with an alcohol then. By palladium coupling with 2-bromo-1-ethynylbenzene (**5**), a bisbromophenylacetylene (**6**) was obtained. Then the ester was reduced to an alcohol and was protected with tert-butyldimethylsilyl group. Through bromine exchange with lithium, a dilithium compound was formed and was quenched with dichlorodisilane to form a cyclic compound (**9**) in 40% yield. With the photoisomerization of the disilaacetylene, a functional disila-indeno[2,1-*a*]indene (**10**) was obtained at a quantitative yield. Deprotection of the alcohol and esterification of **10** with methacrylic chloride afforded monomer **11** which was quantitatively converted into poly((3,3,3′,3′-tetramethyl-3,3′ -disila-indeno[2,1-a]indenyl)methyl methacrylate) (**12**) using anionic polymerization in THF with ethyl magnesium bromide as initiator. The molecular weights of the resulting polymer was $M_n = 6.4 \times 10^3$ and $M_w = 1.1 \times 10^4$.

4. Synthesis of polysiloxane side chain polymers

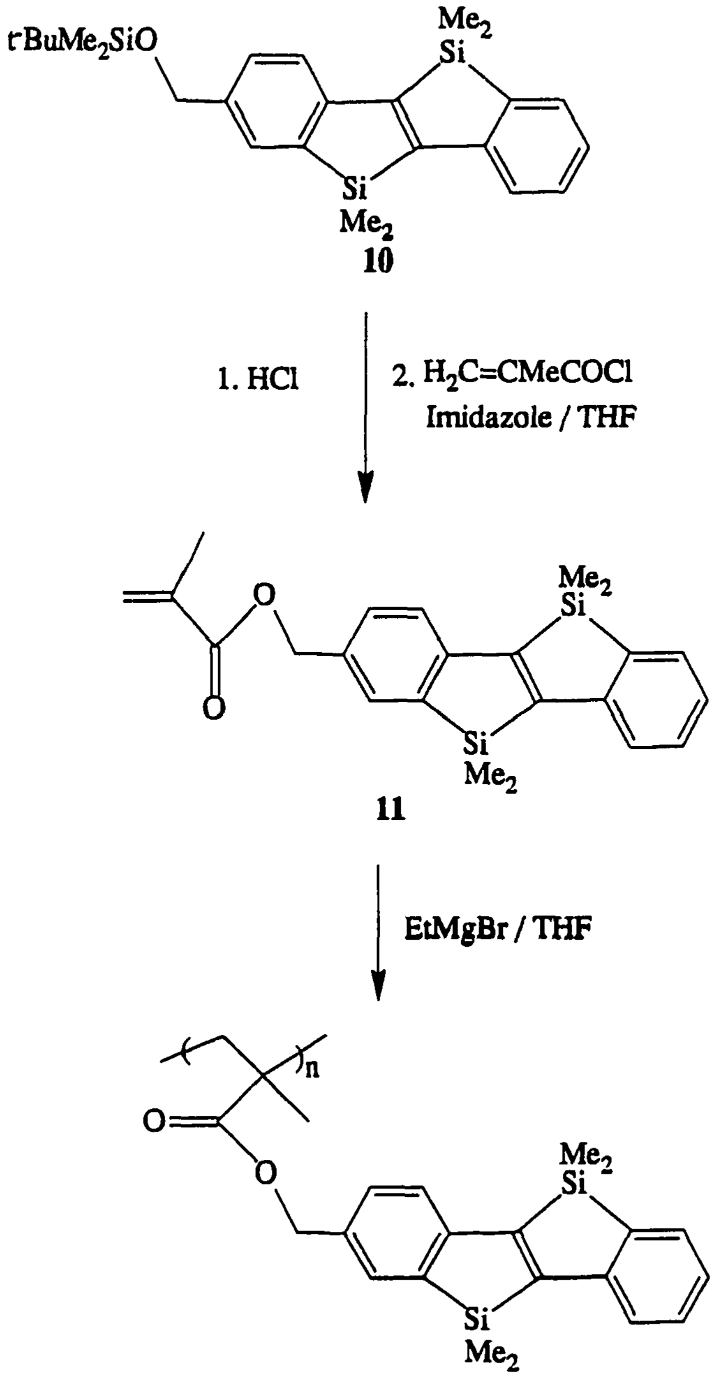
A siloxane chain is flexible and very stable in extreme chemical and thermal environments. Disila-indeno[2,1-*a*]indene was incorporated onto a siloxane polymer by the synthetic route shown in schemes **3**, **4** and **5**. 3-Bromo-4-iodotoluene was converted to 4-bromomethyl-3-bromo-1-iodobenzene with N-bromosuccimide in carbon tetrachloride. Through reaction with allyl alcohol, an allyl benzyl ether (**13**) was obtained. By palladium coupling, lithium-bromine exchange, and reaction with 1,2-dichlorodisilane, a cyclodisilaacetylene was obtained and was photochemically isomerized to a disila-indeno[2,1-*a*]indene. The allyloxy derivative of carbinol, ether **16**, was attached to poly(dimethylsiloxane-co-methyl-siloxane)(**19**), prepared by ring-opening copolymerization of octamethylcyclotetrasiloxane and 1,2,3,4-tetramethylcyclotetra-siloxane with trifluoroacetic acid as catalyst.[32] Side chain attachment was accomplished in quantitative yield by hydrosilylation using chloroplatinic acid (CPA) as the catalyst. The ratio of monomer **16** to silyl hydride unit in **19** employed in this reaction was 1:2. The molecular weight of the resulting polymer **20**, as measured by GPC in THF was $M_n = 1.3 \times 10^4$ and $M_w = 2.1 \times 10^4$).

Both polymers **12** and **20** are strongly photoluminescent materials which form spin-cast films.

Scheme 2


Me
Br
NH2
1. NaNO2/HCl
2. KI
Me
Br
I
3
1. KMnO4
2. MeOH
CO2Me
Br
I
4
Br
H
(5)
(Ph3P)2PdCl2
CuI, Et3N
Br
Br
CO2Me
6
1. LAH
2. t-BuMe2SiCl
Br
Br
CH2OSiMe2Bu
7
1. 2 BuLi
2. ClSiMe2SiMe2Cl (8)
Me
Me
Si–Si
Me
Me
CH2OSiMe2Bu
9
hν / 254 nm

Scheme 2 (continued)

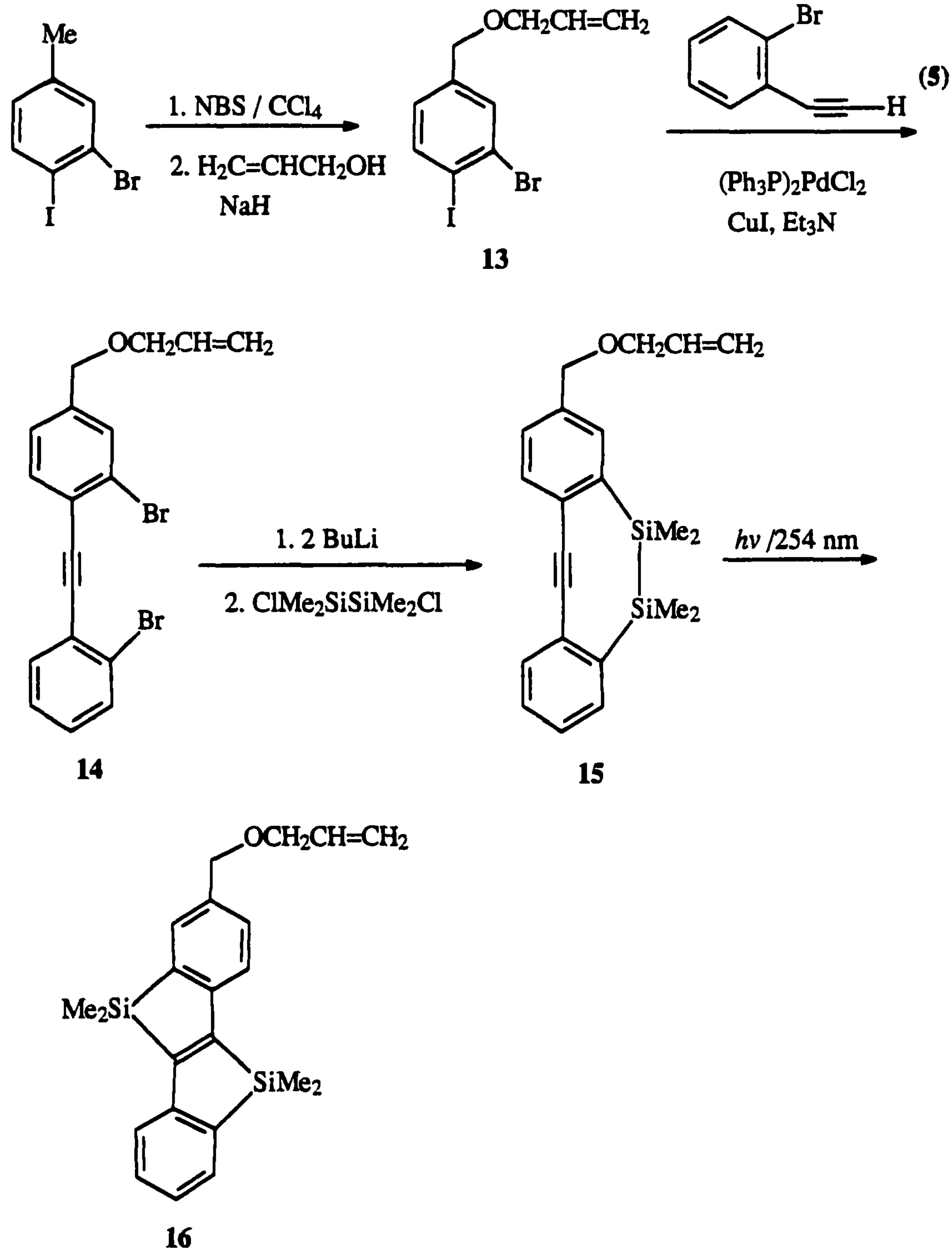


10

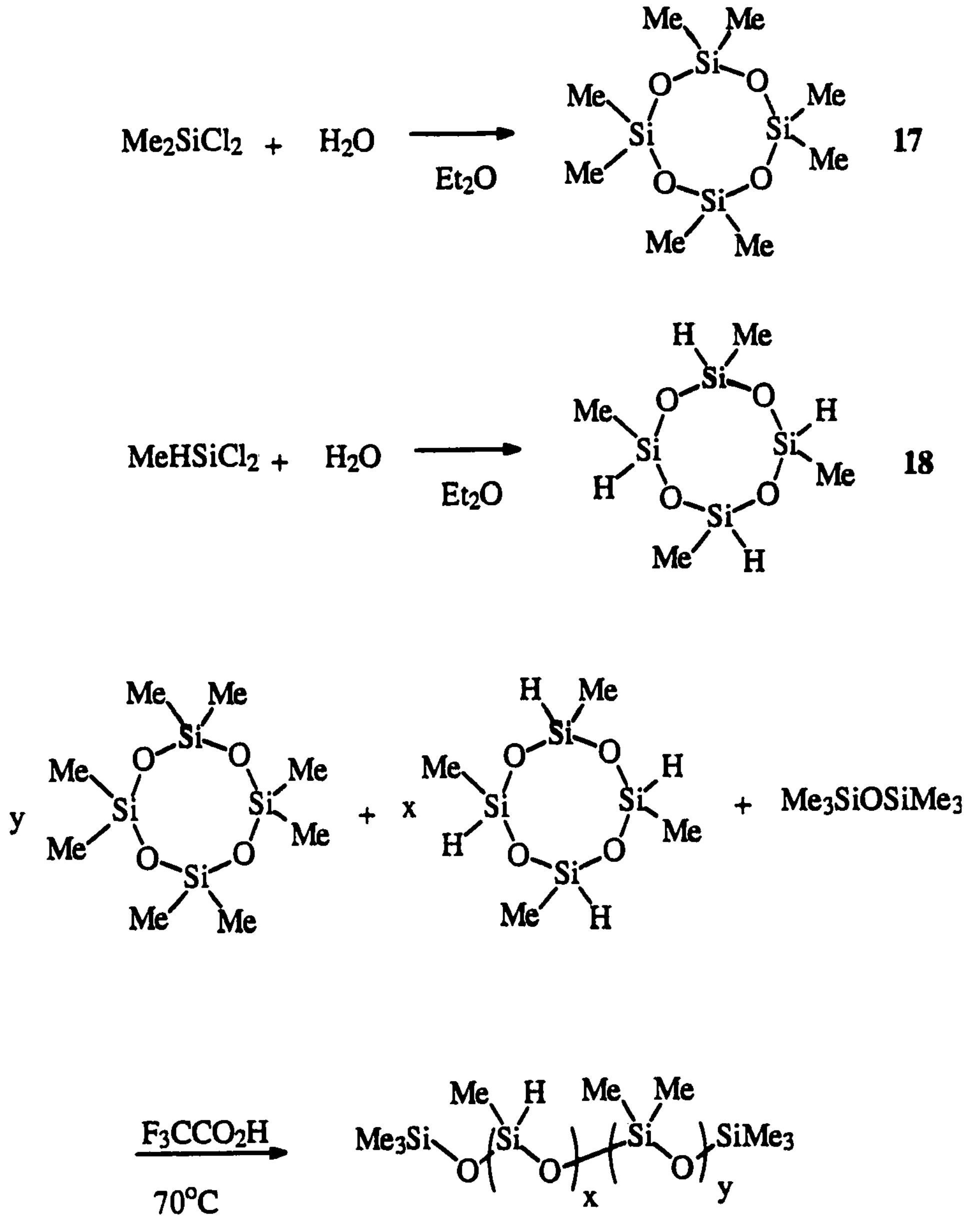
11

12

Scheme 3


Me
Br
I
1. NBS / CCl4
2. H2C=CHCH2OH
NaH
OCH2CH=CH2
Br
I
13
Br
H
(5)
(Ph3P)2PdCl2
CuI, Et3N
OCH2CH=CH2
Br
Br
14
1. 2 BuLi
2. ClMe2SiSiMe2Cl
OCH2CH=CH2
SiMe2
SiMe2
15
hv /254 nm
OCH2CH=CH2
Me2Si
SiMe2
16

Scheme 4

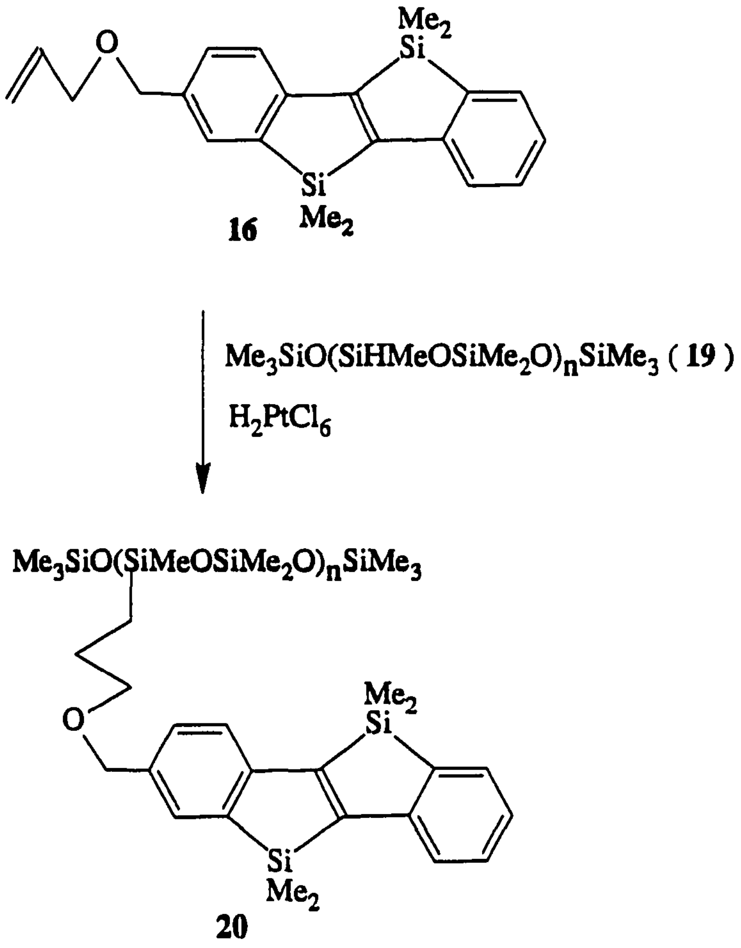


17

18

19

Scheme 6



5. Summary

Novel, blue, light-emitting molecules containing the 3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,1-a]indene unit were synthesized with our recently discovered intramolecular addition of disilanes to acetylenes. Blue-light-emitting LEDs were fabricated with CVD technology. Polysiloxane and polymethacrylate polymers containing 3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,1-a]indene moities as pendant groups were synthesized. Due to their high chemical stabilities and quantum yields, these polymers are excellent candidates for fabrication of blue-light LEDs and efforts toward this goal are currently in progress.

6. Experimental

General Procedures. ^1H and ^{13}C NMR spectra were acquired on a Varian VXR-300 spectrometer. In order to assure the quantitative feature of the ^{13}C NMR spectra, the relaxation agent chromium (III) acetylacetonate was added in $CDCl_3$ with a relaxation delay of 5 seconds.

The exact masses were obtained from a Kratos MS 50 mass spectrometer with 10,000 resolution. The infrared spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer from neat sample. The UV/Vis spectra were obtained on a Hewlett Packard 8452A diode array UV/Vis spectrometer. Reactions were monitored by Hewlett Packard 5890 series II GC and Hewlett Packard tendem GC-IR-MS (5890A GC-5965A IR-5970 Series MS) parallel connected.

Molecular weight of the polymers were determined by gel permeation chromatography (GPC) with 6 Microstyragel columns in series of 500A, $2X10^3$A, $2X10^4$A, 10^5A. THF was used as eluent at a flow rate of 1.0 ml/min. The system was calibrated by polystyrene standards. The detection system used was a Waters Associates differential refractometer.

THF was distilled over sodium-benzophenone and ether was distilled over CaH_2 right before use. Other reagents were used as received from Aldrich or Fisher Chemical Co. without further purification unless specified otherwise.

Synthesis of 3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,1-*a*]indene (2) was developed by us and the details are being reported in a separate manuscript.[30]

Fabrication of LEDs by vacuum chemical vapor deposition. An indium tin oxide (ITO) coated glass (1x1 cm) was used as substrate. The 3x10 mm of strip of ITO was removed by oxidation in a mixture of nitric acid and hydrochloride acid. The substrates were sequentially washed with water, surfactant, acetone, and isopropanol in an ultrasonic bath. The 6 substrates were placed in a bell-jar which was evacuated to $1\text{x}10^{-5}$ torr. The hole transport material N,N′-di-(3-methylphenyl)-N, N′-diphenyl-4,4′-diaminobiphenyl (TPD) was deposited onto the substrates at the rate of 10 Å/second until a film of 20 nm thickness was obtained. Then, 3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,1-*a*]indene (2) was deposited at the rate of 15 Å/second to produce a film of 40 nm thickness. Finally, an aluminum film of 100 nm thick was obtained. Using conductive silver paint, copper wires were connected to the anode and cathode. The LEDs started to emit a strong blue light at 12 volts in air.

Synthesis of 3-bromo-4-iodotoluene (3). The 3-bromo-4-iodotoluene was prepared from 2-bromotoluidine by a similar procedure of Bard et al.[33] To a 500 ml round flask with a magnetic stirrer, 11.16 g (60 mmol) of 2-bromotoluidine was charged. Then, 28 ml of concentrated hydrochloric acid and 40 g of ice were added consecutively. At 0°C, 20 ml of aqueous sodium nitride (4.56 g, 66 mmol in 20 ml of water) was added to the solution dropwise. After stirring 20 minutes at 0°C, the solution was dropwise added to an aqueous potassium iodide solution (99.6 g of KI in 120 ml of water) at 0°C for 40 minutes. The solution was stirred at room temperature overnight, and was extracted with methylene chloride (2X200ml). The combined organic extracts were washed with saturated sodium bicarbonate aqueous solution and water, and dried over $MgSO_4$. After removing the solvent with a rotatory evaporator, the product was purified with a flash chromatography over silica gel. The product 3-bromo-4-iodotoluene was obtained at the yield of 14.4 g (81%).

Synthesis of methyl 3-bromo-4-iodobenzoate (4). To a 500 ml round bottom flask with a magnetic stirrer, 150 ml of pyridine, 150 ml of water and 5.94 g (20 mmol) of 3-bromo-4-iodotoluene (3) were added consecutively. Controlling the solution at 80°C, 15.8 g (100 mmol) of potassium permanganate was added in portion of 1.6 g in 20 minutes. Vacuum filtration was used to remove the MnO_2 first. The filtrate was acidified with 10% of hydrochloric acid until PH = 5 and a white solid was formed. The white solid of 3-bromo-4-iodobenzoic acid obtained by vacuum filtration and was dried in air. Placed the compound into 150 ml of methanol in a 250 ml round bottom flask with a magnetic stirrer, 15 ml of concentrated sulfuric acid was slowly added. The solution was refluxed for 4 hours. Methylene chloride (2x100 ml) was used to extract the product (note: a little water was added to help to separate the layers). After drying over sodium sulfate and solvent removal with a rotatory evaporator, flash chromatography was used to purify the product. Methyl 3-bromo-4-iodobenzoate (4) was obtained (4.3 g, percentage yield of 63% based on 3-bromo-4-iodotoluene (3)). Exact mass 341.85713 (calc. For $C_8H_6O_2BrI$ 341.85754)

Synthesis of 2-bromo-1-ethynylbenzene (5). 2-Bromo-1-ethynylbenzene was synthesized by the procedure of Diercks and Volhardt.[34] Please see part I of this thesis for the experimental details.

Synthesis of 1-(2′-bromo-4′-methoxycarbonylphenyl)-2-(2″-bromophenyl)acetylene (6). To 100 ml of DMF in a 250 ml of round bottom flask with a magnetic stirrer, 2.89 g (15.12 mmol) of 1-bromo-2-ethynylbenzene and 4.3 g (12.6 mmol) of methyl 3-bromo-4-iodobenzoate were added. Under argon atmosphere, 140 mg of $PdCl_2(PPh_3)_2$ and 150 mg of copper (I) iodide were added. Then, 20 ml of triethylamine was injected into the solution. After being stirred overnight, it was worked up with saturated aqueous ammonium chloride solution. After flash-chromatographic purification, 4.12 g (83%) of 1-(2′-bromo-4′-methoxycarbonylphenyl)-2-(2″-bromophenyl)acetylene (6) was obtained: GCMS *m/z* 396 (50), 395 (21), 394 (100), 392 (54), 365 (39), 363 (79), 361 (42), 256 (40), 254 (40), 175 (40), 174 (31), 128 (20), 127 (20), 87 (21).

Synthesis of 1-(2′-bromo-4′-tert-butyldimethylsiloxymethylphenyl)-2-(2″-bromophenyl)acetylene (7). To a suspension of $LiAlH_4$ (0.3 g, 7.5 mmol) in anhydrous ethyl ether (20 ml) in a 50 ml round bottom flask with a magnetic stirrer, a solution of 1-(2′-bromo-4′-methoxycarbonylphenyl)-2-(2″-bromophenyl)acetylene (2.364 g, 6 mmol) in 3 ml of anhydrous ethyl ether was added. After being stirred at room temperature for half an hour, the mixture was refluxed overnight. At room temperature, 20 ml of water was very carefully added. The product was extracted with ethyl ether (4x20 ml). Combining all the extracts, the solution was washed with water and dried over sodium sulfate. After removing the solvent with a rotatory evaporator, the 1-(2′-bromo-4′-hydroxymethylphenyl)-2-(2″-bromophenyl)acetylene was obtained. After the compound was dried with vacuum overnight, 30 ml of THF was added. And then 0.9 g (6 mmol) of tert-butyldimethylsilyl chloride and 2 g of imidazole were added. The solution was stirred overnight at room temperature. After workup with ether and aqueous ammonium chloride solution and purification with flash chromatography, 2.5 g of 1-(2′-bromo-4′-tert-butyldimethylsiloxymethylphenyl)-2-(2″-bromophenyl)acetylene was obtained in 81% yield: GCMS *m/z*: 480(M^+), 425(24), 423(46), 421(24), 393(14), 351(49), 349 (100, base), 347(52), 189(62); ^{1}H NMR (300 MHz, $CDCl_3$), δ 0.100 (s, 6H), 0.939 (s, 9H), 4.710 (s, 2H), 7.145-7.617(m, 7H); ^{13}C NMR (75.429 MHz, $CDCl_3$) δ: -5.310, 25.881, 63.915 (-C-O), 91.725 (-C≡), 92.387 (-C≡), 123.378, 124.526, 125.220, 125.428, 125.474, 126.994, 129.603, 129.857, 132.488, 133.387, 133.575, 143.879; exact mass 481.99203 (calc. For $C_{21}H_{24}OBr_2Si$ 481.99222).

Synthesis of 5,5,6,6-tetramethyl-5,6-disila-benzo[*c*]-(4′-tert-butyldimethylsiloxymethyl)benzo[1′,2′-*g*]cyclooctyne (9). To 50 ml of THF in a 125 ml round bottom flask, 2.5 g (5 mmol) of 1-(2′-bromo-4′-tert-butyldimethylsiloxymethylphenyl)-2-(2″-bromophenyl)acetylene was added under argon atmosphere. After it was cooled down to –78°C, 4 ml (2.5M, 10 mmol) of butyl lithium was injected into the solution over 10 minutes. After being stirred for one hour at the temperature, 0.76 ml (5 mmol) of 1,2-dichlorotetramethyldisilane was injected into the solution over 5 minutes. It was gradually warmed up to room temperature, and stirred overnight. Aqueous ammonium chloride (100 ml) was poured into the solution and ether (3 x 30ml) was used to extract organic layer. After removal of solvent, the product was purified with flash column chromatography over silica gel. The 5,5,6,6-tetramethyl-5,6-disila-benzo[*c*]-(4′-tert-butyldimethylsiloxymethyl)benzo[2′,1′-*g*]cyclooctyne (9) was obtained with a yield of 0.91 g (42%). GCMS *m/z*: 436 (8, M^+), 421(100, base), 379(41), 321(24), 305(16), 131(35). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.099 (s, 6H), 0.213 (s, 6H), 0.244 (s, 6H), 0.942 (s, 9H), 4.746 (s, 2H), 7.311-7.508 (m, 7H).

Synthesis of 6-tert-butyldimethylsiloxymethyl-3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,*1*-*a*]indene(10). A solution ($2x10^{-3}$M) of 446 mg of 5,5,6,6-tetramethyl-5,6-disila-benzo[*c*]-(4′-tert-butyldimethylsiloxymethyl)benzo[2′,1′-*g*]cyclooct-3,7-dieyne dissolved in 50 ml hexanes (HPLC grade) was prepared in a quartz tube capped with a septum. The air in the solution was removed by bubbling argon through it for half an hour. The tube was then connected to an argon balloon and exposed to 254nm UV (a Rayonet photochemical reactor equipped with sixteen 5W low pressure Hg lamp). The reaction was monitored by frequent sampling and analyzed by a capillary GC. The reaction lasted about 1 hour before the starting material was gone. After removing the solvent with rotatory evaporator, the 6-tert-butyldimethylsiloxymethyl-3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,*1*-*a*]indene was obtained at quantitative yield. GCMS *m/z*: 436 (67, M^+), 421(100, base), 379(38), 321(45), 305(27), 131(21). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.095 (s, 6H), 0.111 (s, 6H), 0.444 (s, 6H), 0.938 (s, 9H), 4.744 (s, 2H), 7.162-7.566 (m, 7H). ^{13}C NMR (75.429 MHz, $CDCl_3$) δ: -5.159, -5.087, -3.480, -3.455, 26.033, 64.778 (-C-O), 125.913, 126.025, 128.249, 128.304, 128.417, 131.595, 131.675,139.803, 142.515, 145.127, 149.331.

Synthesis of 6-(iso-propenylcarbonyloxymethyl)-3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,*1*-*a*]indene(11). To 50 ml of 95% Ethanol in a 250ml round bottom flask with a magnetic stirrer, 0.151 g (0.34 mmol)of 6-tert-butyldimethylsiloxymethyl-

3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,*1*-*a*]indene was dissolved. Then, 2 ml of concentrated (37%) hydrochloric acid was added at room temperature. After 5 minutes, TLC showed that the reaction was complete. The reaction was worked up with water and ether. After the product was dried over night with vacuum, it was dissolved in 20 ml of ethyl ether. To the solution, 0.07 ml of methacrylic chloride and 0.05 g of imidazole were added consecutively. After being stirred for 4 hours, The reaction was worked up with ether and water. The product was purified with flash chromatography. The monomer 6-(iso-propenylcarbonyloxymethyl)-3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,*1*-*a*]indene was obtained with 0.102 g (79%).

Synthesis of the poly((3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,*1*-*a*]indenyl)methyl methacrylate) (12). To 20 ml of THF in a 50 ml round bottom flask with a magnetic stirrer, 0.102 g of 6-(iso-propenylcarbonyloxymethyl)-3,3,3′,3′-tetramethyl-3,3′-disila-indeno[2,*1*-*a*]indene was dissolved under argon flow. The solution was cooled down to –78°C, and 0.3 ml (2M) of ethylmagnisium bromide was added. After warmed to room temperature, the solution was stirred for 3 more hours. It was worked up with water and ethyl ether. The polymer was deposited from methanol. The molecular weight measured with GPC was Mn=$6.4x10^3$ and Mw=$1.1x10^4$.

Synthesis of poly(dimethylsiloxane-co-methyl-siloxane) (19).[32] 4-bromomethyl-2-bromo-1-iodobenzene was synthesized first. To 200 ml of carbon tatrachloride in a 500 ml round bottom flask, 17.5 g (58.9 mmol) of 3-bromo-4-iodotoluene, 12.58 g (70.68) of N-bromosuccimide (NBS) and 0.3 g of benzoyl peroxide (BPO) were added. The mixture was refluxed for 12 hours. After filtration of insoluble materials, the filtrate was concentrated in vacuum to leave the residue as brownish oil.

After column chromatography, 9.1 g of 4-bromomethyl-2-bromo-1-iodobenzene was obtained at 42% yield.

Synthesis of 3-bromo-4-iodophenylmethyl allyl ether(13). To 100 ml of N,N-dimethylformamide (DMF), 11.13 g of 4-bromomethyl-2-bromo-1-iodobenzene, 10 ml of allyl alcohol were added. Then 3.6 g of sodium hydride was added carefully. After being stirred for 4 hours, the solution was quenched very carefully with 50 ml of water. The product was extracted with ethyl ether (3x100ml). After removing the solvent with a rotatory evaporator, the product was purified with flash chromatography. The yield was 5.43 g.

Synthesis of 4-(2′-bromophenylethynyl)-3-bromophenylmethyl allyl ether (14). To 100 ml of DMF in a 250 ml round bottom flask with a magnetic stirrer, 5.43g (15 mmol) of 3-bromo-4-iodophenylmethyl allyl ether, 3.53 g of 2-bromo-1-ethynylbenzene were added. Under argon flow, 300 mg of $Pd(PPh_3)_2Cl_2$ and 200 mg of CuI and 3 ml of triethylamine were added consecutively. After being stirred at room temperature overnight, the solution was worked up with water and ethyl ether. After purification with flash chromatography, 5.82 g (95%) of 4-(2′-bromophenylethynyl)-3-bromophenylmethyl allyl (**14**) ether was obtained.

Synthesis of 5,5,6,6-tetramethyl-5,6-disila-benzo[*c*]-(4′-allyloxylmethyl)benzo[1′,2′-*g*]cyclooctyne (15). To 50 ml of THF in a 125 ml round bottom flask, 3.91 g (9.6 mmol) of 4-(2′-bromophenylethynyl)-3-bromophenylmethyl allyl ether was added under argon atmosphere. After it was cooled down to –78°C, 7.68 ml (2.5M, 19.2 mmol) of butyl lithium was injected into the solution over 10 minutes. After stirred for half an hour at the temperature, 1.5 ml (9.6 mmol) of 1,2-

dichlorotetramethyldisilane was injected into the solution over 5 minutes. It was gradually warmed up to room temperature, and stirred overnight. It was worked up with saturated aqueous ammonium chloride and purified with flash column chromatography. The 5,5,6,6-tetramethyl-5,6-disila-benzo[*c*]-(4′-allyloxylmethyl)benzo[2′,1′-*g*]cyclooct-3,7-dieyne was obtained with a yield of 1.57 g (45%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.235 (s, 6H), 0.242 (s, 6H), 5.207 (q), 5.242 (q), 5.299 (q), 5.357 (q), 5.975 (octuplet), 7.336-7.590 (m). ^{13}C NMR (75.429 MHz, $CDCl_3$) δ: -3.640, -3.615, 71.499, 72.138, 98.887, 98.991, 117.354, 127.435, 127.464, 127.491, 127.660, 128.294, 128.392, 128.747, 133.326, 133.953, 134.639, 137.373, 149.284, 149.471.

Synthesis of 6-allyloxymethyl-3,3,3′,3′-tetramethyl-3,3′-disila-indeno[*2,1*-*a*]indene (16). A solution ($2x10^{-3}$M) of 362 mg of 5,5,6,6-tetramethyl-5,6-disila-benzo[*c*]-(4′- allyloxylmethyl)benzo[2′,1′-*g*]cyclooct-3,7-dieyne dissolved in 50 ml hexanes (HPLC grade) was prepared in a quartz tube capped with a septum. The air in the solution was removed by bubbling argon through it for half an hour. The tube was then connected to an argon balloon and exposed to 254nm UV (a Rayonet photochemical reactor equipped with sixteen 5W low pressure Hg lamp). The reaction was monitored by frequent sampling and analyzed by a capillary GC. The reaction lasted about 1 hour before the starting material was gone. After removing the solvent with rotatory evaporator, the 5-allyloxyloxymethyl-3,3,3′,3′-tetramethyl-3,3′-disila-indeno[*2,1*-*a*]indene was obtained at quantitative yield.

Synthesis of tetrahydridotetramethylcyclotetrasiloxane (18) To a mixture of 25 ml of ethyl ether and 50 g of ice in a 250 ml round bottom flask with magnetic stirrer, 10.45 ml of dichloromethylsilane was added dropwise over 15 minutes. After additional 15 minutes stirring, The aqueous layer was removed and organic layer was washed with water until it was neutral. After dried over sodium sulfate and removing solvent, 5.8 g of product was obtained. The tetrahydridotetramethylcyclotetrasiloxane (51%), pentahydridopentamethylcyclopentasiloxane (26%) and hexahydridohexamethylcyclohexasiloxane (9%) were the main compounds in the mixture, which analyzed with a GC-MS. The GCMS of **tetrahydridotetramentylcyclotetrasiloxane** *m/z* : 240 (22, M^+), 239 (65), 225 (100, base peak), 179 (23), 119 (17).

Synthesis of octamethylcyclotetrasiloxane (17) To a mixture of 50 ml of ethyl ether and 100 g of ice in 250 ml round bottom flask with magnetic stirrer, 24.25 ml (200 mmol) of dichlorodimethylsilane was added dropwise over 30 minutes. After additional 20 minutes stirring, The aqueous layer was removed and organic layer was washed with water until it was neutral. After dried over sodium sulfate and removing solvent, 14.2 g of product was obtained. The hexamethylcyclotrisiloxane (D3, 14%), octamethyltetrasiloxane (D4, 60%), decamethylpentasiloxane (15%) and dodecamethylcyclohexasiloxane (D6, 2%) were the main compounds in the mixture, which analyzed with a GC-MS. The GCMS of cyclotetrasiloxane *m/z* : 281 (100, base peak, M^+-15), 265 (11), 73 (8).

Synthesis of poly(dimethylsiloxane-co-methylsiloxane) (19) To a 50 ml round bottom flask with magnetic stirrer, 3.7 g (50 mmol of dimethylsiloxane units) of cyclodimethylsiloxanes, 3.0 g (50 mmol of methylsiloxane units) of cyclomethylhydridosiloxanes, and 0.16 g (1 mmol) of hexamethyldisilyl ether, and 0.38

ml (5 mmol) of trifloroacetic acid was added consecutively. The solution was stirred at 70° overnight and a viscous solution was formed. It was washed with water and methanol. The molecular weight measured with a GPC was Mn=2.54x10^{3}, Mw=2.80x10^{3}, and M (theoretical)=6.7x10^{3}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.058-0.179 (m, H_3C-Si), 4.667-4.699 (m, H-Si). Ratio of integration of H_3C and H-Si was 11 to 1 (theoretically 9 to 1). ^{13}C NMR (75.429 MHz, $CDCl_3$) δ: 0.638-1.241.

Synthesis of poly(dimethylsiloxane-co-methyl-(3-(3′,3′,3″,3″-tetramethyl-3′3″-disila-indeno[2,1-e]indenyl)methoxy)propylsiloxane) (20) To 25 ml of THF in a 100 ml round bottom flask with a magnetic stirrer, 1.07 g of poly(dimethylsiloxane-co-methylsiloxane) and 0.72 g of the 6-allyloxymethyl-3,3,3′,3′-tetramethyl-3,3′-disila-indeno[*2,1-a*]indene were added. Under argon flow, catalytic amount of chloroplatinic acid (CPA) was added. The solution was stirred overnight at 55°C. Then it was washed with water and deposited with methanol. The molecule weight was measured with GPC. Mn=1.3x10^{-4} and Mw=2.2x10^{-4}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.057-0.145 (m, 94H), 0.438 (d, J=1.2 Hz, 8H), 1.339 (q, J=2.7 6H), 1.502 (t, J=7.2), 3.677 (t, J=5.7, 8H), 4.498 (s, 1H), 7.166-7.561 (m, 5H).

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III. SYNTHESIS AND THERMAL AND PHOTOCHEMICAL STUDIES OF 3-METHYLENE-2-SILAOXETANES

A paper to be submitted to the Journal of American Chemical Society

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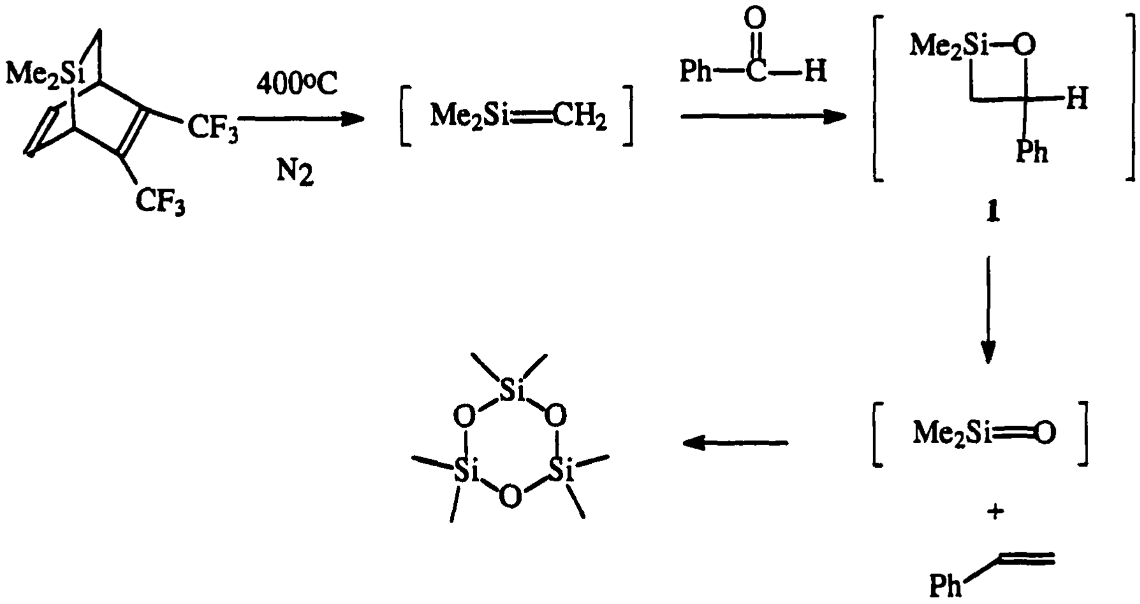
ABSTRACT

A stable 3-methylene-2-silaoxetane molecule was synthesized by the catalytic intramolecular addition of a disilane to an acetylene. Thermochemical and photochemical properties of what is formally the reaction product of silenes and ketenes were determined. The activation energy of decomposition of the 3-methylene-2-silaoxetane into a silanone and an allene was found to be about 49.24±1.91 kcal/mol and Log(A) was 15.37±0.6 s^{-1}. This process was also studied by *ab initio* calculations which showed that the decomposition was a highly non-synchronized concerted process. The four-membered ring system expanded to a five-membered ring photochemically.

1. Introduction

In 1972, Barton and co-workers for the first time suggested that 2-silaoxetane(1) could be an intermediate for the reaction of silenes with ketones (Scheme 1).[1] A year later, Sommer and co-worker offered a similar suggestion.[2] Since then, there has been a great deal of interest in isolating and studying this intermediate.[3-13]

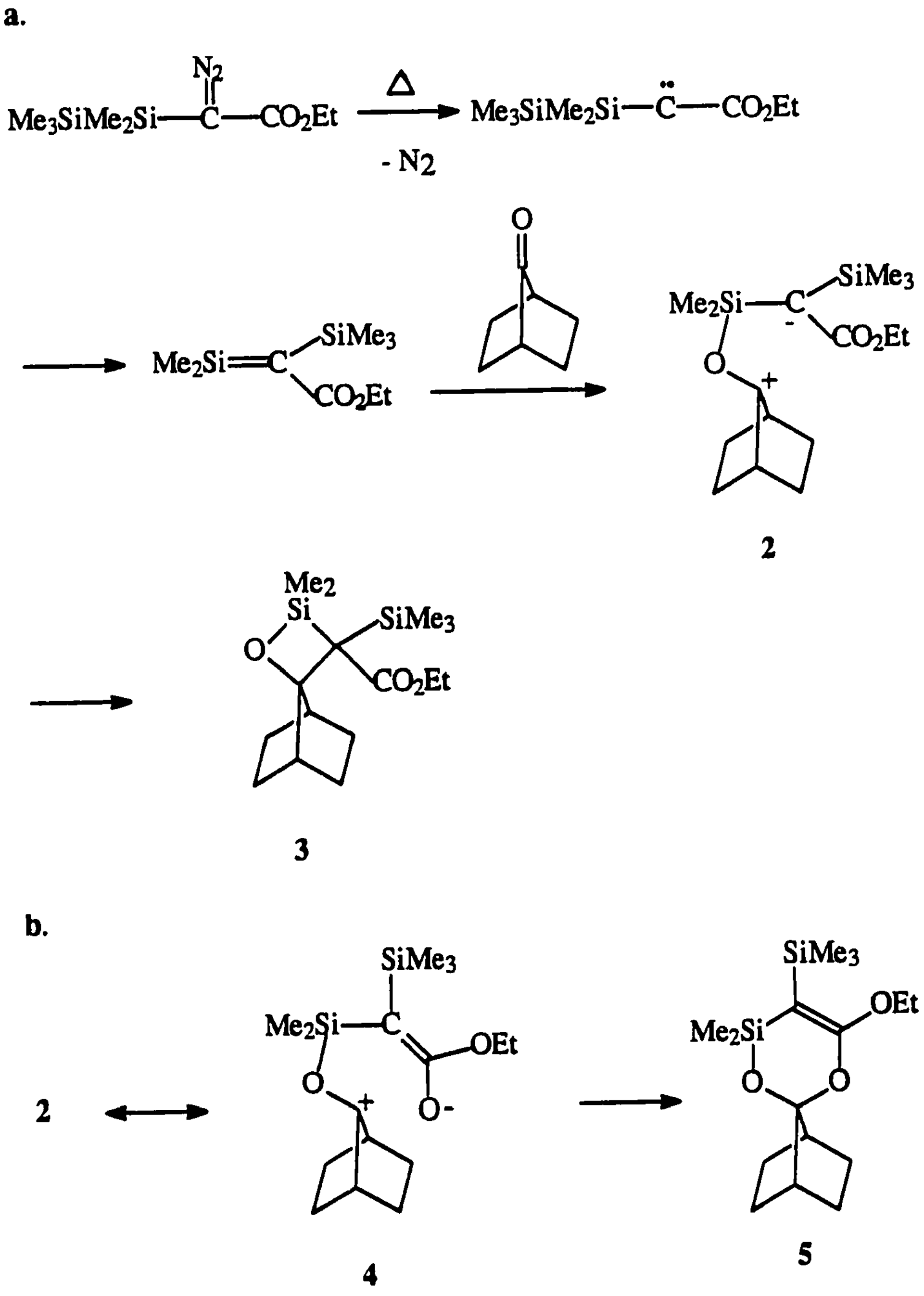
Scheme 1



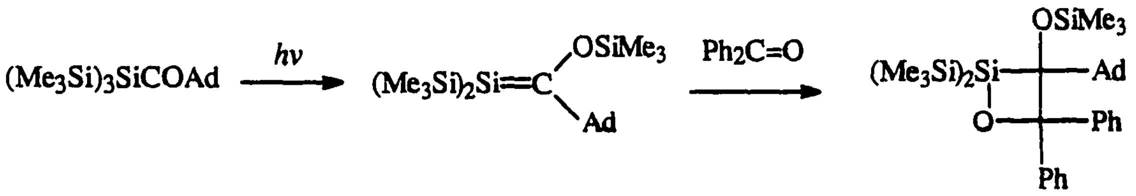
One of the first efforts was by Ando and co-workers in 1982.[7] Ando claimed that the first 2-silaoxetane (3) was isolated by the following procedure (Scheme **2a**). However, the desired product (3) was turned out to be a six-membered ring (5) instead (Scheme **2b**).[10] In 1987, Ando reported the synthesis of another 2-silaoxetane, 3-methylene-2-silaoxetane, by oxidation of alkyldenesilirane.[11] The compound was characterized with the NMR spectroscopy. Because of lack of sufficient support data, it was difficult to convince people that the compound was the one claimed. While a great deal of evidence existed for 2-silaoxetane,[1-9] its isolation remained unattained until 1987 when Brook reported the first crystal structure of a silaoxetane, 2,2-bis(trimethylsilyl)-4,4-diphenyl-3- adamantyl-3-(trimethylsiloxy)-2-silaoxetane[12] (**6**) (Scheme 3). Unfortunately, this small four-membered ring system had huge substitutes which might twist the small ring from its normal conformation and also make it impossible to relate the properties of the molecule to that of the unfettered system. Because **6** is the only 2-silaoxetane which was isolated, there exists a general belief that only sterically hindered 2-silaoxetanes are stable, such as **6**.[13] However, based on *ab initio* calculations, Streittwieser and co-worker concluded that 2-silaoxetane was very stable (50 kcal/ml) compared to its products of decomposition (olefin and silanone).[14]

To explore the thermal and photochemical stability of 2-silaoxetane, it was necessary to synthesize a simpler analog. Here, we have used a catalytic process to successfully synthesize a 2-silaoxetane and isolated it by crystallization. For the first time the decomposition of this kind of compound was studied kinetically. Since Streittwieser's *ab initio* calculations in 1985, the 2-silaoxetanes have not been further studied theoretically. Here, *ab initio* calculations were also carried out to understand the process of thermal decomposition of the molecule, that is, whether the molecule decomposes via a stepwise or concerted process.

Scheme 2


a.
N2
Me3SiMe2Si—C—CO2Et
Δ
- N2
Me3SiMe2Si—C—CO2Et
Me2Si=C
SiMe3
CO2Et
O
Me2Si—C
SiMe3
CO2Et
O
+
-
2
Me2
Si
O
SiMe3
CO2Et
3
b.
2
Me2Si—C
SiMe3
OEt
O
+
O-
4
Me2Si
SiMe3
OEt
O
O
5

Scheme 3



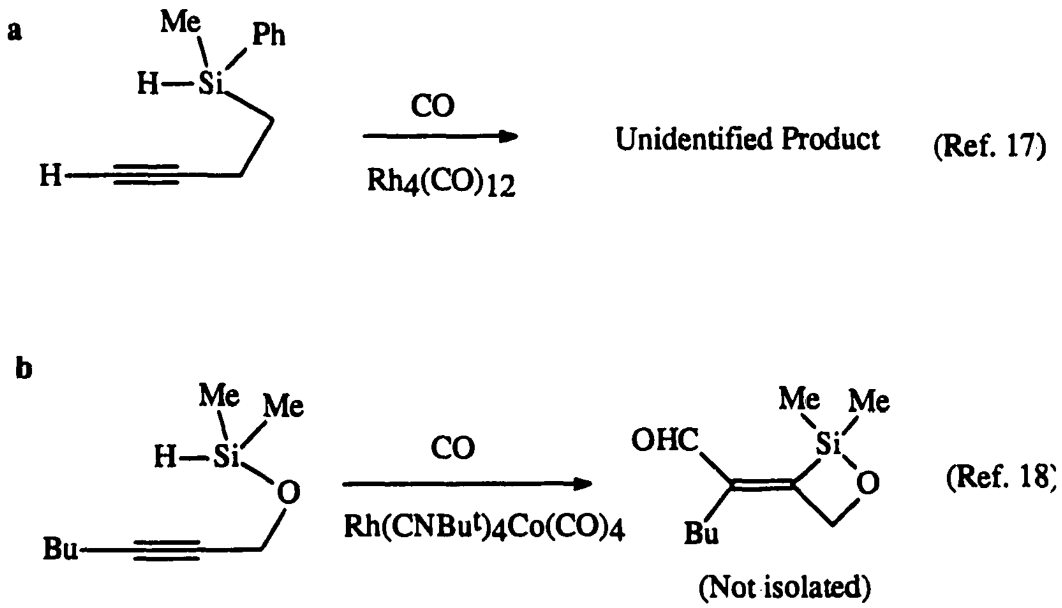
6

Ad = Adamantyl Group

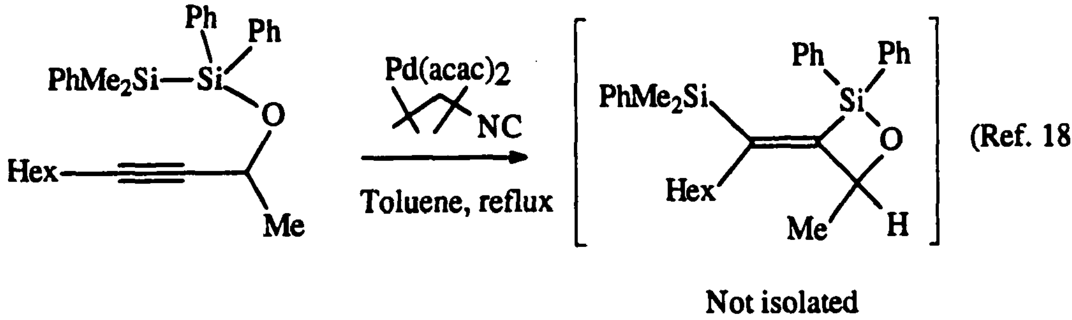
2. Results and Discussion

Catalytic addition reactions of disilanes and hydridosilanes to acetylenes are well known for their high efficiencies and mild requirements.[15,16] However, attempts to synthesize 2-silaoxetanes by intramolecular catalytic additions experienced some difficulties. Matsuda and co-workers first obtained some "complex mixture of unidentified products" (Scheme **4a**),[17] and then they reported they got some "very unstable" product (Scheme **4b**).[18] Ito and coworkers reported that they observed the four-membered ring in the reaction mixture by ^{1}H and ^{13}C NMR but failed to isolate it by chromatography and distillation (Scheme 5).[19] Based on the catalytic intramolecular addition reaction, different substitutes were used in order to synthesize and isolate the 2-silaoxetane. (Scheme 6). (After our work was complete, Ito reported another 2-silaoxetane synthesis in which the starting material and product were very similar to ours. He isolated it with silica gel and confirmed the molecular structure by NMR.)[20]

Scheme 4

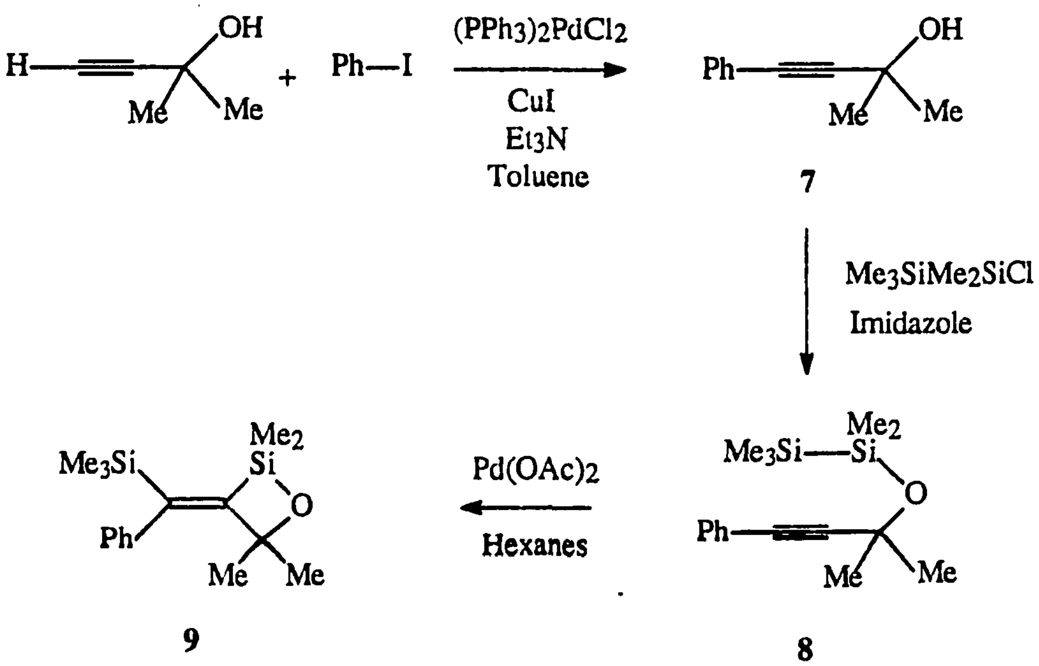


Scheme 5



A 2-silaoxetane (9) was synthesized by the palladium-catalyzed reaction in high yield, which is shown in Scheme 6. Compound 9 is not stable toward chromatography, but could be purified by re-crystallization from hexane. It was characterized with NMR, MS, and X-ray diffraction. The crystal structure is shown in Figure 1 and Tables 1-3. The silaoxetane four-membered ring is planar and it is more strained by the *exo*-π-bond compared to **6**. For **9**, the ^{13}C NMR is very distinguishing. The NMR assignments and comparisons with its precursor are shown in Figure 2. The chemical shifts of the atoms which involve silaoxetane ring formation were changed significantly. The chemical shift of the *endo* methylene carbon in compound **9** is also close to that of 1,1-dimethyl-2-methylene-1-silacyclobutane,[21,22] which has a similar structure (δ164.033 *vs*. 158.50 and 157.11). As mentioned earlier, Ando reported synthesis of a similar compound (**10**) by oxidation of an alkylidenesilirane (Scheme 7), but the reported chemical shift of the *endo* methylene carbon is quite different (δ149.90) (Figure 3).[11] Actually, it is difficult to distinguish it from its isomer (**11**) only by NMR. However, the structures of the compounds reported by Ando were only "confirmed by the NMR."[22] Possibly the structure was not the one the author claimed because the chemical shift of a cycloalkene substituted by a silyl group or other alkyl groups, usually occurs at ca. 5-10 ppm up field relative to exo-methylene systems (Figure 4).[23] Possibly, the molecule Ando synthesized and confirmed with NMR is a sila-oxa-cyclopentene system (**12**) (Figure **5**) instead of a 3-methylene-2-silaoxetane system.

Scheme 6



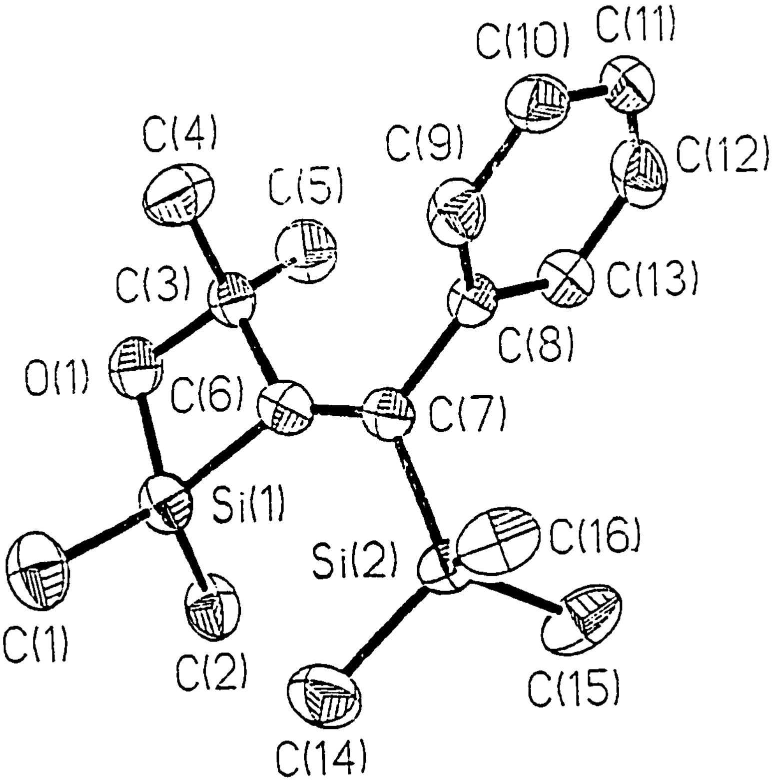


Figure 1. Crystal structure of 2-silaoxetane (**9**)

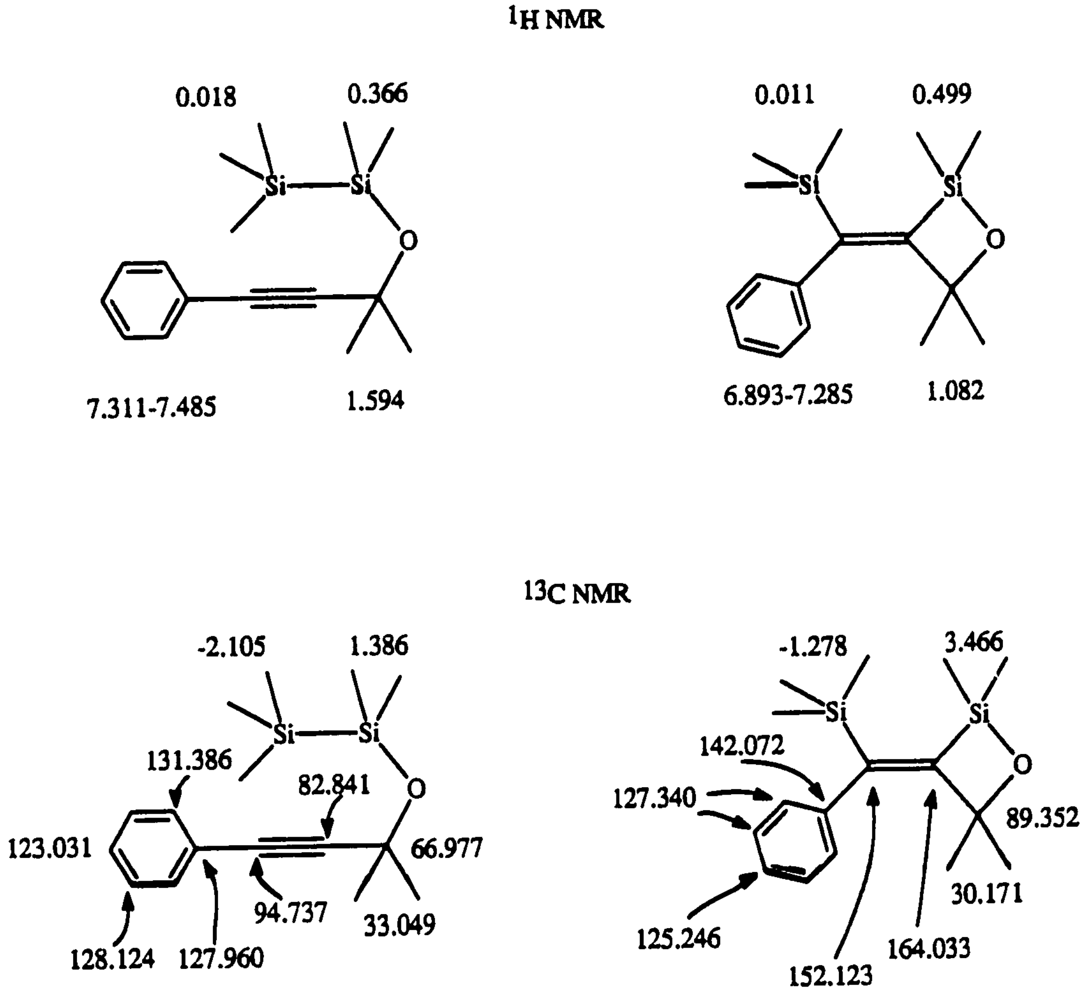
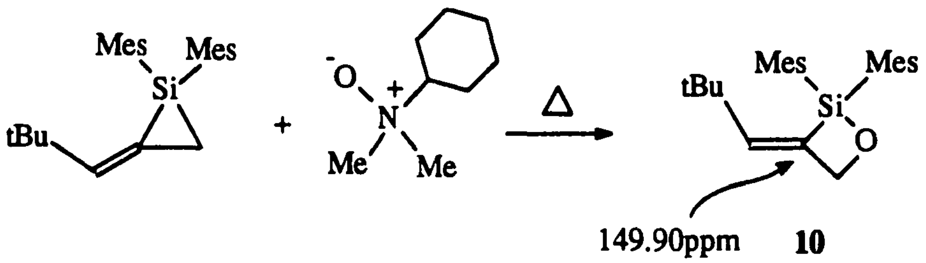


Figure 2. NMR assignments and comparisons between disilane (8) with 2-silaoxetane (9).

Scheme 7



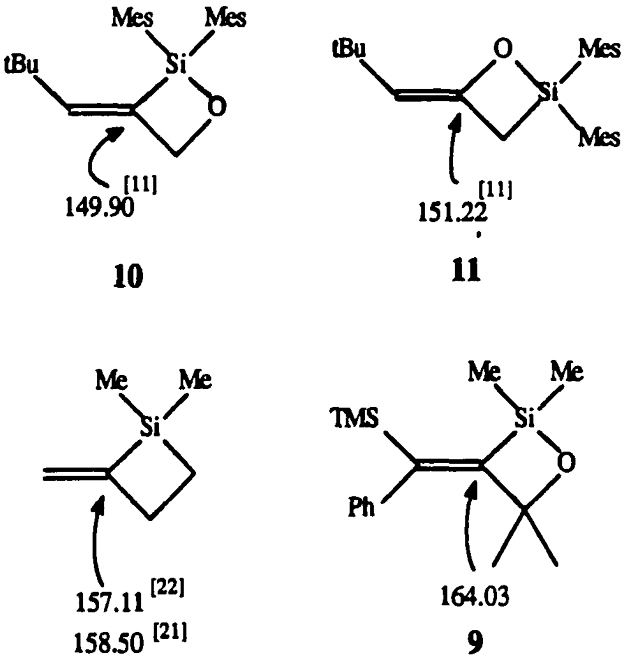


Figure 3. the ^{13}C Chemical shift comparisons between methylene silacyclobuatane with corresponding silaoxetanes

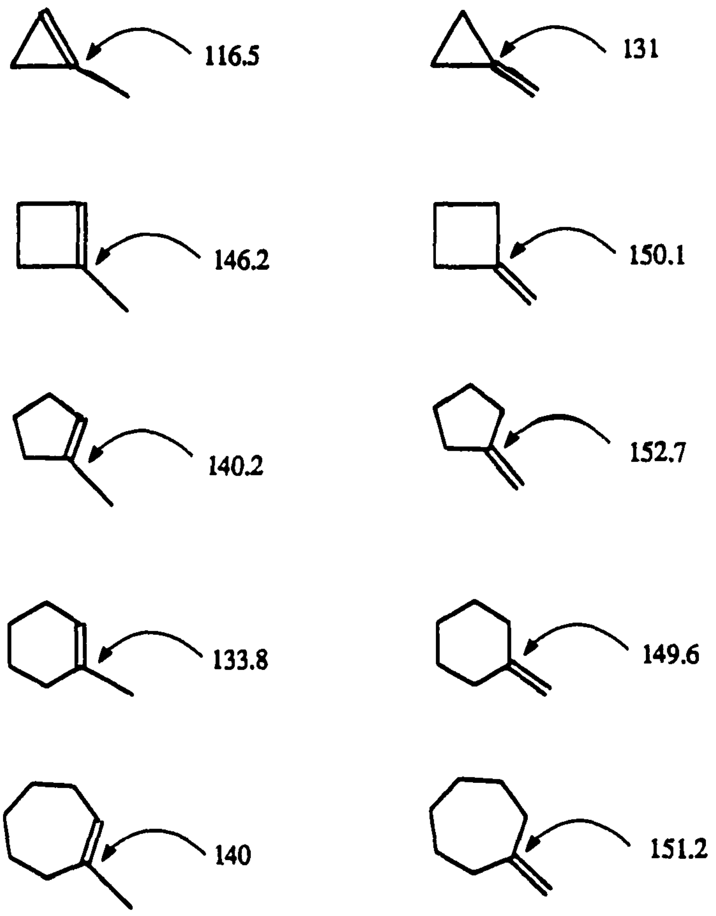
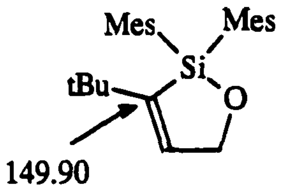


Figure 4. ^{13}C chemical shift (ppm) comparisons for the double bonds in the rings with the double bonds in *exo* positions (Ref 23).



12

Figure 5. Possible structure for **10**.

Table 1. Crystal Data, Measurements, and Structure Refinements for Silaoxetane **9** [a]

Empirical Formula	$C_{16}H_{26}OSi_2$
Crystal System	Orthohombic
Space Group	$P2_12_12$
a	11.829(2) Å
b	26.284(2) Å
c	11.426(10) Å
U	3552.5(32) Å^3
Z	8
Formula Weight	290.55
Density(calc.)	1.086 g/m^3
F(000)	1264
θ	3.36 to 56.76 degree
Standard Reflections	3 measured every 79 reflections
Index Range	$-12 \leq h \leq 0$; $0 \leq k \leq 28$; $-12 \leq l \leq 12$
Reflections Collected	5135
Independent	4754
Structure solution [b]	Direct methods
Refinement Method	Full-matrix least-squares on F^2
Parameter Refined	382
Final R Indices [c]	R1 = 0.0710, wR2 = 0.1701
Max Δ/σ	0.000
Max peak final ΔF	0.430 e/Å^3

[a] Siemens P4RA diffractometer was used; θ-2θ scan type; Cu Kα radiation (λ = 1.54178Å; Graphite Monochromator; T = 213(1) K. [b] Refinement calculations were performed on a Digital Equipment MicroVAX 3100 computer using SHELXTL-Plus and SHELXL-93. All X-ray scattering factors and anomalous dispersion terms were obtained from the "International tables for Crystallography", Vol. C. [c] $R1 = \Sigma \,||Fo| - |Fc|| / \Sigma |Fo|$. $wR2 = [\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]]^{0.5}$, where $w = 1 / [\sigma^2(Fo^2) + (a * P)^2 + b * P + d + e * \sin \theta]$.

Table 2. Atomic Coordinates for 2-silaoxetane 9

Atom	x	y	z
Si (1)	0.2353(2)	-0.1071(1)	0.6666(1)
C (1)	0.1052(6)	-0.1007(3)	0.7568(7)
C (2)	0.3633(6)	-0.0948(3)	0.7524(7)
O (1)	0.2420(4)	-0.1623(1)	0.5941(3)
C (3)	0.2424(5)	-0.1396(2)	0.4752(5)
C (4)	0.1389(6)	-0.1588(3)	0.4097(7)
C (5)	0.3519(6)	-0.1562(3)	0.4163(7)
C (6)	0.2370(5)	-0.0835(2)	0.5121(5)
C (7)	0.2385(5)	-0.0408(2)	0.4465(5)
C (8)	0.2489(5)	-0.0432(2)	0.3150(5)
C (9)	0.1525(6)	-0.0455(3)	0.2437(6)
C (10)	0.1646(7)	-0.0474(3)	0.1230(7)
C (11)	0.2689(7)	-0.0476(2)	0.0712(6)
C (12)	0.3627(6)	-0.0449(3)	0.1396(7)
C (13)	0.3533(6)	-0.0420(2)	0.2612(6)
Si (2)	0.2333(2)	0.0250(1)	0.5110(1)
C (14)	0.1883(7)	0.0251(3)	0.6670(6)
C (15)	0.3739(6)	0.0544(3)	0.4989(8)
C (16)	0.1283(6)	0.0639(3)	0.4310(7)

Table 3. Bond Lengths (Å) and Angles (deg) for 2-silaoxetane 9

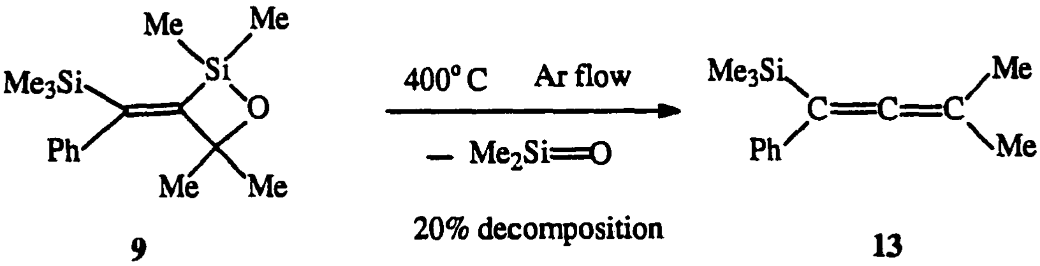
Bond Lengths			
Si(1)-O(1)	1.671(4)	Si(1)-C(2)	1.833(7)
Si(1)-C(1)	1.860(7)	Si(1)-C(6)	1.871(6)
Si(1)-C(3)	2.349(6)	O(1)-C(3)	1.485(6)
C(3)-C(4)	1.521(9)	C(3)-C(5)	1.524(9)
C(3)-C(6)	1.535(7)	C(6)-C(7)	1.349(8)
C(7)-C(8)	1.508(7)	C(7)-Si(2)	1.882(6)
C(8)-C(13)	1.379(9)	C(8)-C(9)	1.403(9)
C(9)-C(10)	1.387(10)	C(10)-C(11)	1.369(10)
C(11)-C(12)	1.359(10)	C(12)-C(13)	1.397(10)
Si(2)-C(15)	1.839(7)	Si(2)-C(16)	1.850(7)
Si(2)-C(14)	1.860(7)		
Bond Angles			
O(1)-Si(1)-C(2)	112.3(3)	O(1)-C(3)-C(4)	108.3(5)
O(1)-Si(1)-C(1)	113.1(3)	O(1)-C(3)-C(5)	106.9(5)
O(1)-Si(1)-C(6)	79.7(2)	O(1)-C(3)-C(6)	97.7(4)
O(1)-Si(1)-C(3)	38.9(2)	O(1)-C(3)-Si(1)	45.0(2)
C(2)-Si(1)-C(1)	111.8(3)	C(4)-C(3)-C(5)	111.8(5)
C(2)-Si(1)-C(6)	115.9(3)	C(4)-C(3)-C(6)	115.0(5)
C(2)-Si(1)-C(3)	122.2(3)	C(4)-C(3)-Si(1)	123.4(5)
C(1)-Si(1)-C(6)	120.1(3)	C(5)-C(3)-C(6)	115.6(5)
C(1)-Si(1)-C(3)	125.4(4)	C(5)-C(3)-Si(1)	123.1(5)
C(6)-Si(1)-C(3)	40.7(2)	C(6)-C(3)-Si(1)	52.7(3)
C(3)-O(1)-Si(1)	96.0(3)	C(6)-C(7)-C(8)	121.4(5)
C(7)-C(6)-C(3)	130.1(5)	C(6)-C(7)-Si(2)	123.1(4)
C(7)-C(6)-Si(1)	143.2(4)	C(8)-C(7)-Si(2)	115.5(4)
C(3)-C(6)-Si(1)	86.6(3)	C(13)-C(8)-Si(9)	118.0(5)
C(10)-C(9)-C(8)	119.7(6)	C(13)-C(8)-C(7)	121.0(5)

Table 3. (Continued).

C(11)-C(10)-C(9)	121.5(7)	C(9)-C(8)-C(7)	120.9(5)
C(12)-C(11)-C(10)	119.2(6)	C(16)-Si(2)-C(14)	106.3(4)
C(11)-C(12)-C(13)	120.6(7)	C(15)-Si(2)-C(7)	109.1(3)
C(8)-C(13)-C(12)	120.9(7)	C(16)-Si(2)-C(7)	109.7(3)
C(15)-Si(2)-C(16)	109.7(4)	C(14)-Si(2)-C(7)	112.7(3)
C(15)-Si(2)-C(14)	109.3(4)		

The first kinetic decomposition study of a 2-silaoxetane was carried out to evaluate its stability and to understand the mechanism of decomposition. The gas-phase reaction was performed using a stirred flow reactor (SFR) system using helium as carrier gas.[24,25] (Note: after we noted that the decomposition of **9** in GC depended on the contamination on the GC column, a new column was used for the GC analysis and decomposition on GC column was less than 1 %.) The kinetic constants are given in Table **4**. The activation energy *E*a was found to be about 49 Kcal/mol (shown in Figure **6** and Scheme 7). The molecule is thermally much more stable than often suggested in the literature, and no significant decomposition was observed below 350°C.

Scheme 7



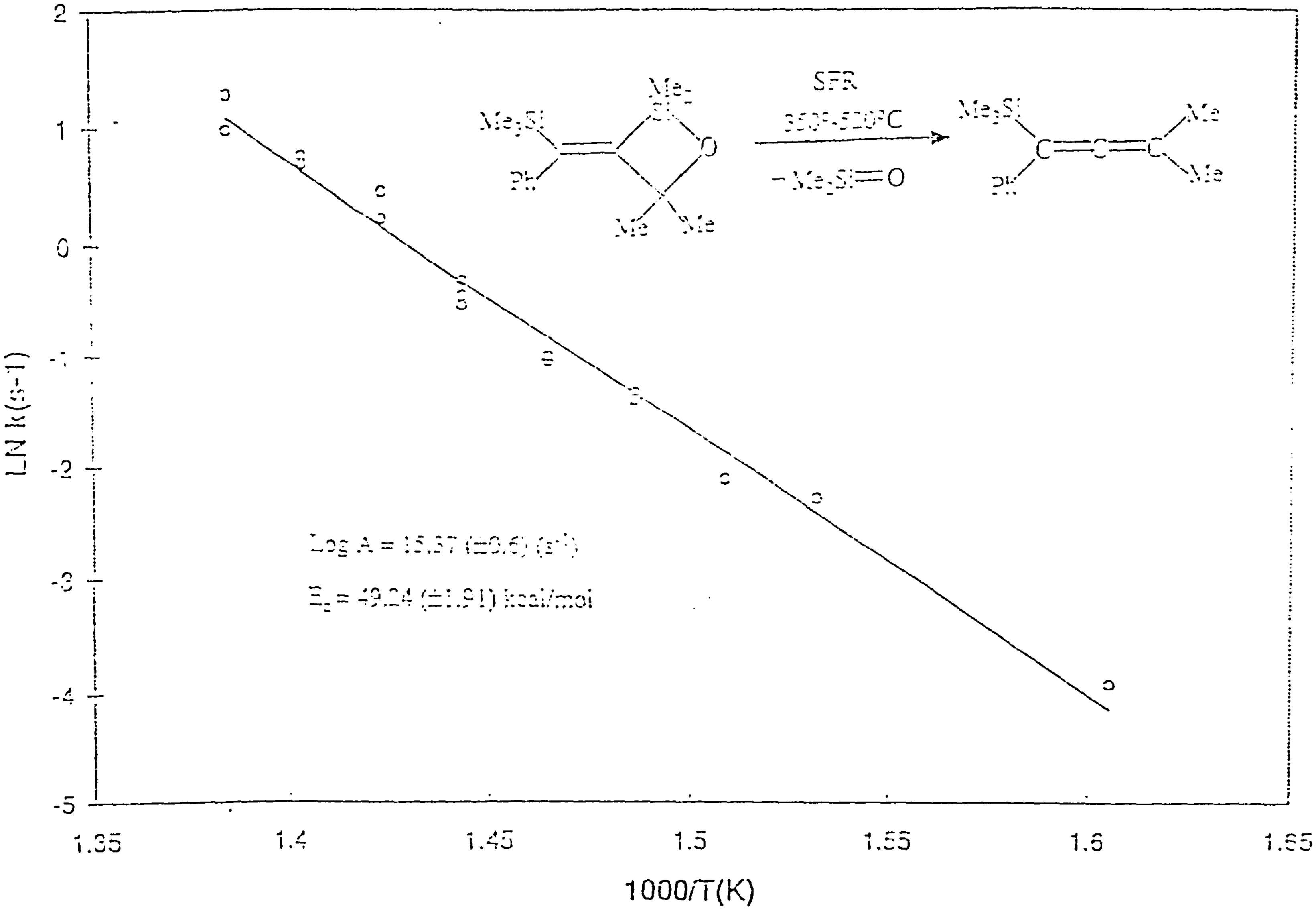


Figure 6. Kinetics of the decomposition of 2-silaoxetane **9**.

For the decomposition of 9, the activation entropy S^* from the kinetics experiment was 8.15, suggesting that the reaction is close to a stepwise ring-opening process. If the ring does not completely open to a 1,4-diradical intermediate, it comes very close to it.

Calculations based on *ab initio* methods were carried out for the decomposition processes of silaoxetane. Figure 7 shows the structures of model molecules, which were done with RHF/6-31G(d).[26] The transition state of the decomposition was also found with the same calculation level. It is interesting to note that the oxygen-carbon bond length increases about 0.74 Å from 1.434 Å in the starting material to 2.174 Å in the transition state, while the silicon-carbon bond length only increased by about one third (0.27 Å). At the same time, the carbon-silicon-oxygen angle increases from 80° to 97°. At the transition state, the interaction between oxygen (O1) and carbon (C4) is very weak, and the oxygen atom has lone-pair character. The intrinsic reaction coordinate (IRC) calculation was carried out to study the entire reaction path. The results are shown in Figure 8. As the reaction proceeds the carbon-oxygen bond length increases much faster than any other bond in the molecule. The breaking rate (slope in the Figure) of the silicon-carbon bond significantly increases after the transition state (reaction coordinate number 7). Thus, the process is very close to a stepwise process, or a highly non-synchronized concerted process. This is consistent with what was found experimentally.

Vibrational analysis was carried out for the starting material, products and the transition state. The zero point vibrational energies, entropies and enthalpies were calculated at 298.15 K. The electron correlation energies were calculated at Mϕller-Plesset fourth order perturbation theory with 6-31G(d) basis set (MP4/6-31G(d)), which includes single, double, triple and quadruple excitations in the perturbation correction. All results are shown in Table 5 and 6. Electron correlation significantly reduces the barrier of the process by about 7 Kcal/mol. The zero point energy correction also reduces the barrier by about 2 Kcal/mol. As a whole, the calculated activation enthalpy ($\Delta H^{\neq}$) of the process is 38.34 Kcal/mol, which is significantly lower than the experimental value (49.24 Kcal/mol) probably because there is no exo-ethylene group in the model molecule.

Table 5. Total energies for 2-silaoxetane, transition state and products (a.u.)

Method	2-silaoxetane	Transition state	Ethylene	Silanone
RHF/6-31G(d)	-521.107476	-521.031867	-78.031718	-443.019543
MP4SDTQ/6-31G(d)	-521.971383	-521.907121	-78.318697	-443.602774
Zero point Energy	0.142947	0.139798	0.054773	0.081800

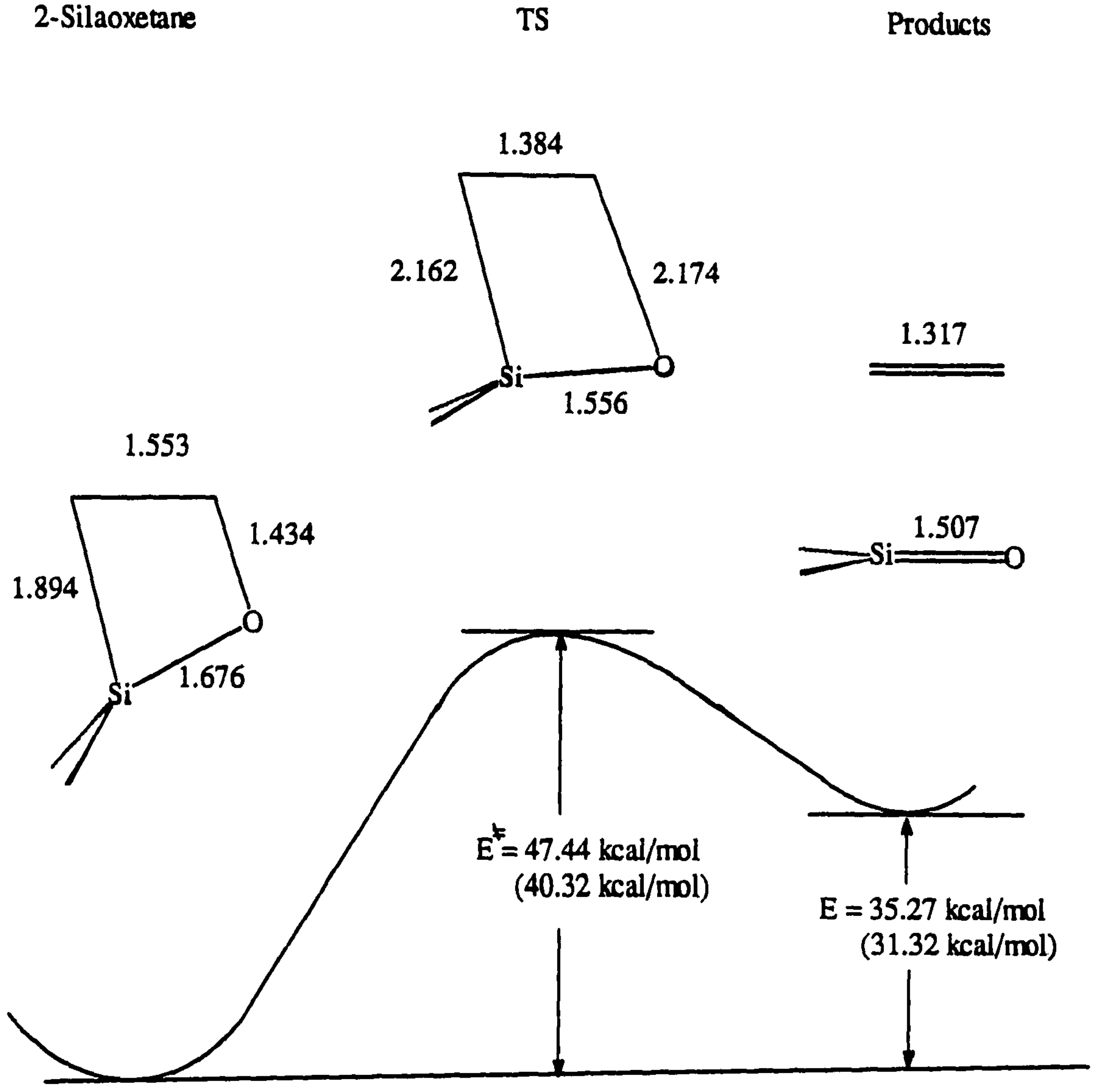


Figure 7. The optimized geometries calculated by using RHF/6-31G(d) and relative energies calculated with RHF/6-31G(d) and with MP4SDTQ/6-31G(d) (in parenthesis)

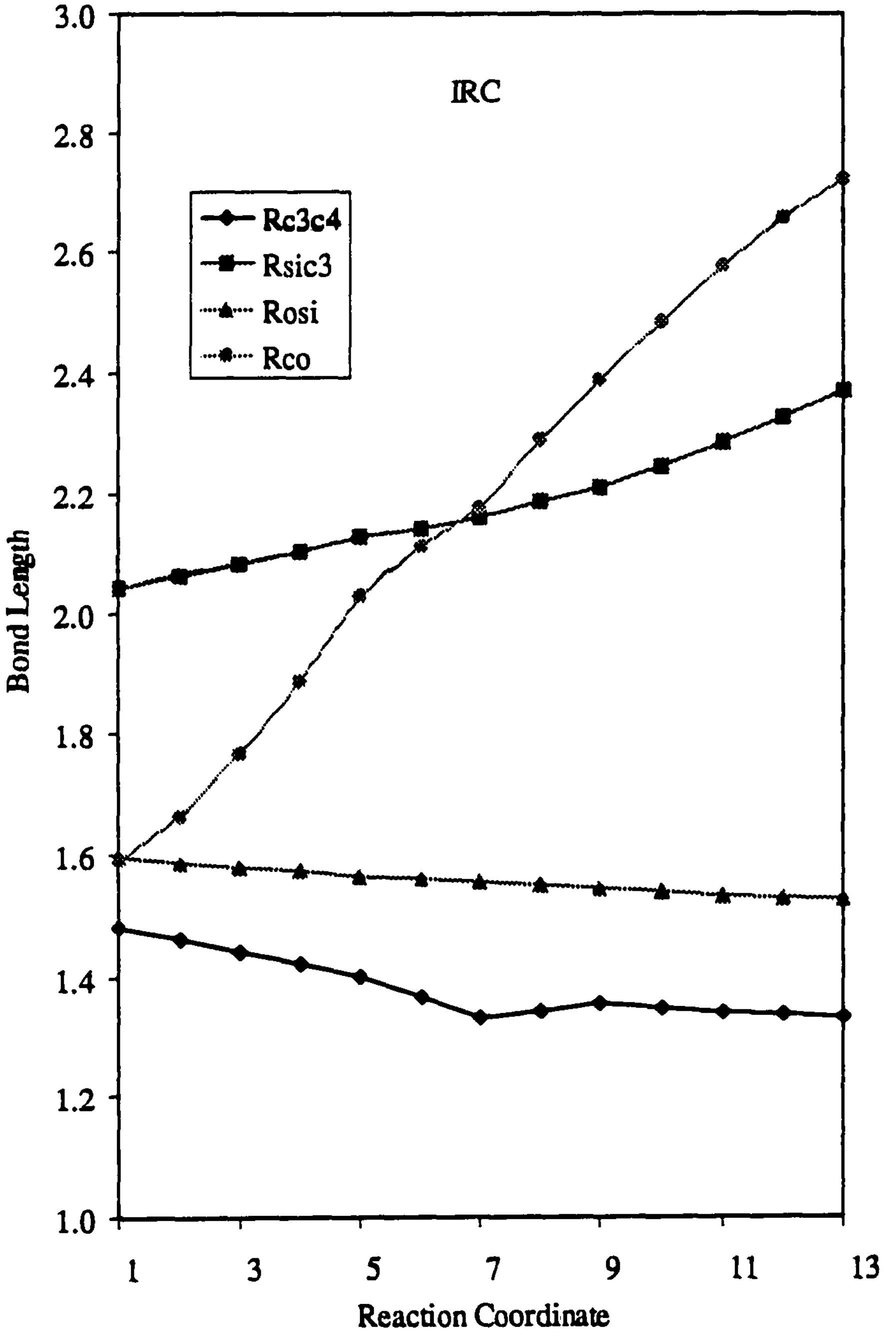


Figure 8. The bond length changes as the reaction proceeds from starting material to product at transition state (point 7) vicinity using IRC method

Table 6. Relative Energies and Enthalpies and Entropies (at 298.15 K and 1.0 atm)

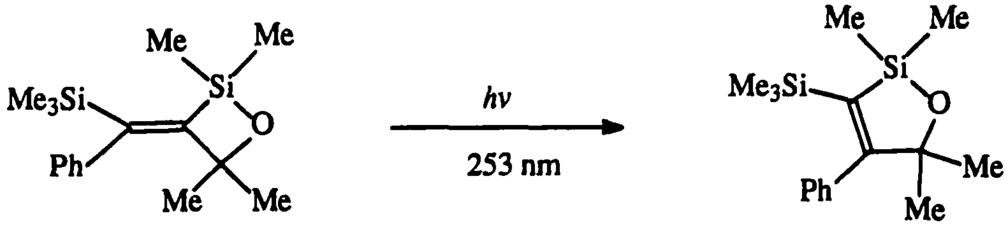
Properties	2-Silaoxetane	Transition State	Product
ΔE (Kcal/mol) (RHF/6-31G(d))	0.0	47.44	35.27
ΔE (Kcal/mol) (MP4(SDTQ))	0.0	40.32	31.32
ΔH (Kcal/mol) (RHF/6-31G(d))	0.0	45.46	31.27
ΔH (Kcal/mol) (MP4(SDTQ))	0.0	38.34	27.32
ΔS (Cal/mol*K)	0.0	0.42	48.35

At a relatively low level, RHF/3-21G, Streitwieser and co-workers found that the products were 50 Kcal/mol of energy higher than the 2-silaoxetane. At the higher calculation level of RHF/6-31G(d), also including the electron correlation and zero-point energy corrections, the enthalpy (Δ*H*) is 27.32 Kcal/mol. That is, the 2-silaoxetane molecule is not as stable as Streittwieser predicted, but it is still a fairly stable molecule.

The photochemical stability of the 2-silaoxetane was also studied with the surprising result that ring expansion produced the five-membered ring (**14**) (Scheme **8**). The X-ray structure of **14** is shown in Figure **9** and Table **7-9**. Instead of a 1,2-shift of silicon, the phenyl group migrated. Two possible mechanisms are proposed. One is that the silicon in the ring shifts to produce a carbene (**15**), followed by 1,2-phenyl shift

(Scheme **9a**). However, for β-carbenes, the shift of silyl-group is preferred rather than phenyl group migration. Another possible mechanism (Scheme **9b**) is that a 90° twist around the double bond occurs as usual to release energy when the olefin absorbs a photon, and a three-membered ring is formed. Then silicon is shifted and the ring is expanded. As part of the chromophore, the phenyl group absorbs the energy and participates in the rearrangement first. This also avoids the conflicts with the preference of silyl group over phenyl group in the 1,2-shift processes.

Scheme 8

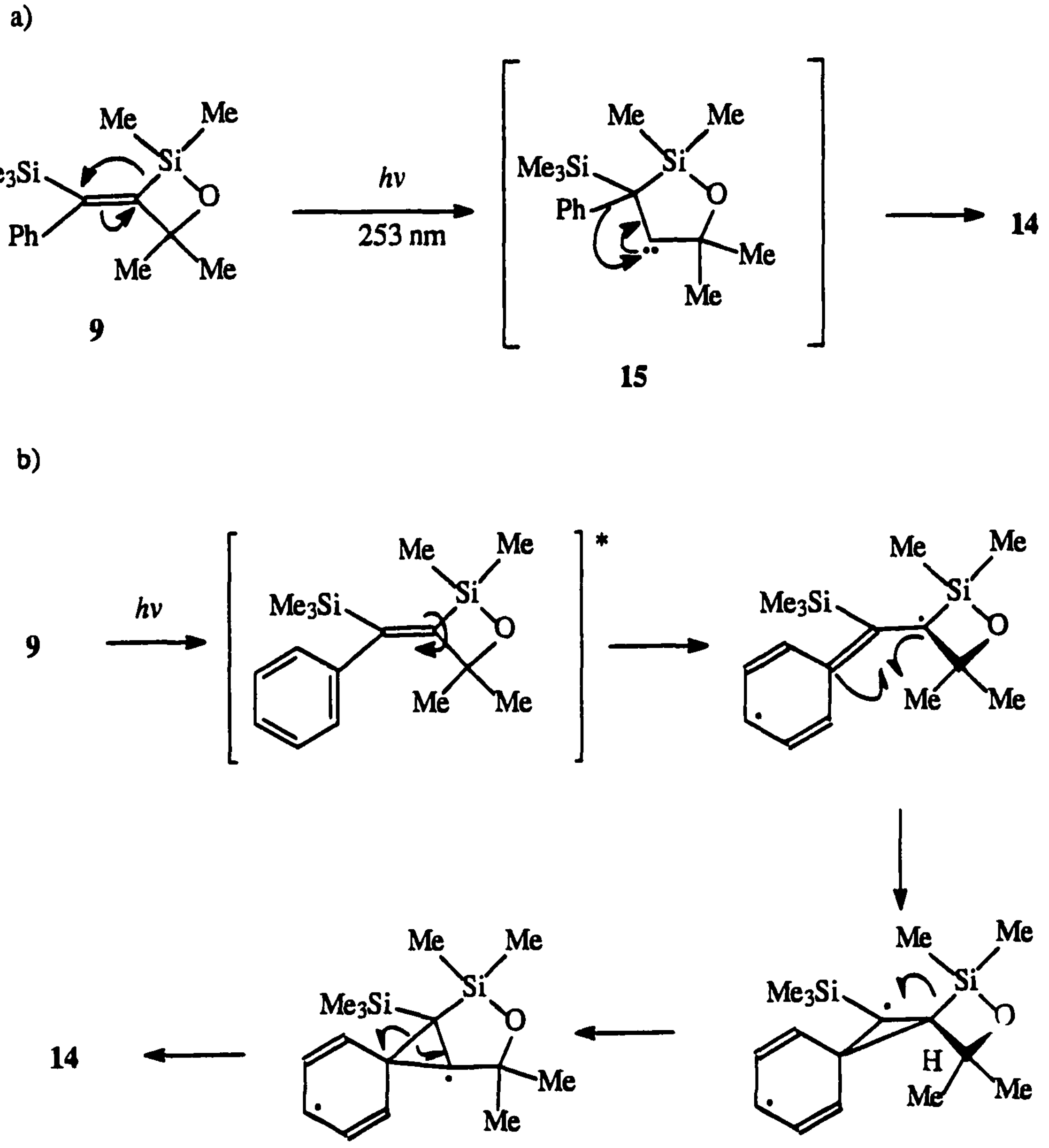


9 **14**

3. Conclusion

A 2-silaoxetane, which is a well-known intermediate of silylenes reacting with ketones, was synthesized with a palladium-catalyzed disilane addition to acetylene. A kinetic study shows that the 2-silaoxetane molecule is thermally fairly stable (*E*a = 49.24 kcal/mol), which is different from the popular conception that this intermediate is not thermally stable. A theoretical study with RHF/6-31G(d) and MP4 found that the decomposition process is a highly non-synchronized concerted process. The molecule underwent ring-expansion photochemically with 1,2-phenyl migration instead of the silyl group, which was unusual.

Scheme 9



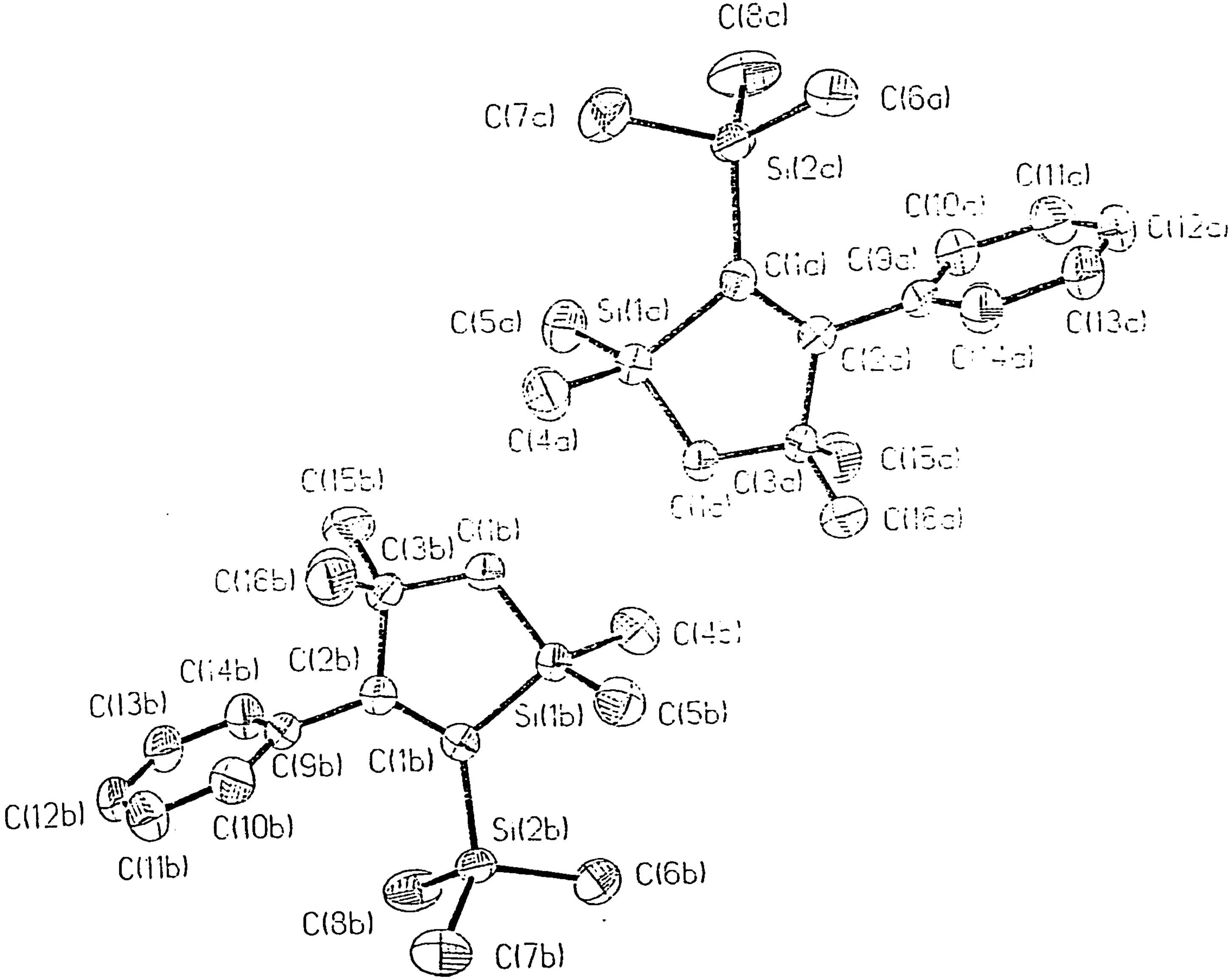


Figure 9. The crystal structure of molecule 14

Table 5. Crystal Data, Measurements, and Structure Refinements for molecule **14** [a]

Empirical Formula	$C_{16}H_{26}OSi_2$
Crystal System	Monoclinic
Space Group	C2/c
a	27.093(5) Å
b	11.120(10) Å
c	26.971(3) Å
β	119.770(10)°
U	7053.3(16) Å^3
Z	16
Formula Weight	290.55
Density(calc.)	1.094 g/m^3
F(000)	2528
θ	3.76 to 56.75 degree
Standard Reflections	3 measured every 97 reflections
Index Range	$-1 \le h \le 29$; $-1 \le k \le 12$; $-29 \le l \le 25$
Reflections Collected	5710
Independent reflections	4706
Structure solution [b]	Direct methods
Refinement Method	Full-matrix least-squares on F^2
Parameter Refined	344
Final R Indices [c]	R1 = 0.0416, wR2 = 0.1123
Max Δ/σ	0.000
Max peak final ΔF	0.284 e/Å^3

[a] Siemens P4RA diffractometer was used; θ-2θ scan type; Cu Kα radiation (λ = 1.54178Å; Graphite Monochromator; T = 213(2) K. [b] see note b in Table 1. [c] See note c in Table 1.

Table 6. Atomic Coordinates for molecule **14**

Atom	x	y	z
Si (1)	0.1300(1)	0.7900(1)	0.0721(1)
Si (2)	0.1404(1)	0.9273(1)	0.1880(1)
O (1)	0.1235(1)	0.8751(1)	0.0172(1)
C (1)	0.1352(4)	0.9287(2)	0.1162(1)
C (2)	0.1307(1)	1.0259(2)	0.0841(1)
C (3)	0.1241(1)	1.0031(2)	0.0247(1)
C (4)	0.1945(1)	0.6988(2)	0.1009(1)
C (5)	0.0660(1)	0.7028(2)	0.0508(1)
C (6)	0.1877(1)	1.0458(2)	0.2374(1)
C (7)	0.1706(1)	0.7787(3)	0.2213(1)
C (8)	0.0678(1)	0.9411(3)	0.1782(1)
C (9)	0.1300(1)	1.1538(2)	0.1009(1)
C (10)	0.0796(1)	1.2075(2)	0.0909(1)
C (11)	0.0789(1)	1.3263(2)	0.1063(1)
C (12)	0.1283(1)	1.3614(2)	0.1325(1)
C (13)	0.1785(1)	1.3404(2)	0.1431(1)
C (14)	0.1794(1)	1.2218(2)	0.1273(1)
C (15)	0.0681(1)	1.0530(2)	-0.0224(1)
C (16)	0.1742(1)	1.0538(2)	0.0209(1)

Table 7. Bond Lengths (Å) and Angles (deg) for **14**

Bond Lengths			
Si(1)-O(1)	1.655(2)	Si(1)-C(4)	1.845(3)
Si(1)-C(5)	1.850(3)	Si(1)-C(1)	1.857(2)
Si(2)-C(8)	1.856(3)	Si(2)-C(6)	1.859(3)
Si(2)-C(7)	1.865(3)	Si(2)-C(1)	1.870(2)
O(1)-C(3)	1.437(3)	C(1)-C(2)	1.351(3)
C(2)-C(9)	1.495(3)	C(2)-C(3)	1.544(3)
C(3)-C(15)	1.519(4)	C(3)-C(16)	1.520(3)
C(9)-C(10)	1.388(3)	C(9)-C(14)	1.388(3)
C(10)-C(11)	1.388(3)	C(11)-C(12)	1.370(4)
C(12)-C(13)	1.364(4)	C(13)-C(14)	1.390(3)
Bond Angles			
O(1)-Si(1)-C(4)	110.57(11)	O(1)-C(3)-C(15)	107.9(2)
O(1)-Si(1)-C(5)	110.72(11)	O(1)-C(3)-C(16)	107.8(2)
O(1)-Si(1)-C(1)	95.22(9)	O(1)-C(3)-C(2)	107.2(2)
C(4)-Si(1)-C(5)	109.69(12)	C(15)-C(3)-C(16)	111.4(2)
C(4)-Si(1)-C(1)	115.89(11)	C(15)-C(3)-C(2)	111.1(2)
C(5)-Si(1)-C(1)	113.94(12)	C(16)-C(3)-C(2)	111.3(2)
C(8)-Si(2)-C(6)	110.27(14)	C(10)-C(9)-C(14)	118.0(2)
C(8)-Si(2)-C(7)	108.8(2)	C(10)-C(9)-C(2)	120.6(2)
C(8)-Si(2)-C(1)	108.84(12)	C(14)-C(9)-C(2)	121.3(2)
C(6)-Si(2)-C(7)	107.54(13)	C(11)-C(10)-C(9)	120.7(2)
C(6)-Si(2)-C(1)	114.02(11)	C(12)-C(11)-C(10)	120.1(3)
C(7)-Si(2)-C(1)	107.22(11)	C(13)-C(12)-C(11)	120.3(2)
C(3)-O(1)-Si(1)	114.39(13)	C(12)-C(13)-C(14)	119.9(3)
C(2)-C(1)-Si(1)	105.8(2)	C(9)-C(14)-C(13)	121.0(3)
C(2)-C(1)-Si(2)	127.3(2)	C(1)-C(2)-C(9)	125.4(2)
Si(1)-C(1)-Si(2)	126.84(12)	C(1)-C(2)-C(3)	117.4(2)

4. Experimental

General Procedures. ^{1}H and ^{13}C NMR spectra were acquired on a Varian VXR-300 spectrometer. In order to assure the quantitation of the ^{13}C NMR spectra, the relaxation agent chromium (III) acetylacetonate was added in $CDCl_3$ with a relaxation delay of 5 seconds.

Exact masses were obtained from a Kratos MS 50 mass spectrometer with 10,000 resolution. The infrared spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer from neat sample. The UV/Vis spectra were obtained on a Hewlett Packard 8452A diode array UV/Vis spectrometer. Reactions were monitored by Hewlett Packard 5890 series II GC and Hewlett Packard tendem GC-IR-MS (5890A GC-5965A IR-5970 Series MS) parallel connected.

THF was distilled over sodium-benzophenone and ether was distilled over CaH_2 right before use. Other reagents were used as received from Aldrich or Fisher Chemical Co. without further purification unless specified otherwise.

3,3,5,5,6,6-hexamethyl-1-phenyl-5,6-disila-4-oxa-1-heptyne (**8**). To a dry 250ml round bottom flask flushed with argon, 100ml of toluene, 5.60ml (50mmol, 10.20g) of iodobenzene and 7.25ml (75mol, 6.3g) of 2-methyl-3-butyn-2-ol were added to the solution. Under an argon atmosphere, 351mg (1%) of $(PPh_3)_2PdCl_2$ and 191mg (2%) of CuI were added to the solution. Then, 20.8ml of triethylamine was injected into the solution, which was then stirred overnight at room temperature. The reaction mixture was slowly added to a 500ml round flask containing 200ml of aq saturated NaCl. It was extracted twice with 100ml Et_2O. The combined organic layer was washed with water and dried over sodium sulfate. After removing the solvent, and drying under vacuum overnight, 7.95g of 2-phenylethynyl-propan-2-ol (7) was obtained.

Dry compound 7 was dissolved in 100 ml of dry THF in a 250ml round bottom flask and then 8.33g (50mmol) of chloropentamethyldisilane was injected into the solution. Under argon, 6.8g (100mmol) of imidazole was added to the solution which then was stirred overnight at room temperature. The reaction solution was poured into a 200ml aq saturated NaCl and then was extracted with 150ml Et_2O and dried over $NaSO_4$. After removing the solvent, the product was purified by silica flash column chromatography with hexane and ethyl acetate (20:1) as eluent. The compound **8**, 3,3,5,5,6,6-hexamethyl-1-phenyl-5,6-disila-4-oxa-1-heptyne was obtained as a pale liquid (13.80g, yield 95%). ^1H NMR δ 0.018 (9H, s), 0.366 (6H, s), 1.594 (6H, s), 7.311-7.485 (5H). ^{13}C NMR δ -2.105 (3C), 1.386 (2C), 33.049 (2C), 66.977 (1C), 82.841 (1C), 94.737(1C), 123.031 (1C), 127.960 (1C), 128.124 (2C), 131.386 (2C). Mass spectrum: 275 (4, M^+-15), 217 (29), 159 (32), 147 (100, base), 77 (5), 75 (23), 73 (47). Exact mass 290.15241 (calc. for $C_{16}H_{26}OSi_2$ 290.15222).

Chloropentamethyldisilane.[27] Chloropentamethyldisilane was synthesized according to Sakurai's procedure,[27] and the experimental details was given in part I of the thesis.

2,2,4,4-tetramethyl-3-((*Z*)-phenyltrimethylsilyl)methylene-2-silaoxetane (9). To 20ml of hexanes in a 50ml round bottom flask, 0.58g (2mmol) of compound **8** was added. Under argon flow, 5mg (1%, 20μmol) of $Pd(OAc)_2$ and 46mg (15%, 300μmol) of

1,1,3,3-tetramethyl-*n*-butyl isocyanide were added to the solution. The solution was stirred overnight at room temperature. After washing with water twice and removing the solvent, **9** was obtained by recrystallization from hexanes. The melting point was 102.5°C. ^{1}H NMR δ 0.011 (9H, s), 0.499 (6H, s), 1.082 (6H, s), 6.893-7.285 (5H, mutiple). ^{13}C NMR δ -1.278 (3C), 3.466 (2C), 30.171 (2C), 89.352 (1C), 125.246 (1C), 127.340 (4C), 142.072 (1C), 152.123 (1C), 164.033 (1C). Mass spectrum: 290 (22, M$^+$), 277 (18), 276 (47), 275 (96), 233 (21), 232 (71), 219 (25), 218 (64), 217 (100. base), 160 (23), 159 (92), 158 (24), 147 (37), 143 (41), 73 (50). Exact mass 290.15147 (calc. for $C_{16}H_{26}OSi_2$ 290.15222). The X-ray data are shown in table **1-3**.

Kinetics of decomposition of 9. 2.9mg (10μmol) of **9** was dissolved in the 1ml of hexanes (0.01M). The Stirred Flow Reactor (SFR) was carried out according to the literature.[24, 25] The reactor volume was 4 cm^3, the flow rate was 102ml/min, and the vapor pressure was 20 psi. The reaction was carried out from 250 through 450°C.

Table 4. Kinetic data for decomposition of compound **9**

Temperature (Celsius)	k (s^{-1})
350	0.0198
380	0.1018
390	0.1208
400	0.2619
400	0.2455
410	0.3489
410	0.3649
420	0.6316
420	0.5793
420	0.7256
430	1.2365
430	1.5568
440	2.1041
440	1.9590
450	2.6237
450	3.5644

3-methyl-1-phenyl-1-trimethylsilyl-buta-1,2-diene (13). Compound **9** decomposed on a silica column, and **13** was obtained at quantitative yield. ^{1}H NMR (300 MHz) δ 0.244 (s, 9H), 1.797 (s, 6H), 7.179-7.333 (m, 5H). ^{13}C NMR δ -0.594 (3C), 19.330 (2C), 90.720 (1C), 98.092 (1C), 125.339 (1C), 127.305 (2C), 127.896 (2C), 138.432 (1C), 207.243 (1C). Mass spectrum: *z/m* 216 (13), 201 (2), 143 (10), 128 (26), 115 (17), 73 (100, base).

1-Phenyl-2-trimethylsilyl-3,3,5,5-tetramethyl-4-oxa-3-sila-cyclolpentene (14). 290mg (0.01M) of compound **9** was dissolved in 100ml of hexanes in a quartz tube. Argon was bubbled through the solution for half an hour to remove dissolved gases. The solution was radiated at 254nm in a Rayonet photochemical reactor equipped with sixteen

5W low pressure Hg lamp under argon atmosphere. The reaction was monitored by frequent sampling and analyzed by a capillary GC. The reaction lasted about 20 hours before the starting material was gone. After purification with column chromatography, compound **14** was obtained in 85% yield. ^{1}H NMR δ 0.014 (9H, s), 0.504 (6H, s), 1.090 (6H, s), 6.904-7.291 (5H, m). ^{13}C NMR δ -0.466 (3), 1.450(2C), 28.533 (2C), 87.030 (1C), 126.244 (1C), 126.877 (2C), 127.768 (2C), 135.269 (1C), 140.967 (1C), 175.950 (1C). Mass Spectrum, *m/z* 290 (4, M^+), 275 (100, base), 232 (21), 217 (75), 159 (53), 143 (22), 75 (22), 73 (42), 58 (10). Exact mass 290.15162 (calc. for $C_{16}H_{26}OSi_2$ 290.15222). The X-ray structure is shown in Figure **9**.

Theoretical calculation methods. All geometries were determined at the Hartree-Fock self-consistent field (SCF) method, using the 6-31G(d) basis set and analytic gradients. Stationary points were analyzed by the eigenvalues of the hessian matrix. The negative eigenvalues correspond to imaginary vibrational frequecies. The stationary point is a minimum if there is no negative eigenvalue. It is a transition state if there is one negative eigenvalue. And it is a higher order saddle point if there are more than one negative eigenvalue. The intrinsic reaction coordinate (IRC) method was used to determine if the transition state connects the expected minima, to understand the reaction process. Zero point vibrational energies were calculated at RHF/6-31G(d). The single point calculations were executed with Mϕller-Plesset fourth order perturbation theory using 6-31G(d) basis set at the RHF/6-31G(d) geometries. All calculations were carried out with the program GAUSSIAN 92.

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GENERAL CONCLUSION

In this dissertation, the thermal and photochemical additions of disilanes to acetylenes were studied for the first time. The trans-addition of disilanes to acetylenes was discovered. The reaction was performed with the 5,5,6,6-tetramethyl-3,3,8,8-tetraphenyl-4,7-dioxa-5,6-disila-cyclooctayne (**1**) under argon flow at 600°C to give product 1,1,4,4-tetramethyl-3,3,6,6-tetraphenyl-2,5-dioxa-1,4-disila-dicyclo[3,3,0]octa-7-ene (**2**). *Ab initio* calculations with MP4/6-31G** was carried out to find the transition state structure. The activation energy was determined to be 34 kcal/mol. We also found that the intramolecular trans-addition of disilanes to acetylenes also photochemically occurred when the acetylene is conjugated with an aromatic group.

Based on the discovery of intramolecular addition of disilanes to acetylenes, a novel, blue light-emitting molecules containing the 3,3,3′,3′-tetramethyl-3, 3′-disila-indeno[2,1-*a*]indene unit were synthesized. The light-emitting diodes (LEDs) were fabricated with vapor deposition technique. The chromophore was also incorporated into polysiloxanes and polymethacrylate as pendent groups. Due to their high chemical stabilies and quantum yields, these polymers are excellent candidates for fabrication of polymer-based blue-light LEDs.

A small, highly-strained 2-silaoxetane with the catalytic addition of disilane to acetylene was synthesized and isolated via re-crystallization. This led us for the first time thermal chemically and photochemically to study the reaction intermediate of silylenes with ketones. The activation energy of decomposition of the 2-silaoxetane was found to be about 49.24 kcal/mol and Log(A) was 15.37. This process was also studied by *ab initio* calculations. This theoretical study showed that the decomposition was a highly non-synchronized concerned process. The four-membered ring system was expanded to a five-membered ring photochemically.

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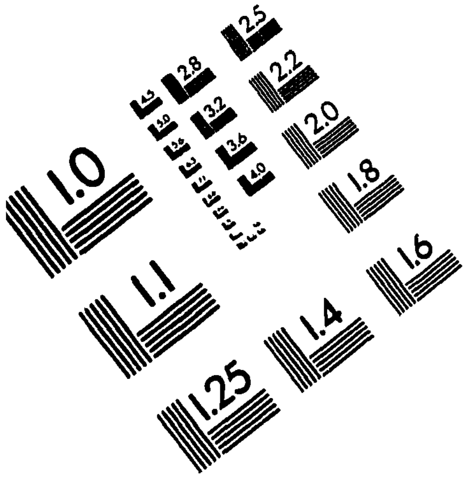
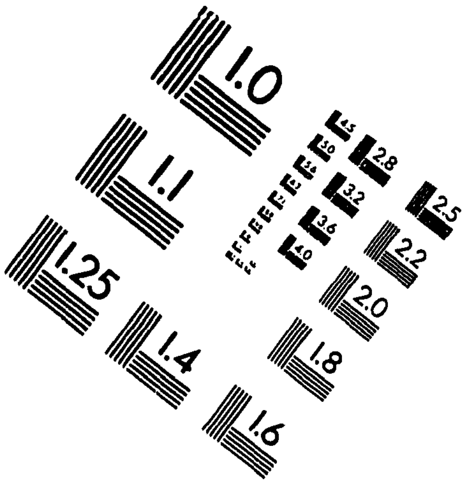
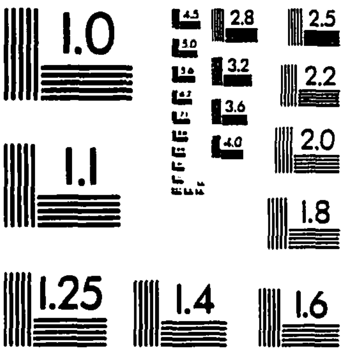
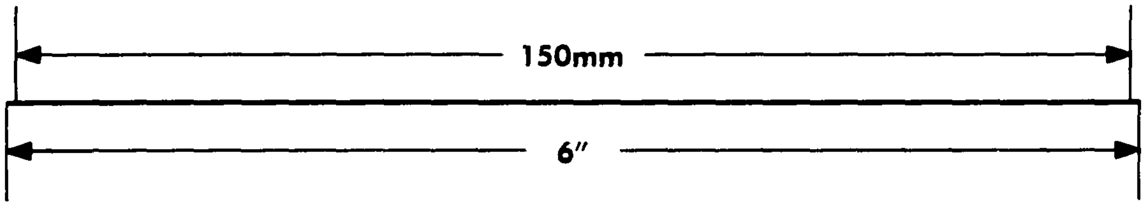
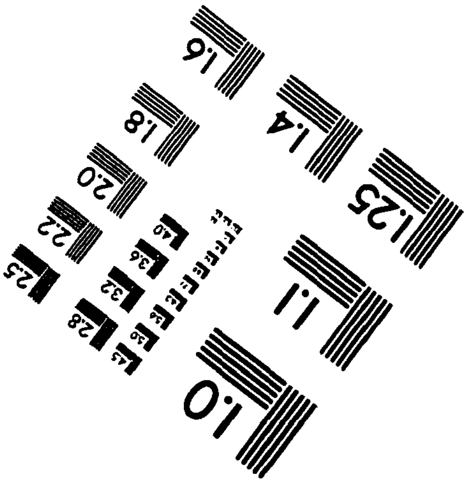
IMAGE EVALUATION TEST TARGET (QA-3)

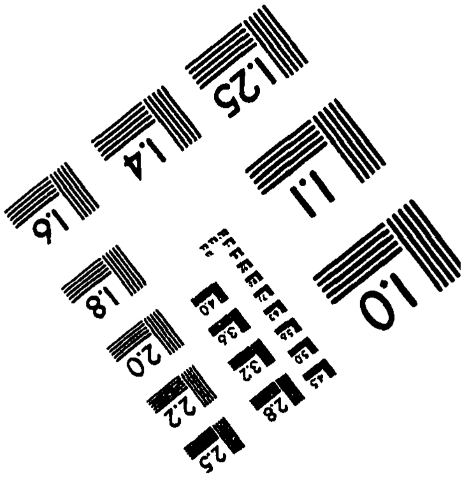












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