Synthesis, Photochemical Decomposition and DFT studies of 2,2,3,3-Tetramethyl-1,1-bis(dimethylphenylsilyl)silacyclopropane

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Abstract

The compound, 2,2,3,3-tetramethyl-1,1-bis(dimethylphenylsilyl)silacyclopropane (**1**), is a potential photochemical source of silylenes either through a 2+1 fragmentation of the silacyclopropane ring core or through α -elimination from the aryltrisilane chain. Upon 254 nm photolysis, the silacyclopropane (**1**) exclusively undergoes 2+1 ring fragmentation with the formation of bis(dimethylphenylsilyl)silylene and tetramethylethylene. This clearly shows the heightened photoreactivity of the silacyclopropane ring compared with the aryltrisilane chain. The extruded bis(dimethylphenyl)silylene is intercepted with trapping agents such as triethylsilane, methoxytrimethylsilane and bis(trimethylsilyl)-acetylene to form thermally stable adducts. Time Dependent-Density Functional Theory (TD-DFT) calculations at the B3LYP/6-31G* level reveal that an electron is excited from a Si-C σ orbital of the silacyclopropane ring (HOMO) to the empty π^* orbitals of phenyl group (LUMO). This weakens the Si-C bonds of the silacyclopropane ring which is believed to result in the observed 2+1 photofragmentation.

Key words

silacyclopropane, transient silylene, 2+1 fragmentation, silacyclopene, TD-DFT

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1. Introduction

The photochemical generation of transient silylenes is an important area of silicon chemistry. There are two common types of precursors used for this purpose [1]. The first one includes linear, branched and cyclic polysilanes [2, 3]. These precursors can undergo α elimination of Si-H and Si-Si bonds to give transient silylenes. One example is the aryl substituted oligosilanes, particularly 2-aryltrisilanes and 2-aryltetrasilanes (Scheme 1). These precursors are photochemical sources for silylenes, with the chromophore provided by the aromatic group [4, 5].

[Insert Scheme 1]

The second type of silylene precursor includes strained three membered ring compounds. Silacyclopropanes [6], silacyclopropenes [7], disilacyclopropanes [8] and cyclotrisilanes [9] fall into this category as molecules which undergo 2+1 type photofragmentation to give a silylene and the corresponding multiple bond compound. These compounds are also known to decompose thermally to extrude silylenes. Silacyclopropanes as silylene generators are one of the best studied of these systems originating with the first reported synthesis by Seyferth of hexamethylsilacyclopropane in 1975 [6, 7, 10-14]. Since this initial synthesis, a variety of silacyclopropanes have been used as silylene sources.[2, 15-20]. In general, all of these silacyclopropane-based silylene precursors possess the silacyclopropane ring as their effective chromophore. However, the study of a single compound possessing two independent substructures for

silylene generation; a silacyclopropane ring core and an aryltrisilane chain, remains unnoticed in the literature.

We report here the synthesis and photochemical decomposition pathway of 2,2,3,3-tetramethyl-1,1-bis(dimethylphenylsilyl)silacyclopropane (**1**) which possesses both the silacyclopropane ring core and the aryltrisilane chain. The potential photofragmentation of this compound may result from either the bis(dimethylphenylsilyl)silylene (Path **A**) and tetramethylethylene or the cyclic silylene 2,2,3,3-tetramethyl silacycloprop-1-ylidene (Path **B**) and tetramethyldiphenyldisilane (Scheme 2). TD-DFT calculations were performed in order to better understand the photochemical fate of (**1**).

[Insert Scheme 2]

2. Material and Methods

2.1. General information

Chlorosilanes, triethylsilane, methoxytrimethylsilane and bis(trimethylsilyl)acetylene were purchased from Gelest and used without further purification. All other reagents were purchased from Aldrich and were used without purification. Cyclohexane and C₆D₁₂ were dried over sodium, vacuum transferred, and stored under argon. CDCl₃ was distilled from CaH₂ and stored under argon. Hexane and THF were distilled directly from sodium benzophenone. Magnesium turnings (~1/8 in, 99.95% on trace metal basis) were purchased from Aldrich.

Photolyses were performed using a Rayonet RS photochemical reactor equipped with 17 low-pressure 254-nm radiation mercury lamps. All NMR spectra were recorded on a Bruker Avance 300 spectrometer and referenced to TMS as a chemical shift standard. $^{29}\text{Si}\{^1\text{H}\}$ NMR of all compounds was recorded using inverse gated coupling technique. Preparative HPLC was performed using a Varian Prostar 210 HPLC with a binary solvent delivery system with a reverse phase semi-preparative column (column module C18 8U 21.4 X 250). The eluent had a combined solvent flow rate of 23 mL/min. GCMS was performed using a Varian Saturn 2100 instrument. Infrared spectra were recorded as neat samples between NaCl plates using a Nexus 670 Avatar FTIR Spectrometer. EI-MS and HRMS were recorded at the Georgia Tech mass spectrometry facility. Elemental analysis was performed at Schwarzpof Microanalytical Laboratory and the Tulane University Coordinated Instrumentation Facility. Uv-Vis spectra were obtained using a Cary 50 Uv-Vis spectrophotometer.

2.2. Synthesis of 2,2-diisopropyl-1,1,3,3-tetramethyl-1,3-diphenyltrisilane (3)

Lithium (4.0 g, 0.58 mol) was washed with ether to remove the oil and was added in pieces to an argon filled 200 mL Schlenk flask containing 100 mL of dry THF. Phenyltrimethylchlorosilane (8.0 g, 0.050 mol) was then added with stirring at room temperature. After a few minutes of addition, the solution turned dark brown and was subsequently stirred overnight at room temperature to give the dimethylphenylsilyllithium. Diisopropyldichlorosilane (6.0 g, 0.030 mol) and 30 mL of THF were placed in a separate 500 mL Schlenk flask and cooled to -25 °C. The dimethylphenylsilyllithium was then added to the flask over a 3 h period and stirred overnight. The reaction mixture was quenched by the addition of 100 mL of water and

the trisilane (**3**) was extracted with hexane (2x100mL) and dried with anhydrous MgSO₄. The solvent was removed by rotary evaporation. Pure **3** was obtained as a colorless liquid by vacuum distillation at 125-140 °C (350 mTorr). Yield 5.6 g (62%) ¹H NMR (δ, C₆D₆) 0.40-0.47 (s, 12H) 0.99-1.07 (d, 12H, J = 7 Hz) 1.17-1.3 (m, 2H) 7.12-7.24 (m, 6H), 7.42-7.51 (m, 4H) ¹³C{¹H} NMR (δ, C₆D₆) 0.5, 13.3, 21.6, 128.4, 129.0, 134.9, 141.3 ²⁹Si{¹H} NMR (δ, C₆D₆) -27.4, -19.1. GCMS(EI): m/z (relative abundance) 369 (27, M⁺-Me) 327 (32), 299 (100), 224 (25), 135 (10), 105 (10) Elemental analysis for C₂₂H₃₆Si₃: observed (calculated). C, 68.28 (68.67) H, 9.39 (9.43).

2.3. Synthesis of 2,2-bis(2-bromopropan-2-yl)-1,1,3,3-tetramethyl-1,3-diphenyltrisilane(2)

The trisilane (**3**) (2.8 g 7.4 mmol), N-bromosuccinimide (2.9 g 16 mmol), AIBN (0.040 g, 0.23 mmol) and 45 mL of CCl₄ were placed in a 100 ml Schlenk flask, fitted with a condenser. The mixture was stirred for 15 min. and then heated to reflux for 30 min. and the mixture was then cooled to 0 °C. The precipitated succinimide was separated from the clear solution by filtration. Rotary evaporation of the filtrate and subsequent crystallization in toluene yielded (**2**) as colorless crystals. M.p. 165-170 °C. Yield 1.7 g (42%) ¹H NMR (δ, C₆D₁₂) 0.61-0.75 (s, 12H) 1.74-1.92 (s, 12H) 7.12-7.28 (m, 6H), 7.41-7.56 (m, 4H) ¹³C{¹H} NMR (δ, C₆D₁₂) 1.3, 35.9, 57.2, 128.1, 129.1, 136.1, 138.7 (δ, C₆D₁₂) ²⁹Si{¹H} NMR (δ, C₆D₆) -18.3, -8.3. MS(EI): m/z (relative abundance) 527 (16, M⁺-Me), 463 (45), 421 (18), 328 (36), 285 (11), 231 (31), 135 (100), 105 (18), 43 (11) HRMS for C₂₁H₃₁⁷⁹Br₂Si₃ (M⁺-Me): observed (calculated) 525.00450 (525.00401)

Elemental analysis for C₂₂H₃₄Br₂Si₃: observed (calculated). C, 48.28 (48.70) H, 6.29 (6.32).

2.4. Synthesis of 2,2,3,3-tetramethyl-1,1-bis(dimethyl(phenyl)silyl)silacyclopropane (**1**)

Magnesium turnings (99%, 0.75 g, 31 mmol) and 20 mL of THF were placed in a 100 mL Schlenk flask under nitrogen. A small amount of 1,2-dibromoethane (0.70 mL) was added to the solution which was then stirred for 1 h in order to activate the magnesium. Compound (**2**) (4.0 g, 7.0 mmol), dissolved in 20 mL of THF, was added to the magnesium slurry over a period of 3 h at 15 °C. The reaction mixture was stirred for an additional 5 h at room temperature. The solvent was removed from the reaction mixture by applying vacuum. Chilled hexane (25 mL, 0 °C) was added, stirred for 10 min, and allowed to settle. The clear solution was decanted and filtered through a Schlenk fritted funnel. The extraction with chilled hexane was repeated one more time. The solvent was then removed from the combined filtrate and dried under vacuum to give (**1**) as colorless semi-liquid. Compound (**1**) was stored at -30 °C in a glove box due to its air and thermal instability. Yield 2.2 g (80%) ¹H NMR (δ, C₆D₆) 0.33-0.40 (s, 12H) 1.33-1.50 (s, 12H) 7.14–7.23 (m, 6H), 7.43-7.53 (m, 4H). ¹³C{¹H} NMR (δ, C₆D₆) 0.6, 24.2, 28.4, 127.9, 128.7, 134.3, 140.1 ²⁹Si{¹H} NMR (δ, C₆D₆) -123.9, -13.9. IR (NaCl, cm⁻¹) 3068 (s), 2954 (m), 2854 (s), 1423 (s), 1245 (s), 1111 (s), 1077 (s), 819 (m), 739 (m). MS(EI): m/z (relative abundance) 382 (8, M⁺), 367 (7) 298 (100), 283 (19), 239 (73), 162 (20), 84 (25) 69 (35) HRMS for C₂₂H₃₄Si₃ (M⁺): observed (calculated) 382.19412 (382.19683)

2.5. Thermolysis experiments

In a typical procedure, a mixture of (**1**) (0.10 g, 0.26 mmol), the trapping agent (6 times the molar ratio of (**1**)), and freshly distilled cyclohexane (4.0 mL) was placed into a pyrex custom-made thick walled pyrolysis tube (10ml, 17mm o.d. x 180mm height with a 10mm o.d. stem). The tube was attached to a teflon stopcock via a Cajon union. The tube assembly was attached to a high vacuum line and the solution was degassed in three freeze-pump-thaw cycles. The tube was then sealed with a torch and heated to 120 °C for 20 h. The ampule was opened after cooling to room temperature and the pyrosylate was transferred to a 10 ml Schlenk flask. The solvent as well as the excess trapping agent were removed by vacuum. Crude samples (**4**) and (**5**) were purified by reverse phase HPLC to give colorless liquids.

2.6. Characterization of (**4**)

Analytically pure (**4**) was obtained by HPLC separation using a CH₃OH:THF mixture (93:7). Retention time 8.3 - 9.6 min. Yield 0.10 g (80%) ¹H NMR (δ, C₆D₆) 0.38-0.43 (s, 6H) 0.43-0.5 (s, 6H) 0.52-0.65 (q, 6H, J = 8 Hz) 0.86-0.98 (t, 9H, J = 8 Hz) 2.84-2.94 (s, 1H) 7.08-7.34 (m, 6H) 7.39-7.64 (m, 4H) ¹³C{¹H} NMR (δ, C₆D₆) 0.4, 6.1, 8.6, 128.2, 129.0, 134.2, 140.8, ²⁹Si{¹H} NMR (δ, C₆D₆) -16.8, -14.0, 3.0. IR (NaCl, cm⁻¹) 3069 (s), 2950 (m), 2069 (Si-H, s), 1462 (s), 1428 (s), 1107 (s), 1008 (s), 881 (s), 765 (m). MS(EI): m/z (relative abundance) 414 (5, M⁺), 399 (14), 299 (70), 278 (100), 239 (37), 197 (23) 135 (99), 59 (18) 43 (5) HRMS for C₂₂H₃₈Si₄ (M⁺) : observed (calculated) 414.20326 (414.20507).

2.7. Characterization of (5)

Analytically pure (5) was obtained by HPLC separation using a CH₃OH:THF mixture (95:5). Retention time 5.8–7.3 min. Yield 0.080 g (80%) ¹H NMR (δ, C₆D₁₂) 0.03-0.05 (s, 9H) 0.31-0.45 (d, 12H, J = 6Hz) 3.33-3.37 (s, 3H) 7.14-7.22 (m, 6H) 7.35-7.42 (m, 4H) ¹³C{¹H} NMR (δ, C₆D₁₂) -2.1, -2.1, -0.3, 54.9, 127.4, 128.1, 133.8, 139.5 ²⁹Si{¹H} NMR (δ, C₆D₁₂) -19.3, -15.1, 3.0 IR (NaCl, cm⁻¹) 3068 (s), 3048 (s), 2950 (s), 2891 (s), 2817 (s), 1426 (s), 1245 (s), 1106 (s), 1075 (Si-OMe, s), 835 (d), 761 (s), 733 (s), 696 (s), 644 (s). MS(EI): m/z (relative abundance) 402 (11, M⁺), 387 (100), 329 (16), 298 (38), 236 (76), 193 (34), 177 (33), 135 (87) 105 (9), 73 (20) HRMS C₂₀H₃₄OSi₄ (M⁺) : observed (calculated) 402.16808 (402.16867).

2.8. Characterization of (6)

Compound (6) was isolated after removing the solvent and the trapping agent from the reaction mixture as an extremely air and moisture sensitive liquid. It was pure enough to characterize and no HPLC purification was attempted due to the high reactivity of 6 towards air and moisture. Yield 0.11 g (90%). ¹H NMR (δ, C₆D₁₂) 0.12-0.18 (s, 18H) 0.18-24 (s, 12H) 7.20-7.30 (m, 6H) 7.34-7.42 (m, 4H) ¹³C{¹H} NMR (δ, C₆D₁₂) -0.8, 0.0, 128.6, 129.4, 135.0, 140.5, 164.7 ²⁹Si{¹H} NMR (δ, C₆D₁₂) -178.9, -17.0, -11.1. IR (NaCl, cm⁻¹) 3065 (s), 3046 (s), 2953 (s), 2886 (s), 1583 (s), 1423 (s), 1245 (s), 1106 (s), 1066 (m), 836 (m), 739 (m). MS(EI): m/z (relative abundance) 468 (53, M⁺), 454 (34), 391 (19), 303 (23), 236 (62), 155 (22), 135 (100), 43 (6) HRMS for C₂₄H₄₀Si₅ (M⁺) : observed (calculated) 468.19267 (468.19763).

2.9. NMR tube photolysis experiments

In typical procedure, a solution of (**1**) (0.030 mM) and trapping reagent (6 times the molar ratio of (**1**)) in cyclohexane-*d*₁₂ (0.70 mL) was placed in a quartz NMR tube fitted with a J-Young valve. The tube was connected to a Teflon high vacuum stopcock. The stopcock tube was then attached to a high vacuum line and the solution was degassed by three freeze-pump-thaw cycles. The solution was then photolyzed in a Rayonet photochemical reactor at 254 nm. The progress of the photolysis was monitored by NMR spectroscopy in 2 h time intervals throughout the experiment. Quantitative formation of tetramethylethylene with respect to decomposition of (**1**) was calculated by comparing ¹H NMR ratio of trapping agent to (**1**) (decreasing) and trapping agent to tetramethylethylene (increasing) before and after photolysis.

2.10. Photolysis of (**1**) in the presence of triethylsilane

Silacyclopropane (**1**) (0.10 g, 0.26 mmol), triethylsilane (0.20 g, 3.2 mmol), and 8.0 mL of hexane were placed in a quartz tube. The quartz tube was then attached to a high vacuum line and the solution was degassed in three freeze-pump-thaw cycles. The solution was photolyzed at 254 nm for 16 h at 15 °C. The solvent and excess triethylsilane were removed by vacuum. Analytically pure (**4**) was obtained by HPLC separation using a CH₃OH:THF mixture (93:7). Retention time 8.3 - 9.6 min.

2.11. X-ray structure determinations: general data

The solid state structure of (**2**) was determined by X-ray crystallography. An ORTEP drawing of (**2**) is given in Fig. 1, while experimental details and relevant metrical data are presented in Table 1. General procedures for crystal alignment, unit cell determination and refinement and collection of intensity data have been published [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in idealized positions with fixed isotropic temperature factors. Each bromoisopropyl group is rotationally disordered over two sites (for Br1 occupancy ratio 91/9, for Br2, 64/36). These were modeled as rigid groups using metrical parameters obtained from DFT calculations and with assignment of approximate isotropic displacement parameters to the methyl carbon atoms.

2.12 Computational Details

All the TD-DFT reported in this paper used the GAUSSIAN03 [22] program system through WebMo interface [23]. Geometries for model compound (**1**) have been optimized by implementing the density functional calculations using B3LYP method at 6-31G* level. The GIAO (gauge-independent atomic orbital) nuclear magnetic shielding tensors were calculated at the B3LYP/6-31G* level using the optimized structures at the B3LYP/6-31G*. ²⁹Si chemical shift tensors were converted into the corresponding isotropic chemical shifts assuming $\sigma = 386.5$ for SiMe₄ [24, 25].

2. Results and Discussion

3.1. Synthesis of silacyclopropane (**1**)

The synthesis of silacyclopropane (**1**) is shown in Scheme 3. The dimethylphenylsilyl lithium was prepared by the reaction of dimethylphenylchlorosilane

with lithium metal in THF by a procedure reported by Murakami *et.al.* [26]. The silyllithium was then reacted with dichlorodiisopropylsilane to give 2,2-diisopropyl-1,1,3,3-tetramethyl-1,3-diphenyltrisilane (**2**). The trisilane (**2**) was brominated using N-bromosuccinimide (NBS) in CCl₄ in the presence of 2,2'-azobisisobutyronitrile (AIBN) under reflux to give 2,2-bis(2-bromopropan-2-yl)-1,1,3,3-tetramethyl-1,3-diphenyltrisilane (**2**).

[Insert Scheme 3]

Silacyclopropane (**1**) was obtained in 80% yield from the reaction of (**2**) with activated magnesium in dry THF following the procedure pioneered by Seyferth [10]. Compound (**1**) is an air and moisture sensitive colorless semi-liquid and is thermally unstable at room temperature. The structure of (**1**) is fully supported by ¹H NMR, ¹³C{¹H} NMR and ²⁹Si{¹H} NMR and EI-MS spectra. The ²⁹Si{¹H} NMR chemical shift of -123.9 ppm is very typical for the ring silicon atom of silacyclopropanes [2, 10, 15, 16, 18] and is also consistent with the chemical shift of -110.4 calculated from Density Functional Theory (DFT). The EI-MS of (**1**) shows the parent ion (M⁺) at 382 amu and the base peak, corresponding to bis(dimethylphenylsilyl)silylene, at 298 amu.

2.2. X-ray crystal structure of **2**

A single crystal X-ray structure diffraction study was carried out on the dibromide (**2**) (Figure 1). Compound (**2**) crystallized in a monoclinic unit cell with P2₁/C space group symmetry. The crystal structure revealed a mild disorder arising from the positional scrambling of the methyl and bromine atoms within the bromoisopropyl

groups. Despite this disorder, the refinement was well behaved and proceeded to an R value of 0.0537. The Si1-Si2 (2.381(4) Å) and Si2-Si3 bonds (2.389 (4) Å) are slightly longer than the normal Si-Si bond length of 2.33 Å [27]. The silicon to bromoisopropyl carbon bond lengths (Si1-C17 and Si3-C20) of 1.93(1) Å are also longer than a typical Si-C single bond length of 1.87 Å [28]. The longer Si-Si and Si-C bonds reflect the sterically congested nature of this species.

[Insert Figure 1]

[Insert Table 1]

Silylene Trapping Reactions

3.3.1. Thermolysis of (1) and the characterization of trapping products

The thermolysis of **(1)** was carried out in cyclohexane at 120 °C for 20 h in the presence of trapping agents. The silylene was trapped by a 6-fold excess of either triethylsilane, methoxytrimethylsilane or bis(trimethylsilylacetylene) to give the expected adducts **(4)**, **(5)** and **(6)**, respectively, from the reaction with the transient bis(silyl)silylene (Scheme 4).

[Insert Scheme 4]

Compounds **(4)**, **(5)** and **(6)** were fully characterized by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR including DEPT135, $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopy, infrared spectroscopy (IR) and mass spectroscopy. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the silacyclopropene **(6)**, showed a

resonance at -178.9 ppm which is very typical for a silacyclopentene ring [2, 7, 29] and is also consistent with the chemical shift of -168.5 ppm calculated from DFT. The other two silicon resonances are observed at -17.0 and -11.1 ppm.

3.3.2. Photolysis of silacyclopentane (**1**) in the presence of trapping reagents

Compound (**1**) was photolyzed at 254 nm in cyclohexane-*d*₁₂ at 15 °C in the presence of the trapping agents triethylsilane, methoxytrimethylsilane and bis(trimethylsilyl)acetylene. The photochemical reaction was monitored by ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra. Loss of tetramethylethylene and the formation of (**4**), (**5**) and (**6**) were observed from their respective trapping agents (Scheme 4). In the case of triethylsilane, the adduct (**4**) was photochemically stable and was isolated. Adducts (**5**) and (**6**), however, underwent decomposition upon further photolysis to give uncharacterized products. However the formation of (**5**) and (**6**) was confirmed by comparing the ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra at an early photolysis stage (5.5 h), with authentic samples of (**5**) and (**6**) obtained from their respective thermolysis reactions (section 3.3.2). Quantitative formation of tetramethylethylene with respect to the decomposition of (**1**) was observed in the ¹H NMR by comparing the integrated ratio of trapping agent to (**1**) and trapping agent to tetramethylethylene before and after photolysis. Neither the adduct of the cyclic silylene nor (Me₂PhSi)₂, products from a Si-Si α-elimination, were observed in the ¹H NMR spectrum.

UV-Vis spectrum and TD-DFT studies of silacyclopentane (**1**)

In order to better understand the dominance of silacyclopentane ring cleavage in the photochemical silylene extrusion of (**1**), TD-DFT calculations were performed on (**1**) and compared with its UV-Vis spectrum. Figures 2 and 3 represent the experimental UV-Vis

spectrum and the calculated MO diagram of the frontier orbitals of (**1**) based on TD-DFT calculations, respectively. Table **2** is the comparison of λ_{max} obtained from experiment and the MOs responsible for the transition as calculated by TD-DFT. The longest wavelength absorption (270 nm) in silacyclopropane (**1**) can be assigned to the transitions of the HOMO to LUMO (dark transition), LUMO+1 and LUMO+2. Careful analysis revealed that the HOMO has a predominant contribution from the *p* orbitals of the Si-C bonds of the silacyclopropane ring, whereas the LUMO is predominantly carbon 2p in character derived from the π^* orbitals of phenyl ring. Since photoreactivity stems from the lowest singlet state LUMO according to Kasha's rule, we propose that the excitation of electron from the silacyclopropane ring to the π^* orbitals of phenyl group creates a net partial positive charge on the silacyclopropane ring (**C**) and a significant weakening of the silacyclopropane Si-C bonds. This results in the breaking of a Si-C bond leading to an intermediate singlet diradical (**D**) (Scheme **5**) on the way to the extrusion of the silylene. This mechanism is analogous to the one proposed by Kira *et. al.* for the microscopic reverse reaction: formation of the silacyclopropane from the silylene and the alkene [30].

[Insert Figure 2]

[Insert Figure 3]

[Insert Table 2]

[Insert Scheme 5]

3. Conclusion

Silacyclopropane (**1**) upon photolysis, undergoes exclusively a 2+1 fragmentation to extrude bis(dimethylphenylsilyl)silylene (**A**), thereby demonstrating that the silacyclopropane ring is a highly effective photochemical silylene generator. TD-DFT calculations show that the low energy excitations results in the promotion of an electron from the Si-C bonds of the silacyclopropane ring (HOMO) to a set of delocalized π^* orbitals on the phenyl rings (LUMO). The subsequent weakening of the silacyclopropane Si-C bonds thereby favors the 2+1 fragmentation. The extruded silylene can be conveniently trapped with triethylsilane, methoxytrimethylsilane and bis(trimethylsilyl)acetylene.

4. Supporting Materials

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1059615 for the compound (**2**). Copies of this information may be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. A PDF containing details of the TD-DFT calculation and detailed crystallographic data is available free of charge via the internet at <http://www.sciencedirect.com>.

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CAPTIONS FOR FIGURES AND SCHEMES

Figure 1 Molecular structure of (**2**) with atomic numbering (ORTEP, 50% probability ellipsoids; H atoms are omitted for clarity). Selected bond distances (Å) and bond angles (deg) for **2**: Si1-Si2 = 2.381(4), Si2-Si3 = 2.389(4), Si2-C17 = 1.93 (1), Si2-C20 = 1.93 (1) Si1-Si2-Si3 = 106.1 (1), Si1-Si2-C17 = 112.2 (3), Si1-Si2-C20 = 109.1 (3), C17-Si2-C20 = 109.7 (4).

Figure 2 UV-Vis spectrum of silacyclopropane (**1**) in CH₂Cl₂

Figure 3 Partial MO diagram of silacyclopropane (**1**) based TD-DFT calculations

Scheme 1 Photolysis of aryltrisilanes to give arylsilylenes

Scheme 2 Potential photochemical decomposition pathways for **1**

Scheme 3 Synthetic route to the silacyclopropane (**1**)

Scheme 4 Trapping reactions for the bis(phenyldimethylsilyl)silylene generated from the decomposition of (**1**)

Scheme 5 Proposed stepwise mechanism for the photochemical generation of silylene (**A**) from (**1**)

CAPTIONS FOR TABLES

Table 1. Experimental crystallographic data for compound (**2**)

Table 2: Comparison of λ_{max} and excitation energy from experimental and TD-DFT calculation for silacyclopropane (**1**)

Figure 1

Figure 2

Figure 3

Scheme 2

Scheme 3

Scheme 4

Scheme 5

Table 1

	Compound (2)
Formula	C ₂₂ H ₃₄ Br ₂ Si ₃
Molecular weight	542.58
Crystal dimensions [mm]	0.18 x 0.29 x 0.34
Crystal System	Monoclinic
Space group	P2 ₁ /c (No. 14)
Cell dimensions	
<i>a</i> (Å)	9.0647(5)
<i>b</i> (Å)	12.2012(7)
<i>c</i> (Å)	22.930(1)
α (°)	90
β (°)	94.880(1)
γ (°)	90
<i>V</i> (Å ³)	2526.9(2)
<i>Z</i>	4
ρ (calc) (g/cm ³)	1.426
Radiation	(λ = 0.71073)
Mo K α (mm)	3.357
θ range (°)	2.3, 28.8
Scan type	$\omega/2\theta$
Total data collected	44078
Unique data	6530
Observed data [<i>I</i> > 2.0 σ (<i>I</i>)]	5659
F(000)	1112
Temperature (K)	100
<i>R</i>	0.0537
<i>R</i> _w ^a	0.1460

$$^a R_w = \{ [\sum w(F_o^2 - F_c^2) / \sum wF_o^2] \}^{1/2}; w = 1 / [\sigma^2(F_o^2 + (xP)^2)], \text{ where } P = (F_o^2 + F_c^2) / 3$$

Table 2

Expt		DFT				
λ_{max}	Excitation energy(eV)	λ_{max} (dft)	Excitation energy(eV)	Orbital transitions	Oscillator strength	% contri bution
270	4.6	281	4.4	HOMO - LUMO	0.004	98
		264	4.7	HOMO - LUMO+1	0.035	91
		253	4.9	HOMO-LUMO+2	0.059	86

Graphical Abstract