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Notes

Thermal Generation and Trapping of Transient 9-Silaanthracene Derivatives

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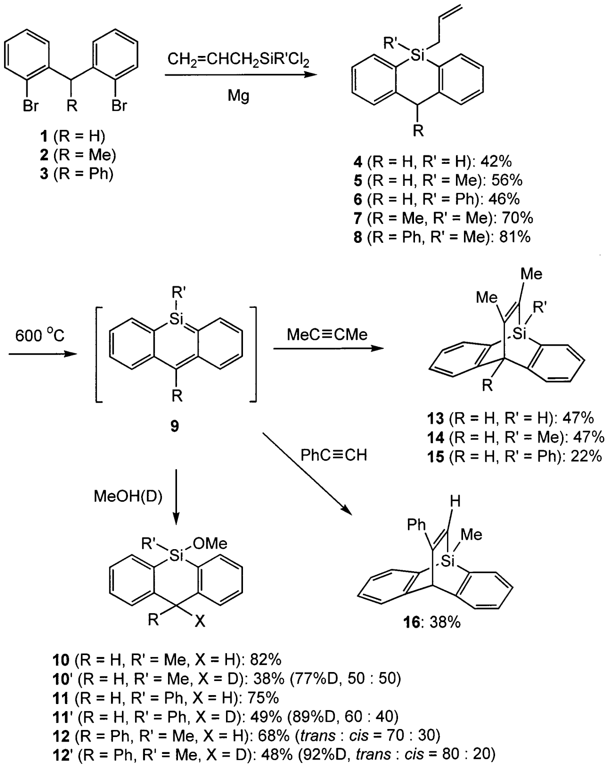
Summary: Thermal generation of 9-silaanthracene derivatives by 1,4-elimination of propene from 9-allyl-9,10-dihydro-9-silaanthracene derivatives is described. The formation of the transient 9-silaanthracene was deduced by the isolation of the trapping products from the copyrolysate of the respective allylsilane with methanol or alkynes.

Introduction

A great deal of attention has been focused on silicon compounds containing a silicon−carbon double bond as part of a delocalized system.[1] A current topic in this area is the isolation of kinetically stabilized silabenzene and 2-silanaphthalene reported by Tokitoh et al.[2] Very recently, they also succeeded in isolating a 9-silaanthracene derivative.[3] Our recent efforts have been directed toward the synthesis of 9-silaanthracenes. We have reported an observation of the UV−vis absorption and fluorescence spectra of 9-silaanthracenes produced by UV photolysis of 9,10-dihydro-9-silaanthracenes.[4] Another report on the generation of 9-silaanthracenes by Maier and co-workers involved flash vacuum thermolysis of suitable precursors at 800−1000 °C and subsequent isolation of the product in an argon matrix at 15 K.[5] Thermally induced retro-ene elimination of propene from an allylsilane has often been employed in the generation of silaaromatics.[6] Recently, we have also reported the first generation and trapping of 9-silaphenanthrene via the retro-ene process.[7] In this paper, we describe the thermal generation of 9-silaanthracenes from 9-allyl-9,10-dihydro-9-silaanthracenes and their reaction with methanol and alkynes.

Scheme 1



Results and Discussion

As shown in Scheme 1, the novel allylsilane precursors **4**−**8** were prepared from the bis(2-bromophenyl)methanes **1**−**3** and appropriate allyldichlorosilanes in the presence of magnesium in moderate to good yields (42−81%). The structures were confirmed by their ^{1}H, ^{13}C, and ^{29}Si NMR and MS data.

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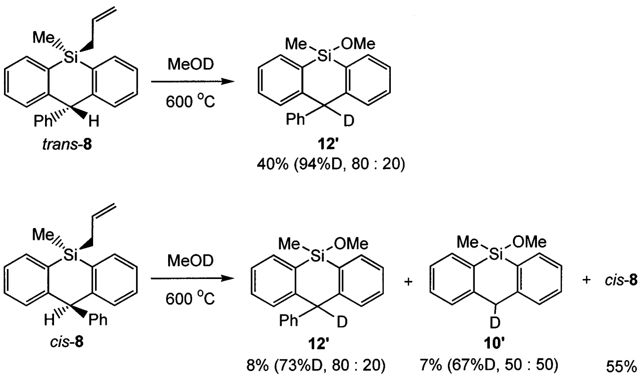
Copyrolysis of allylsilane **5** and methanol was carried out in a vertical quartz tube packed with quartz glass wool heated to 600 °C in a tube furnace with a 30 mL/min flow of nitrogen gas. Chromatography of the pyrolysate on silica gel eluted by a mixture of hexane and ethyl acetate (90:10) gave 9-methoxy-9-methyl-9,10-dihydro-9-silaanthracene (**10**), the expected product of addition of methanol to 9-methyl-9-silaanthracene (**9**), in 82% yield based on the reacted **5**. Evidence that the transient 9-silaanthracene **9** is indeed involved in this sequence was obtained from the copyrolysis of **5** and methanol-*d* to afford the corresponding methoxysilane **10′** labeled with deuterium at the 10-position (77% D content) in 38%[8] yield as a 50:50 mixture of isotopomeric diastereomers. Although the initial attack of methanol-*d* on the transient 9-silaanthracene is considered to proceed with syn stereospecificity, further methanolysis of the incipient methoxysilane would afford a mixture of isomers. Another trapping of 9-silaanthracene (**9**) was accomplished by copyrolysis of **5** and 2-butyne. The Diels–Alder-type [4 + 2] adduct **14** was isolated from the copyrolysate in 47% yield. Terminal alkynes such as phenylacetylene and 1-hexyne were also employed as dienophiles. With phenylacetylene, a regiospecific [4 + 2] addition occurred to give the adduct **16** in 38% yield. The terminal alkyne did not react as a C–H acid in the sense of methanol. In the case of 1-hexyne, only a trace amount of the corresponding adduct was detected in the complex reaction mixture.

Copyrolysis of the precursors **4** and **6** with methanol, methanol-*d*, or 2-butyne was similarly carried out, and the results are also outlined in Scheme 1. From the allylsilane **6**, the expected trapping products **11**, **11′**, and **15** were obtained in 75, 49, and 22% yields, respectively. In the case of **4**, the trapping experiment using methanol was unsuccessful. However, the copyrolysis of **4** and 2-butyne resulted in clean formation of the [4 + 2] adduct **13** in 47% yield, indicating the generation of the parent 9-silaanthracene (**9**) in the thermolysis of **4**.

To investigate the stereochemistry of the 1,4-elimination of propene from the 9-allyl-9,10-dihydro-9-silaanthracene framework, we investigated the thermolysis of a 50:50 mixture of cis and trans isomers of **7** bearing a methyl substituent at the 10-position in the presence of methanol or methanol-*d*. However, complete demethylation at the 10-position occurred during the course of the reaction to give methoxysilane **10** or **10′** (74% D content, 50:50 mixture of isomers) in 45 or 36% yield, respectively. Copyrolysis of the isolated *cis*- and *trans*-**7** with methanol-*d* gave similar results, and no stereochemical information could be obtained.

We next employed the corresponding 10-phenyl derivative **8** as a precursor, and it was found that the trapping products **12** and **12′** were obtained with the 10-phenyl substituent intact. The results are also summarized in Scheme 1. Typically, the copyrolysis of a 59:41 mixture of trans and cis isomers of **8**[9] and methanol-*d* was performed under the same conditions as described above, and the adduct **12′** was obtained in 48% yield based on the reacted **8**. The isomer ratio of the recovered **8** (trans:cis = 10:90) indicated the predominant consumption of the trans isomer. In fact, the copyrolysis of the isolated *trans*-**8** and methanol-*d* gave the adduct **12′** in 40% yield, whereas a similar treatment of *cis*-**8** resulted in 55% recovery of the starting material along with the formation of small amounts of the adducts **12′** and the corresponding dephenylated derivative **10′** in 8 and 7% yields, respectively (Scheme 2). These results suggest that the 1,4-elimination of propene from the 9-allyl-9,10-dihydro-9-silaanthracene framework proceeds mainly through a concerted process by a syn pathway.

Scheme 2



In the thermolysis of **8**, formation of the trans adduct **12** or **12′** always predominated in a ratio of 70:30 or 80:20. In these cases, the trans stereochemistry of the initial adduct is appreciably preserved due to the steric retardation of the subsequent methanolysis by the 10-phenyl substituent. Actually, the copyrolysis of the isolated *trans*-**12** and [D$_4$]methanol afforded trans and cis isomers of the corresponding [D$_3$]methoxysilanes in 35 and 25% yields, respectively, along with 40% recovery of *trans*-**12**. The 75:25 ratio of the trans and cis isomers, including the unchanged *trans*-**12**, is in accord with that observed in the thermolysis of **8**.

Finally, we also performed the copyrolysis of the adduct **14** and methanol-*d*. The expected methoxysilane **10′** was obtained in 28% yield, indicating that the transient 9-silaanthracene **9** was also generated by the thermal retro-Diels–Alder process.

Experimental Section

General Procedures. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were measured at 400.0, 100.6, and 79.5 MHz, respectively. All chemical shifts are reported as δ values (ppm) relative to residual chloroform (δ_H 7.26), tetramethylsilane (δ_{Si} 0.00), and the central peak of deuteriochloroform (δ_C 77.0). High-resolution mass spectra (EI) were obtained at an ionization potential of 70 eV.

Bis(2-bromophenyl)methane (**1**)[10] and bis(2-bromophenyl)-phenylmethane (**3**)[11] were prepared according to the literature. All other reagents were of commercial grade and were used as supplied.

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(8) The yields of trapping products with methanol-*d* were somewhat lowered, probably due to the low quality of the commercial methanol-*d*.

(9) The relative configurations of the compounds **8** and **12** were determined by the chemical shift of the methyl group attached to the silicon atom. The signal for the trans isomer suffers a shift of −0.42 or −0.51 ppm, respectively, relative to that of the cis isomer, indicating the former methyl group lies in the shielding region of the phenyl ring.

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1,1-Bis(2-bromophenyl)ethane (2). To a solution of 2,2′-dibromobenzophenone (5.10 g, 14.2 mmol) was added a 1.14 M solution of methyllithium in ether (15.8 mL, 18.0 mmol) over a period of 15 min. After it was stirred overnight, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and the separated organic layer was dried over $MgSO_4$. After removal of the solvent, the crude alcohol was treated with red phosphorus (19.9 g, 646 mmol) in refluxing 57% hydriodic acid (45 mL) for 48 h. After removal of the phosphorus using a Celite pad, the filtrate was extracted with hexane and the organic layer was dried over $MgSO_4$. The concentrated organic layer was chromatographed on silica gel. Elution with hexane gave the title compound **2** (2.35 g, 49%). ^1H NMR ($CDCl_3$): δ 1.58 (d, J = 7 Hz, 3 H), 4.82 (q, J = 7 Hz, 1 H), 7.07−7.13 (m, 4 H), 7.26 (m, 2 H), 7.56 (d, J = 8 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ 20.2, 43.8, 125.5, 127.4, 127.8, 128.5, 133.1, 144.1. HRMS: m/z 337.9280 (M^+, calcd for $C_{14}H_{12}Br_2$ 337.9306).

9-Allyl-9,10-dihydro-9-silaanthracene Derivatives 4−8. The preparation of 9-allyl-9-methyl-9,10-dihydro-9-silaanthracene (**5**) is representative. To a suspension of Mg (870 mg, 35.8 mmol) in THF (20 mL) was added a solution of the dibromide **1** (3.00 g, 9.20 mmol) and allyldichloromethylsilane (2.14 g, 13.8 mmol) over a period of 15 min. After it was stirred overnight, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and the separated organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel. Elution with hexane afforded the compound **5** (1.29 g, 56%) as a colorless oil. ^1H NMR ($CDCl_3$): δ 0.57 (s, 3 H), 1.91 (d, J = 8 Hz, 2 H), 4.05 (d, J = 17 Hz, 1 H), 4.25 (d, J = 17 Hz, 1 H), 4.87 (d, J = 9 Hz, 1 H), 4.89 (d, J = 18 Hz, 1 H), 5.80 (ddt, J = 18, 9, and 8 Hz, 1 H), 7.26−7.35 (m, 6 H), 7.62 (d, J = 7 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ −5.8, 22.2, 41.6, 114.1, 125.6, 128.0, 129.2, 133.6, 133.8, 134.0, 146.0. ^{29}Si NMR ($CDCl_3$): δ −19.9. HRMS: m/z 250.1187 (M^+, calcd for $C_{17}H_{18}Si$ 250.1178). Anal. Calcd for $C_{17}H_{18}Si$: C, 81.54; H, 7.25. Found: C, 81.44; H, 7.30.

Other 9-allyl-9,10-dihydro-9-silaanthracene derivatives were prepared similarly, and the physical and spectral data are as follows.

4: colorless oil; ^1H NMR ($CDCl_3$) δ 2.09 (dd, J = 7 and 3 Hz, 2 H), 4.08 (d, J = 17 Hz, 1 H), 4.19 (d, J = 17 Hz, 1 H), 4.86 (t, J = 3 Hz, 1 H), 4.94 (d, J = 10 Hz, 1 H), 5.01 (d, J = 17 Hz, 1 H), 5.91 (ddt, J = 17, 10, and 7 Hz, 1 H), 7.27−7.37 (m, 6 H), 7.70 (d, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.2, 41.6, 115.0, 125.6, 128.1, 129.6, 130.8, 133.6, 134.6; ^{29}Si NMR ($CDCl_3$) δ −32.6; IR (neat) ν_{Si-H} 2130 cm^{-1}; HRMS m/z 236.1064 (M^+, calcd for $C_{16}H_{16}Si$ 236.1021). Anal. Calcd for $C_{16}H_{16}Si$: C, 81.30; H, 6.82. Found: C, 81.32; H, 6.97.

6: colorless solid; mp 88−90 °C; ^1H NMR ($CDCl_3$) δ 2.37 (d, J = 8 Hz, 2 H), 4.09 (d, J = 18 Hz, 1 H), 4.17 (d, J = 18 Hz, 1 H), 4.86 (d, J = 10 Hz, 1 H), 4.97 (d, J = 17 Hz, 1 H), 5.84 (ddt, J = 17, 10, and 8 Hz, 1 H), 7.25−7.42 (m, 9 H), 7.54 (d, J = 7 Hz, 2 H), 7.63 (d, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.2, 41.6, 115.1, 125.6, 128.0, 128.1, 129.5, 129.7, 132.1, 133.6, 134.3, 134.6, 135.3, 146.6; ^{29}Si NMR ($CDCl_3$) δ −24.9; HRMS m/z 312.1341 (M^+, calcd for $C_{22}H_{20}Si$ 312.1334). Anal. Calcd for $C_{22}H_{20}Si$: C, 84.56; H, 6.45. Found: C, 84.69; H, 6.64.

Compounds **7** and **8** were obtained as a mixture of cis and trans isomers. The isomers were partially separable by column chromatography on silica gel with hexane as eluent.

9-Allyl-9,10-dimethyl-9,10-dihydro-9-silaanthracene (7). Major isomer: colorless oil; ^1H NMR ($CDCl_3$) δ 0.59 (s, 3 H), 1.55 (d, J = 7 Hz, 3 H), 1.98 (d, J = 8 Hz, 2 H), 4.28 (q, J = 7 Hz, 1 H), 4.98 (d, J = 18 Hz, 1 H), 4.99 (d, J = 9 Hz, 1 H), 5.93 (ddt, J = 18, 9, and 8 Hz, 1 H), 7.31−7.45 (m, 6 H), 7.65 (d, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.9, 25.4, 31.8, 47.4, 114.0, 125.4, 128.2, 129.6, 132.1, 134.2, 134.3, 151.9; ^{29}Si NMR ($CDCl_3$) δ −21.7; HRMS m/z 264.1298 (M^+, calcd for $C_{18}H_{20}Si$ 264.1334). Anal. Calcd for $C_{18}H_{20}Si$: C, 81.76; H, 7.62. Found: C, 81.69; H, 7.76. Minor isomer: colorless oil; ^1H NMR ($CDCl_3$) δ 0.56 (s, 3 H), 1.53 (d, J = 7 Hz, 3 H), 2.17 (d, J = 8 Hz, 2 H), 4.26 (q, J = 7 Hz, 1 H), 4.90 (d, J = 10 Hz, 1 H), 5.02 (d, J = 16 Hz, 1 H), 5.90 (ddt, J = 16, 10, and 8 Hz, 1 H), 7.31−7.45 (m, 6 H), 7.73 (d, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −0.7, 22.0, 31.1, 46.9, 114.3, 125.4, 128.0, 129.6, 132.3, 133.8, 134.3, 152.1; ^{29}Si NMR ($CDCl_3$) δ −22.1. Anal. Calcd for $C_{18}H_{20}Si$: C, 81.76; H, 7.62. Found: C, 82.23; H, 7.85.

9-Allyl-9-methyl-10-phenyl-9,10-dihydro-9-silaanthracene (8). Cis isomer: colorless solid; mp 69−71 °C; ^1H NMR ($CDCl_3$) δ 0.52 (s, 3 H), 1.17 (d, J = 8 Hz, 2 H), 4.69 (d, J = 17 Hz, 1 H), 4.81 (d, J = 10 Hz, 1 H), 5.41 (s, 1 H), 5.61 (ddt, J = 17, 10, and 8 Hz, 1 H), 6.84 (d, J = 8 Hz, 2 H), 7.09 (m, 1 H), 7.15 (m, 2 H), 7.33 (m, 2 H), 7.44 (m, 2 H), 7.50 (d, J = 8 Hz, 2 H), 7.61 (d, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −5.6, 22.9, 56.6, 113.7, 125.9, 128.0, 128.2, 129.3, 129.9, 134.13, 134.15, 134.4, 134.8, 146.5, 149.2; ^{29}Si NMR ($CDCl_3$) δ −25.0; HRMS m/z 326.1467 (M^+, calcd for $C_{23}H_{22}Si$ 326.1491). Anal. Calcd for $C_{23}H_{22}Si$: C, 84.61; H, 6.79. Found: C, 84.63; H, 6.95. Trans isomer: colorless oil; ^1H NMR ($CDCl_3$) δ 0.10 (s, 3 H), 2.11 (d, J = 8 Hz, 2 H), 4.89 (d, J = 10 Hz, 1 H), 4.99 (d, J = 16 Hz, 1 H), 5.44 (s, 1 H), 5.86 (ddt, J = 16, 10, and 8 Hz, 1 H), 6.93 (d, J = 7 Hz, 2 H), 7.10 (m, 1 H), 7.17 (m, 2 H), 7.33 (m, 2 H), 7.41 (m, 2 H), 7.45 (m, 2 H), 7.72 (d, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −2.4, 22.1, 56.4, 114.4, 125.8, 128.1, 128.17, 128.23, 129.4, 129.9, 133.7, 134.1, 134.2, 146.6, 149.2; ^{29}Si NMR ($CDCl_3$) δ −21.3.

Copyrolysis of 9-Allyl-9,10-dihydro-9-silaanthracene Derivatives 4−8 and MeOH(D). Typically, a solution of the allylsilane **5** (118 mg, 0.472 mmol) in methanol (2.02 g, 63.1 mmol) was pyrolyzed by dropwise addition over a period of 75 min through a nitrogen flow (30 mL/min) vertical quartz tube (30 × 600 mm) packed with quartz glass wool (30 mm) and heated to 600 °C in a tube furnace. The pyrolysate trapped at 77 K was chromatographed on silica gel (hexane:ethyl acetate = 90:10) to give 9-methoxy-9-methyl-9,10-dihydro-9-silaanthracene (**10**, 74.0 mg) in 82% yield. ^1H NMR ($CDCl_3$): δ 0.60 (s, 3 H), 3.43 (s, 3 H), 4.15 (d, J = 18 Hz, 1 H), 4.26 (d, J = 18 Hz, 1 H), 7.32−7.43 (m, 6 H), 7.75 (d, J = 7 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ −3.6, 40.8, 51.2, 125.7, 128.2, 129.9, 132.4, 133.4, 146.4. ^{29}Si NMR ($CDCl_3$): δ −18.9. HRMS: m/z 240.0992 (M^+, calcd for $C_{15}H_{16}OSi$ 240.0970).

A similar treatment of the allylsilane **5** (132 mg, 0.528 mmol) in MeOD (2.07 g, 62.8 mmol) gave 9-methoxy-9-methyl-9,10-dihydro-9-silaanthracene-10-*d* (**10′**, 30.0 mg) in 38% yield based on the recovered **5** (50.0 mg, 38%). ^1H NMR ($CDCl_3$): δ 0.57 and 0.58 (2 s, 3 H), 3.41 (s, 3 H), 4.11 (br s, 0.5 H), 4.23 (br s, 0.5 H), 7.30−7.42 (m, 6 H), 7.73 (d, J = 7 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ −3.6 and −3.5 (2 s), 40.5 (t, J = 19 Hz), 51.3, 125.8, 128.3, 129.9, 132.5, 133.4, 146.3. HRMS: m/z 241.1011 (M^+, calcd for $C_{15}H_{15}DOSi$ 241.1033).

Copyrolysis of other precursors with methanol or methanol-*d* was similarly carried out, and the results are summarized in Schemes 1 and 2. The physical and spectral data for the obtained methoxysilanes are as follows.

11: colorless solid; mp 86−88 °C; ^1H NMR ($CDCl_3$) δ 3.64 (s, 3 H), 4.22 (d, J = 18 Hz, 1 H), 4.29 (d, J = 18 Hz, 1 H), 7.34−7.47 (m, 9 H), 7.69 (m, 2 H), 7.78 (d, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 40.9, 51.8, 125.8, 127.9, 128.3, 130.1, 130.2, 131.2, 133.6, 134.1, 134.9, 146.8; ^{29}Si NMR ($CDCl_3$) δ −20.4; HRMS m/z 302.1177 (M^+, calcd for $C_{20}H_{18}OSi$ 302.1127). Anal. Calcd for $C_{20}H_{18}OSi$: C, 79.42; H, 6.00. Found: C, 79.45; H, 6.10.

11′: colorless oil; ^1H NMR ($CDCl_3$) δ 3.57 and 3.58 (2 s, 3 H), 4.14 (br s, 0.6 H), 4.22 (br s, 0.4 H), 7.28−7.43 (m, 9 H), 7.62 (m, 2 H), 7.70 and 7.72 (2 d, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 40.6 (t, J = 19 Hz), 51.8, 125.8, 127.9, 128.3, 130.1, 130.2, 131.3, 134.1, 134.2, 134.88 and 134.92 (2 s), 146.7 and 136.8 (2 s); ^{29}Si NMR ($CDCl_3$) δ −20.5; HRMS m/z 303.1151 (M^+, calcd for $C_{20}H_{17}DOSi$ 303.1190).

The methoxysilane **12** was obtained as a mixture of cis and trans isomers. Recrystallization from ethanol gave pure *trans*-**12**.

trans-**12**: colorless solid; mp 127−128 °C; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 3 H), 3.33 (s, 3 H), 5.44 (s, 1 H), 6.88 (m, 2 H), 7.08 (m, 1 H), 7.15 (m, 2 H), 7.37 (m, 2 H), 7.45 (m, 2 H), 7.52 (m, 2 H), 7.77 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.7, 51.3, 56.1, 125.9, 126.1, 128.07, 128.12, 129.86, 129.95, 132.8, 133.7, 146.4, 149.3; ^{29}Si NMR ($CDCl_3$) δ −10.6; HRMS *m*/*z* 316.1257 (M^+, calcd for $C_{21}H_{20}OSi$ 316.1283). Anal. Calcd for $C_{21}H_{20}OSi$: C, 79.70; H, 6.37. Found: C, 79.31; H, 6.49.

cis-**12**: as a mixture with the trans isomer; ^{1}H NMR ($CDCl_3$) δ 0.67 (s, 3 H), 3.23 (s, 3 H), 5.45 (s, 1 H), aromatic proton signals are overlapped with those of the *trans* isomer; ^{13}C NMR ($CDCl_3$) δ −4.4, 50.9, 56.3, 125.8, 125.9, 128.2, 128.3, 129.4, 130.1, 130.2, 134.1, 146.6, 149.9; ^{29}Si NMR ($CDCl_3$) δ −9.6.

12′: as a mixture of trans and cis isomers; HRMS *m*/*z* 317.1340 (M^+, calcd for $C_{21}H_{19}DOSi$ 317.1346). Trans isomer: ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 3 H), 3.33 (s, 3 H), 6.89 (m, 2 H), 7.08 (m, 1 H), 7.15 (m, 2 H), 7.37 (m, 2 H), 7.44 (m, 2 H), 7.51 (m, 2 H), 7.76 (m, 2 H). Cis isomer: ^{1}H NMR ($CDCl_3$) δ 0.67 (s, 3 H), 3.24 (s, 3 H), aromatic proton signals are overlapped with those of the trans isomer.

Copyrolysis of 9-Allyl-9,10-dihydro-9-silaanthracene Derivatives 4−6 and Alkynes. For example, the copyrolysis of **5** and 2-butyne is demonstrated. A solution of the allylsilane **5** (106 mg, 0.425 mmol) and 2-butyne (2.01 g, 37.2 mmol) in cyclohexane (2.01 g) was pyrolyzed by dropwise addition over a period of 35 min through a nitrogen flow (30 mL/min) vertical quartz tube (30 × 600 mm) packed with quartz glass wool (30 mm) and heated to 600 °C in a tube furnace. The pyrolysate trapped at 77 K was chromatographed on silica gel (hexane) to give the adduct **14** (51.8 mg, 47%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.96 (s, 3 H), 1.82 (s, 3 H), 1.99 (s, 3 H), 4.90 (s, 1 H), 7.08 (m, 2 H), 7.14 (m, 2 H), 7.38 (d, *J* = 7 Hz, 2 H), 7.57 (d, *J* = 7 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ −14.0, 14.4, 19.5, 61.9, 124.5, 124.9, 127.2, 130.1, 132.6, 139.0, 151.1, 152.8. ^{29}Si NMR ($CDCl_3$): δ −27.7. HRMS: *m*/*z* 262.1222 (M^+, calcd for $C_{18}H_{18}Si$ 262.1178).

A similar treatment of the allylsilane **5** (108 mg, 0.432 mmol) and phenylacetylene (2.02 g, 19.8 mmol) in cyclohexane (2.02 g) gave the adduct **16** in 38% yield based on the recovered **5** (88.8 mg, 82%). ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 3 H), 5.68 (d, *J* = 2 Hz, 1 H), 6.77 (d, *J* = 2 Hz, 1 H), 7.07−7.63 (m, 13 H). ^{13}C NMR ($CDCl_3$): δ −12.2, 59.0, 124.7, 125.3, 125.5, 127.4, 127.7, 128.4, 128.8, 130.6, 138.8, 142.0, 150.9, 164.3. HRMS: *m*/*z* 310.1139 (M^+, calcd for $C_{22}H_{18}Si$ 310.1178).

Allylsilanes **4** and **6** were similarly thermolyzed in the presence of 2-butyne to give the adducts **13** and **15** in 47 and 22% yields, respectively.

13: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.90 (q, *J* = 1 Hz, 3 H), 1.98 (q, *J* = 1 Hz, 3 H), 4.93 (s, 1 H), 5.22 (s, 1 H), 7.08 (m, 2 H), 7.15 (m, 2 H), 7.38 (d, *J* = 7 Hz, 2 H), 7.68 (d, *J* = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.8, 19.4, 62.3, 124.7, 125.1, 127.5, 131.4, 131.63, 137.2, 150.5, 153.0; ^{29}Si NMR ($CDCl_3$) δ −41.0; HRMS *m*/*z* 248.1029 (M^+, calcd for $C_{17}H_{16}Si$ 248.1021).

15: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 3 H), 2.03 (s, 3 H), 4.97 (s, 3 H), 7.08 (m, 2 H), 7.15 (m, 2 H), 7.42 (m, 2 H), 7.64 (m, 5 H), 8.13 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.4, 19.8, 62.0, 124.6, 125.2, 127.3, 127.8, 128.6, 130.8, 131.1, 132.2, 136.1, 138.1, 151.2, 153.5; ^{29}Si NMR ($CDCl_3$) δ −37.3; HRMS *m*/*z* 324.1349 (M^+, calcd for $C_{23}H_{20}Si$ 324.1334).

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