Synthesis of Silaindenes by Thermally Induced Acetylene–Vinylidene Rearrangements

Thomas J. Barton* and Brian L. Groh

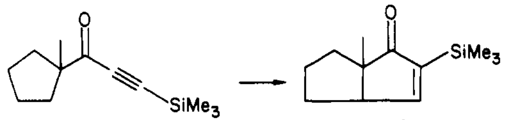
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received July 3, 1984

Flash vacuum pyrolysis (FVP) of (*o*-(dimethylsilyl)phenyl)acetylene at 800 °C produces 1,1-dimethyl-1-silaindene in 84% yield via (largely) insertion of an intermediate vinylidene into the Si–H bond. At 650 °C, this FVP also affords the isomeric 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene (34%) arising from a initial 1,5-H shift from silicon. Deuterium labeling revealed that there are two pathways leading to silaindene. FVP of a silylacetylene produced results consistent with (but not demanding of) a 1,2-silyl shift on the acetylene. 7-(Trimethylsilyl)-1-methylenebenzocyclobutene was synthesized and found to quantitatively isomerize on FVP to (trimethylsilyl)-*o*-tolylacetylene via electrocyclic opening followed by a 1,5-H shift. It is concluded that the title chemistry can provide a convenient synthetic route to unsaturated silacycles.

Although the existence of thermally induced 1,2 migrations on acetylenes to reversibly produce alkylidenecarbenes ($1 \rightleftarrows 2$) has been firmly established since 1978,[1] application of this reaction in organometallic chemistry has not been reported. We have undertaken a program designed to both utilize this rearrangement in the synthesis of unsaturated silacycles[2] and to determine whether the usual superior migratory aptitude of silicon[3] would prove beneficial with regard to the thermal requirements of these isomerizations. The sole example, of which we are aware, of apparent thermally induced 1,2-silyl migration on an acetylene is that of Dreiding,[4] who found that ethynyl ketone 3 isomerized to 4 at 700 °C in 25% yield. As the parent acetylene isomerized analogously at ca. 100 °C lower temperature, the silyl migration route was abandoned in future work.

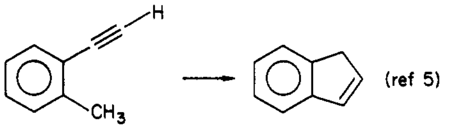
1 2



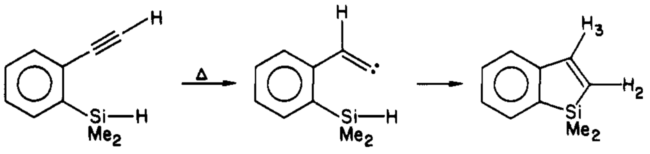
3 4

Our initial efforts in this area were prompted by the report of Brown[5] that gas-phase pyrolysis of *o*-ethynyltoluene (5) afforded indene. We reasoned that if indeed this reaction proceeds through alkylidenecarbene intermediacy, replacement of the methyl group by silyl hydride functionality would provide a more efficient intramolecular carbene trap. Thus, it was hoped that pyrolysis of 6 would provide us with an efficient synthesis of silaindene 8 via carbene 7.

Synthesis of 6 (Scheme I) was accomplished by dimetalation of phenylacetylene by the method of Brandsma[6] followed by quenching with dimethylchlorosilane to afford a 70% yield of (dimethylsilyl)(*o*-(dimethylsilyl)phenyl)acetylene (9). Hydrolysis of 9 produced an 84% yield of silanol 10 that was converted to the chloride 11 (62%) by reaction with PCl_5 in refluxing CCl_4. Reduction of 11 with $LiAlH_4$ afforded the desired silyl hydride 6 in 76% yield.

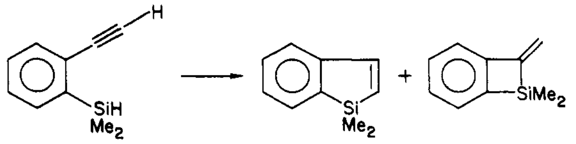


5



6 7 8

Flash vacuum pyrolysis (FVP) of 6 at 800 °C afforded silaindene 8[7] in 84% yield (86% mass recovery) as the only volatile product. Reduction of the pyrolysis temperature to 700 °C still yielded 8 as the major product (77%), but examination of the GC/MS and ^1H NMR spectra of the pyrolysate revealed that an isomer of 8 (17%) was now present. The structure of 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene (12) was assigned on the basis of ^1H NMR spectrum which showed the vinyl hydrogens as two doublets with a geminal coupling of 1.3 Hz and consistent ^{13}C NMR and GC/MS spectra. FVP (800 °C) of a mixture of 6 (8%), 8 (34%), and 12 (58%) afforded a 93% yield of 8 with no remaining 6 or 12. It was not possible to separate this isomer from 8 on a packed GC column, and all attempts at preparative GC resulted in almost complete destruction of the minor isomer. The yield of this isomer was a maximum of 34% at 650 °C, at which temperature 2% unreacted 6 remained, and 8 was formed in 47% yield.



6	*T* °C	8	12
0%	800	84%	0%
0%	700	77%	16%
2%	650	47%	34%
22%	600	42%	28%

---

(1) Brown, R. F. C.; Eastwood, F. W.; Jackman, G. P. *Aust. J. Chem.* **1978**, *31*, 579.

(2) Barton, T. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 9, Chapter 9.2.

(3) Brook. A. G.; Bassindale, A. R. In "Organic Chemistry", DeMayo, P., Ed.; Academic Press: New York, 1980; Essay No. 9, Vol. 2.

(4) Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1979**, *62*, 1852.

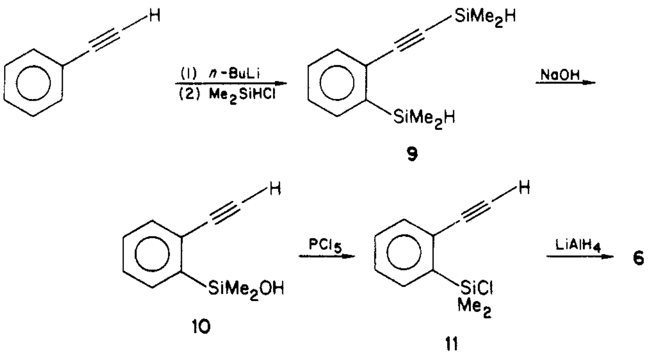
(5) (a) Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J.; McMullen, G. L. *Aust. J. Chem.* **1974**, *27*, 2393. (b) Brown, R. F. C.; Eastwood, F. W.; Jackman, G. P. *Aust. J. Chem.* **1977**, *30*, 1757.

(6) Hommes, H.; Verkruijsse, H. D.; Brandsma, L. *J. Chem. Soc., Chem. Commun.* **1981**, 366.

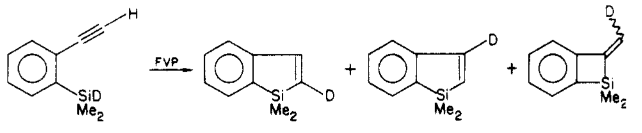
(7) Barton, T. J.; Juvet, M. *Tetrahedron Lett.* **1975**, *45*, 3893.

0276-7333/85/2304-0575$01.50/0 © 1985 American Chemical Society

Scheme I



Since these results clearly implicate **12** as a source of **8**, the question arose as to whether **12** was the sole source of **8**, and the presumed intermediacy of carbene **7** was incorrect.[8] Toward resolution of this question, deuterated **6** (**6-D**) was prepared by LiAlD$_4$ reduction of silyl chloride **11**. Pyrolysis of **6-D** at 800 °C produced a mixture of **8-2D** (73%) and **8-3D** (19%). FVP of **6-D** at 600 °C produced, in addition to **8-2D** and **8-3D**, a 27% yield of **12-D** and a 46% recovery of **6-D** with *no* scrambling.

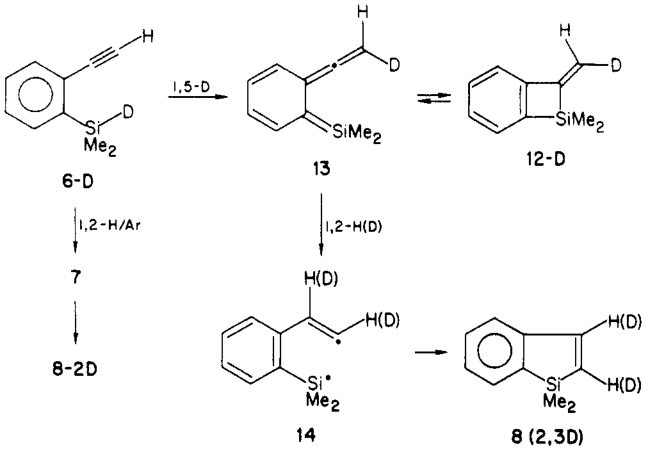


6-D	T °C	8-2D	8-3D	12-D
0%	800	73%	19%	
46%	600	17%	2%	27%

The assignment of the site of deuteration in deuterated **8** is a nontrivial exercise. The two vinyl protons of **8** appear in the NMR spectrum as doublets at δ 6.26 and 7.32 and were assigned respectively as H-2 and H-3 through NOE enhancement of only the δ 6.26 absorption upon irradition of the SiMe$_2$ resonance at δ 0.31. The ^{13}C NMR resonances of C-2 and C-3 were respectively assigned as δ 132.38 and 149.18 from single off-resonance-decoupled (SORD) spectral analysis as described in the Experimental Section. The assignments of **8-2D** and **8-3D** were made from these absorption assignments.

From the **6-D** pyrolysis results, it is apparent that there are two pathways leading to silaindene **8** (Scheme II). The route involving 1,2-hydrogen (or aryl) migration to form carbene **7** followed by Si–H (Si–D) insertion will lead exclusively to **8-2D**, which is indeed the major product. We envision the formation of **12** to arise from a 1,5-sigmatropic shift of D (or H) from silicon to produce allene **13** which can close to form **12**. That the isomerization of **6** to **13** is not significantly reversible under our conditions is evidenced by the absence of deuterium scrambling in recovered **6-D**. As to how allene **13** proceeds to **8**, we suggest that this occurs by 1,2-hydrogen migration and closure of the resulting diradical **14**. Such a diradical process is believed to be operative in the thermal interconversion of allene and propyne.[9] We note that this process predicts that half (neglecting isotope effects) of the **8** formed from **12-D** will be **8-2D** and half **8-3D**. This is in keeping with the pyrolysis results for **6-D**. It should also be noted that **8-2D** (and **7**) could also be formed from an initial 1,2-aryl migration on the acetylene. This possibility cannot be ruled out with the present data but does not bear on the question of allene involvement. Brown[5a] has speculated that the thermolysis of **5** might involve some reversible formation of the all-carbon analogue of allene **13**. However, the possibility that this allene might be on a pathway to indene not involving an alkylidenecarbene has apparently not been considered. Methylenebenzocyclobutene, the carbon analogue of **12**, is not found in the pyrolysis of **5**, although it does produce both **5** and indene on pyrolysis at 550 and 700 °C.[5a]

Scheme II

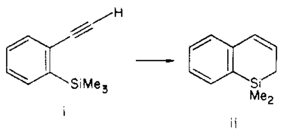


In order to gain information about the relative migratory aptitudes of hydrogen and silicon in acetylene isomerization, silylacetylene **9** was pyrolyzed at 800 °C to afford a mixture of the expected 3-silylsilaindene **16** (62%), silaindene **8** (15%), and 4% of 2-silylsilaindene **18** with no surviving **9** (Scheme III). The formation of **8** is not unexpected as reductive elimination of silylenes from hydridovinylsilanes is an established process.[10] While the gratifying production of **16** was anticipated from a 1,2-silyl (or aryl) shift to form carbene **15**, the formation of **18** reveals that again a competitive process is present. An initial 1,5-hydrogen shift to form allene **17**, followed by 1,2-hydrogen migration and diradical closure, provides a mechanistic rational for **18**. One might expect at least as much 1,2-silyl migration as 1,2-hydrogen migration for allene **17**, and thus this pathway can contribute to the yield of **16**. This contribution probably is not great, as pyrolysis of **9** at 700 °C affords a 30% yield of **1** (64% based on reacted **9**) and only 1% of **18**. However, if the migration of Si in **17** is considerably more facile than the competing 1,2-H migration, it is still possible that **16** arises from this route.

The fate of allene **17** was indirectly probed through the synthesis and FVP of the silyl-substituted methylene benzocyclobutene **21** (Scheme IV). Synthesis of **21** was accomplished by conversion of benzocyclobutenone via a modified Wittig reaction to dibromide **19**, partial reduction to a 1:1 *E*/*Z* mixture of the monobromide **20**, metalation,

---

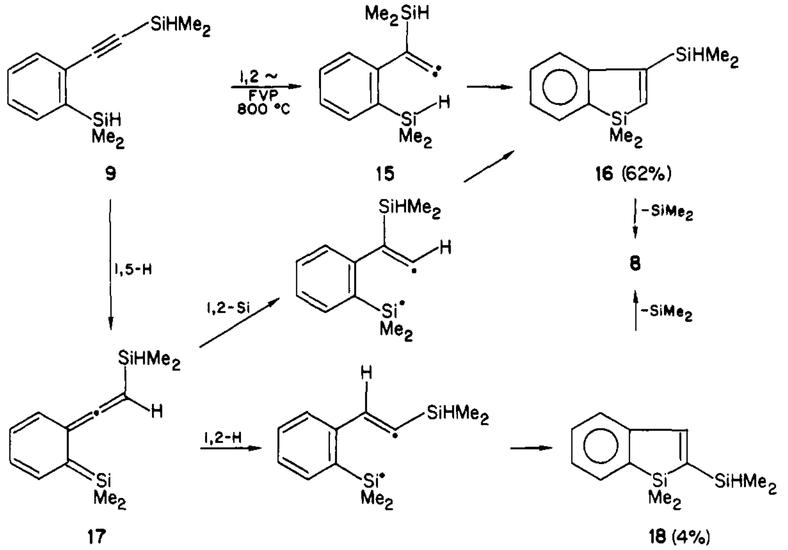
[8] Throughout these discussions, we omit the possibility of radical chain processes leading to the observed products. Although most of our data does not allow this exclusion, we do so because (a) radical processes are not consistent with the major pathway for **6-D** as revealed by the labeling in **8-2D**, (b) the necessary geometries for the various closures are not attractive for the required radical intermediates, and (c) we have very similar chemistry for related systems not capable of silyl radical formation, for example, i → ii.



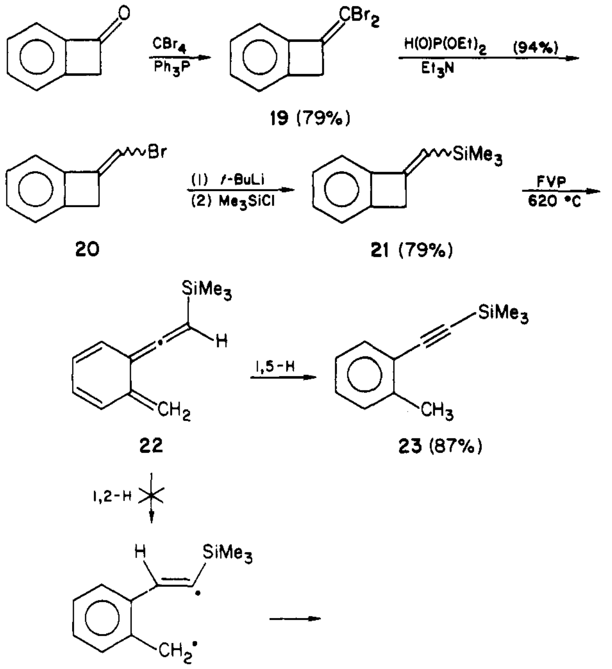
[9] Hopf, H.; Priebe, H,; Walsh, R. *J. Am. Chem. Soc.* **1980**, *102*, 1210.

[10] Ring, M. A.; O'Neal, H. E.; Richborn, S. F.; Sawrey, B. A. *Organometallics* **1983**, *2*, 1891.

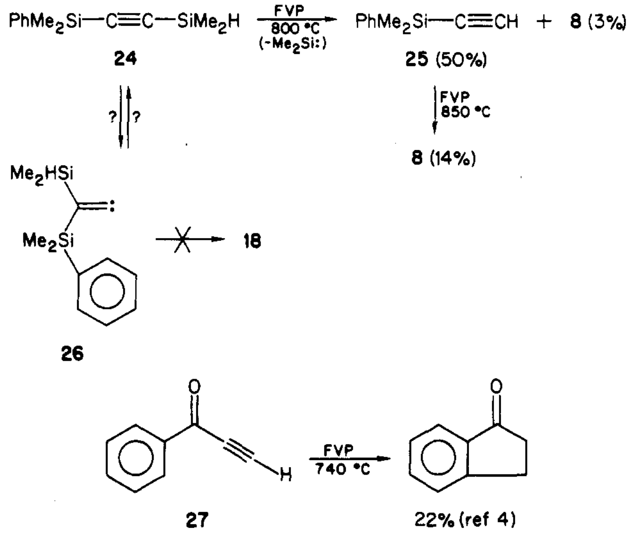
Scheme III



Scheme IV



Scheme V



and quenching with chlorotrimethylsilane to afford a 1:1 mixture of the *E* and *Z* isomers of **21**. At temperatures ranging from 520 to 620 °C, the only product obtained from FVP of **21** was the isomeric acetylene **23** (Scheme IV). At 620 °C this conversion was complete with both the yield and mass recovery being 87%. Thus, the isomerization of the presumed allene intermediate occurs exclusively by a 1,5-hydrogen shift. Apparently, the energy requirements of a 1,2 shift in allene **22** are even higher.

In an attempt to utilize this chemistry to prepare an authentic sample of **18** for spectral comparison with the material obtained in the pyrolysis of **9**, we pyrolyzed bis(silyl)acetylene **24** in hopes that isomerization to vinylidene **26** could be intercepted by C–H insertion on the phenyl ring. However, FVP of **24** at 800 °C afforded in 50% (corrected for 22% unreaced **24**) yield **25**, the product of reductive elimination of dimethylsilylene (Scheme V). No **18** could be detected in the product mixture, but 3% of silaindene **8** was formed. The absence of **18** cannot be taken as evidence against the reversible formation of vinylidene **26**, as the desired insertion into an aromatic C–H is, of course, more difficult than the previous Si–H insertions. The minor formation of **8** is attributed to isomerization of acetylene **25**. Indeed, FVP (850 °C) of **25** afforded **8** in only 14% (corrected for 71% recovery of **25**) yield. Similarly, Dreiding obtained 1-indanone in only 22% yield from the pyrolysis of the analogous ethynyl phenyl ketone **27**.[4]

We are continuing our studies in this area and will later report both mechanistic details and synthetic applicability of this method to other metallocyclic systems.

Experimental Section

General Information. Routine ^1H NMR (60 MHz) spectra were recorded on a Varian EM-360 A or L spectrometer. High-resolution ^1H NMR (300-MHz) spectra were recorded on a Nicolet NT-300 spectrometer. ^{13}C NMR spectra were recorded on a Nicolet NT-300 (75.5 MHz) or a JEOL FX90Q (22.5 MHz) spectrometer. All chemical shifts are reported as parts per million (δ scale) from Me_4Si. GC/MS spectra were obtained by using a Finnigan Model 4000 mass spectrometer. Exact masses were recorded on an AEI-MS-902. IR spectra were recorded on an IBM 98 FTIR or a Beckman 4250 spectrophotometer.

Elemental analyses were performed by Galbraith Laboratories, Inc., or by Mic Anal Organic Microanalysis.

Gas chromatographic analyses were performed on a Hewlett-Packard 5790A fitted with a capillary column. Preparative GC was performed on a GOW MAC 550P or a Varian 1700. Yields were determined by ^{1}H NMR using internal standards or by GC using internal standards after determination of appropriate response factors.

Flash vacuum pyrolysis (FVP) pressures were measured by a vacuum ionization gauge, but it should be emphasized that the pressures were measured behind a liquid-nitrogen trap and, therefore, do not represent the actual pressures of the reaction zone.

Synthesis of (Dimethylsilyl)(*o*-(dimethylsilyl)phenyl)acetylene (9). Phenylacetylene (197 mmol) was dimetalated with use of the procedure developed by Brandsma et al.[6] The dark green suspension of the dianion was then cooled to −65 °C, and dimethylchlorosilane (669 mmol) was added as rapidly as possible while the reaction mixture was kept at or below −50 °C at all times. After addition was complete, the yellow suspension was allowed to warm slowly to room temperature (approximately 4 h). The mixture was then poured into ice-cold, dilute H_2SO_4 and extracted with hexane. The organic portion was washed with cold H_2O and then dried over $MgSO_4$. After removal of solvent, the residual yellow oil was fractionally distilled giving 30.1 g (70%) of **9**: bp 77–78 °C (0.5 torr); ^{1}H NMR ($CDCl_3$) δ 0.32 (d, 6 H, J = 3.8 Hz), 0.41 (d, 6 H, J = 3.8 Hz), 4.29 (h, 1 H, J = 3.8 Hz), 4.52 (h, 1 H, J = 3.8 Hz), 7.26–7.34 (m, 2 H), 7.45–7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −3.27, −3.04, 94.24, 107.16, 128.02, 128.32, 129.09, 132.30, 134.73, 140.55; IR (neat) 3072, 3053, 2962, 2902, 2156, 2137, 1581, 1556, 1460, 1427, 1250, 1128, 1074, 887, 839, 771, 760, 734, 723, 702 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 218 (7), 203 (32), 177 (10), 159 (13), 145 (46), 105 (11), 73 (100); calcd for $C_{12}H_{18}Si_2$ m/e 218.094 71, measd m/e 218.094 86. Anal. Calcd for $C_{12}H_{18}$: C, 65.98; H, 8:31. Found: C, 65.70; H, 8.03. Approximately a 20% yield of (dimethylsilyl)phenylacetylene was also obtained: bp 55–61 °C (0.5 torr); ^{1}H NMR ($CDCl_3$) δ 0.3 (d, 6 H, J = 4 Hz), 4.3 (h, 1 H, J = 4 Hz), 7.4 (m, 4 H); IR (neat) 3060, 2964, 2905, 2164, 2141, 1593, 1487, 1252, 883, 845, 771, 756, 741, 690 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 160 (34), 159 (14), 145 (100) 129 (14), 105 (13).

Preparation of (*o*-(Hydroxydimethylsilyl)phenyl)acetylene (10). Acetylene **9** (69 mmol) was added to a solution of MeOH (750 mL) and aqueous NaOH (250 mL, 0.5 M) with external cooling keeping the reaction temperature below 35 °C. The reaction mixture (complete in 30 min) was acidified with dilute H_2SO_4, extracted several times with pentane, washed with H_2O, and dried over $MgSO_4$. After filtration of the $MgSO_4$ and removal of the solvent, the product was distilled to yield 10.2 g (84%) of **10**: bp 64–67 °C (0.15 torr); ^{1}H NMR ($CDCl_3$) δ 0.48 (s, 6 H), 2.60 (br s, 1 H), 3.28 (s, 1 H), 7.31–7.38 (m, 2 H), 7.50–7.60 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.13, 80.18, 85.22, 125.99, 128.23, 129.25, 133.09, 133.49, 142.26; IR (neat) 3300, 3080, 3060, 2965, 2100, 1585, 1465, 1430, 1260, 1125, 1070, 860, 830, 780, 760 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 176 (15), 161 (100), 115 (11), 102 (4), 91 (9), 75 (6); calcd for $C_{10}H_{11}OSi$ ($M^+ - H$) m/e 175.057 92, measd 175.057 55.

Synthesis of (*o*-(Chlorodimethylsilyl)phenyl)acetylene (11). Acetylene **10** (53.4 mmol) was added in one portion to a stirring solution of PCl_5 (53.4 mmol) in 107 mL of CCl_4 at 0 °C. The solution was then heated to reflux for 14 h. After distillation of the solvent and low boiling components, the residue was distilled at 56–57 °C (0.5 torr) to give 6.47 g (62%) of **11**: ^{1}H NMR ($CDCl_3$) δ 0.79 (s, 6 H), 3.30 (s, 1 H), 7.35–7.42 (m, 2 H), 7.52–7.56 (m, 1 H), 7.76–7.79 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 2.80, 81.66, 84.28, 126.46, 128.36, 130.06, 133.36, 134.46, 138.56; IR (neat) 3310, 3090, 3070, 2980, 2100, 1590, 1460, 1430, 1255, 1120, 1060, 835, 810, 790, 755, 715 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 181 (39), 179 (100), 143 (6), 115 (13), 103 (7), 91 (23), 73 (10), 60 (15), 58 (33); calcd for $C_{10}H_{11}ClSi$ m/e 194.031 86, measd m/e 194.031 62.

Synthesis of (2-(Dimethylsilyl)phenyl)acetylene (6). Acetylene **11** (22.5 mmol) was added dropwise to a stirring suspension of lithium aluminum hydride (22.5 mmol) in Et_2O (30 mL) at 0 °C. After complete addition, the reaction was warmed to room temperature and stirred for 15 h. The reaction mixture was hydrolyzed by adding it to ice-cold, dilute H_2SO_4 and then extracted with pentane, washed with H_2O, and dried with $MgSO_4$. After removal of the drying agent and solvents, the products was distilled to give 2.72 g (76%) of **6**: bp 83–87 °C (10 torr); ^{1}H NMR ($CDCl_3$) δ 0.42 (d, 6 H, J = 3.80 Hz), 3.23 (s, 1 H), 4.54 (h, 1 H, J = 3.80 Hz), 7.29–7.38 (m, 2 H), 7.48–7.57 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −3.88, 80.18, 84.21, 127.60, 128.08, 129.13, 132.82, 134.68, 140.48; IR (neat) 3300, 3072, 3053, 2959, 2903, 2125, 1583, 1556, 1462, 1427, 1248, 1126, 1072, 889, 839, 762, 723, 702, 652 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 160 (9), 159 (7), 145 (100), 129 (7), 119 (11), 105 (8), 77 (5), 53 (16); calcd for $C_{10}H_{12}Si$ m/e 160.070 83, measd m/e 160.070 55. Anal. Calcd for $C_{10}H_{12}Si$: C, 74.93; H, 7.55. Found: C, 74.89; H, 7.69.

Synthesis of (*o*-(Deuteriodimethylsilyl)phenyl)acetylene (6-D). The procedure utilized was the same as used for the synthesis of **6**, but lithium aluminum deuteride was substituted for lithium aluminum hydride. From 10.7 mmol of **11**, 4.71 mmol (44%) of **6-D** was obtained, analytically pure, after preparative GC on a 5 ft × 0.25 in. 15% SE-30 Chromosorb W column at 170 °C: ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6 H), 3.23 (s, 1 H), 7.24–7.34 (m, 2 H), 7.5–7.53 (m, 2 H); IR (neat) 3302, 3074, 3053, 2959, 2903, 2104, 1583, 1547 (Si–D), 1461, 1433, 1425, 1258, 1248, 1126, 1072, 839, 797, 762, 725, 683, 652 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 161 (26), 160 (10), 147 (38), 146 (100), 144 (19), 130 (9), 129 (10), 120 (17), 119 (23), 106 (12), 105 (17), 103 (14); calcd for $C_{10}H_{11}DSi$ m/e 161.077 11, measd m/e 161.077 03. No Si–H was detected by NMR or IR; 1% would have been readily observed.

Synthesis of (Dimethylsilyl)(dimethylphenylsilyl)acetylene (24). A solution of *n*-butyllithium in hexane (32.5 mmol, 2.4 M) was added to (dimethylphenylsilyl)acetylene[11] (29.6 mmol) in ether (60 mL) at −78 °C. After being stirred at −78 °C, the mixture was warmed to room temperature and stirred an additional 30 min. After the solution was cooled to 0 °C, chlorodimethylsilane (37.0 mmol) was added rapidly and stirred for 30 min at 0 °C and then at room temperature for 30 min. Lithium chloride was then removed by filtration, and solvents were removed by distillation. Vacuum distillation of the residue gave 24.0 mmol (81%) of **24**: bp 66–74 °C (1.0 torr); ^{1}H NMR ($CDCl_3$) δ 0.26 (d, 6 H, J = 3.7 Hz), 0.42 (s, 6 H), 4.14 (h, 1 H, J = 3.7 Hz), 7.35–7.43 (m, 2 H), 7.60–7.68 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −3.00, −0.84, 112.70, 113.41, 127.92, 129.50, 133.73, 136.56; IR (neat) 3071, 3051, 2962, 2902, 2141, 1429, 1252, 1113, 885, 839, 820, 781, 771, 737, 698 cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 218 (18), 203 (100), 159 (13), 145 (15), 135 (50), 105 (14), 73 (27); calcd for $C_{12}H_{18}Si_2$ m/e 218.094 71, measd m/e 218.094 99. Anal. Calcd for $C_{12}H_{18}$: C, 65.98; H, 8.31. Found: C, 66.16; H, 8.55.

Synthesis of Benzocyclobutanone. A mixture of benzocyclobutanyl acetate[12] (39.8), Na_2CO_3 (39.8 mmol), MeOH (35 mL), and H_2O (70 mL) was sonicated in a Bransonic B-32 ultrasonic bath at 25–36 °C for 3 h. The reaction mixture was extracted with Et_2O, washed with H_2O, and dried with $MgSO_4$. After removel of $MgSO_4$ and solvent, a crystalline solid, benzocyclobutanol (33.4 mmol, 84%), was obtained after recrystallization from pentane: mp 59–60 °C (lit.[11] 58–60 °C). Without the aid of ultrasound, the reaction requires 20 h at room temperature.[11] Benzocyclobutanol (29.7 mmol) was added rapidly to $CrO_3(C_5H_5N)_2$ (178.2 mmol) prepared in situ in CH_2Cl_2 (445 mL). After 15 min at room temperature, the solution was decanted from the residue, which was subsequently washed with Et_2O (400 mL). The combined organic solutions were then washed successively, three times each, with 150-mL portions of 5% aqueous NaOH, 5% aqueous HCl, and 5% aqueous $NaHCO_3$. After drying of the organic layer with $MgSO_4$ and removal of solvents, the residue was distilled, giving 26.7 mmol (90%) benzocyclobutanone: bp 69–71 °C (2 torr). The bp and IR spectrum matched that given by Newsoroff and Sternhell.[11]

Synthesis of 7,7-Dibromo-1-methylenebenzocyclobutene (19). Triphenylphosphine (17.0 mmol) was added in one portion to a stirring solution of CBr_4 (8.5 mmol) in 50 mL of CH_2Cl_2 at 0 °C. After stirring 15 min, benzocyclobutanone (8.5 mmol) in an an equal volume of CH_2Cl_2 was added dropwise. After being

---

[11] Novikova, O. A.; Kuznetsova, V. P.; Kornev, K. A. *Zh. Obshch. Khim.* **1968**, *38*, 178.

[12] Newsoroff, G. P.; Sternhell, S. *Aust. J. Chem.* **1972**, *25*, 1669.

stirred an additional 10 min, the mixture was slowly added to 500 mL of hexane. The solution was decanted and then concentrated, resulting in the precipitation of more Ph_3PO. Addition of recovered hexane followed by filtration to remove the precipitate and concentration gave the crude product. Crystallization from $EtOH/H_2O$, 4:1, gave 6.7 mmol of **19**: mp 49–51 °C; ^{1}H NMR ($CDCl_3$) δ 3.5 (s, 2 H), 7.1–7.5 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 41.31, 78.96, 119.53, 122.46, 127.82, 130.37, 141.64, 142.45, 142.99; IR (neat) 3080, 3060, 2930, 2830, 1460, 1445, 1415, 1280, 1180, 1150, 1140, 1000, 830, 815, 790, 770, 750, 705 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 276 (25), 274 (48), 272 (27), 195 (99), 193 (100), 113 (82), 97 (12), 95 (13), 86 (17), 72 (10), 61 (19), 57 (17); calcd for $C_9H_6Br_2$ *m/e* 271.883 62, measd *m/e* 271.883 39.

Synthesis of 7-Bromo-1-methylenebenzocyclobutene (20). Freshly distilled diethyl phosphite (8.97 mmol) was dissolved in 4.08 mmol of 7,7-dibromo-1-methylenebenzocyclobutene (**19**). Triethylamine (8.97 mmol) was then added, and the reaction was followed by TLC. After 18 h, the reaction was complete, Et_2O was then added, and Et_3NHBr was removed by filtration. Column chromatography of the filtrate on a silica gel column eluted with hexane gave 3.85 mmol (94%) of **20** as a 1:1 mixture of *E* and *Z* isomers: ^{1}H NMR ($CDCl_3$) δ 3.62 (apparent s, 4 H), 5.95 (unresolved t, 1 H), 6.35 (t, 1 H, J = 2 Hz), 7.0–7.6 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 39.09 (two coincidental peaks), 95.05, 96.13, 118.12, 120.56, 122.51, 122.95, 127.60 (two peaks), 129.39, 129.88, 130.37, 140.50, 142.56, 142.99, 143.69, 144.40; IR (neat) 3090, 2930, 1670, 1465, 1445, 1415, 1330, 1230, 770, 740, 695, 690 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 196 (17), 194 (17), 115 (100), 89 (13), 63 (12); calcd for C_9H_7Br *m/e* 193.973 11, measd *m/e* 193.972 94.

Synthesis of 7-(Trimethylsilyl)-1-methylenebenzocyclobutene (21). A solution of 7-bromo-1-methylenebenzocyclobutene (2.72 mmol) in Et_2O (30 mL) was cooled to −78 °C. A solution of *tert*-butyllithium in pentane (5.71 mmol, 1.9 M) was then added dropwise, and the reaction was allowed to stir for 45 min. Trimethylchlorosilane was then added dropwise, and the mixture was stirred for 20 min before being warmed to room temperature. After being stirred at room temperature for 1 h, the reaction was then extracted with H_2O and additional Et_2O and dried over $MgSO_4$. After filtration of the $MgSO_4$ and removal of the solvent, the residue was chromatographed on silica gel and eluted with hexane, giving 2.14 mmol of **21** as a 1:1 mixture of *E* and *Z* isomers: ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 0.24 (s, 9 H), 3.60 (unresolved d, 2 H), 3.65 (d, 2 H, J = 2 Hz), 5.48 (unresolved t, 1 H), 5.94 (t, 1 H, J = 2 Hz), 7.2–7.5 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ −0.57, −0.14, 40.33, 41.31, 101.66, 117.69, 117.85, 120.40, 120.56, 122.78, 120.00, 127.28, 128.80, 128.96, 129.34, 145.86, 146.02, 146.30, 147.00, 152.09; IR (neat) 3070, 2960, 2920, 1645, 1585, 1445, 1245, 855, 835, 750, 735 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 188 (7), 173 (3), 145 (15), 73 (100), both isomers show identical breakdown patterns and vary only slightly in relative intensities. High-resolution mass spectrum (of the mixture of the isomers) for $C_{12}H_{16}Si$: calcd *m/e* 188.10213, measd *m/e* 188.10176. Anal. (of the isomeric mixture) Calcd for $C_{12}H_{16}$: C, 76.53; H, 8.56. Found: C, 76.49; H, 8.87.

Pyrolysis of (*o*-(Dimethylsilyl)phenyl)acetylene (6). (i) Acetylene **6** (73.6 mg) was pyrolyzed by distillation (40 °C, 8 × 10^{-5} torr), over a 30-min period, through a horizontal quartz tube packed with quartz chips heated to 800 °C. The pyrolysate (63.1 mg, 85.7%) was collected in a cold trap cooled with liquid nitrogen. The clear, colorless pyrolysate was analyzed by GC and ^{1}H NMR and found to contain only 1,1-dimethyl-1-silaindene (**8**, 84%, NMR yield) based on comparison of its spectra (GC/MS, ^{1}H NMR, ^{13}C NMR) with those of an authentic sample and published data.[7]

(ii) Acetylene **6** (36.1 mg) was pyrolyzed by distillation (40 °C, 2 × 10^{-5} torr), over a 15-min period, through a horizontal quartz tube packed with quartz chips heated to 700 °C. The pyrolysate (34.0 mg, 94.2%) was collected in a cold trap cooled with liquid nitrogen. Analysis by GC/MS and ^{1}H NMR showed two isomers present. The major isomer was determined to be 1,1-dimethyl-1-silaindene (**8**, 77%, NMR yield). It was not possible to separate the isomers on a packed GC column, and all attempts at preparative GC resulted in near complete destruction of the unidentified isomer. This isomer was determined to be 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene (**12**, 17%, NMR yield) based on its spectra (subtracted of **8** for ^{1}H NMR and ^{13}C NMR and separately in GC/MS and GC/IR data): ^{1}H NMR ($CDCl_3$) δ 0.49 (s, 6 H), 5.30 (d, 1 H, J = 1.3 Hz), 5.92 (d, 1 H, J = 1.3 Hz); ^{13}C NMR ($CDCl_3$) δ −0.84, 113.02, 118.42, 128.11, 130.58, 131.17, 148.79, 152.24, 155.16; GC/IR (gas phase) 3063, 2974, 2908, 1285, 1254, 1042, 899, 856, 795 cm^{-1}; GC/MS (70 eV), *m/e* (relative intensity) 160 (32), 145 (100), 119 (12), 105 (8), 93 (6), 77 (7), 53 (16).

(iii) Acetylene **6** (106.2 mg) was pyrolyzed by distillation (40 °C, 2 × 10^{-5} torr), over a 40-min period, through a horizontal quartz tube packed with quartz chips heated to 650 °C. The pyrolysate (94.5 mg, 89.0%) was collected in a cold trap cooled with liquid nitrogen. Analysis by ^{1}H NMR revealed starting material **6**, 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene (**12**), and 1,1-dimethyl-1-silaindene (**8**) in 2%, 34%, and 47% yields (NMR), respectively.

(iv) Acetylene **6** (94.7 mg) was pyrolyzed by distillation (40 °C, 1 × 10^{-5} torr), over a 40-min period, through a horizontal quartz tube packed with quartz chips heated to 600 °C. The pyrolysate (88.3 mg, 93.2%) was collected in a cold trap cooled with liquid nitrogen. Analysis by ^{1}H NMR revealed starting material **6**, 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene (**12**), and 1,1-dimethyl-1-silaindene (**8**) in 22%, 28%, and 42% yields (NMR), respectively.

Pyrolysis of (*o*-(Deuteriodimethylsilyl)phenyl)acetylene (6-D). (i) Acetylene **6-D** (112.3 mg) was pyrolyzed by distillation (40 °C, 2 × 10^{-4} torr), over a 40-min period, through a horizontal quartz tube packed with quartz chips heated to 800 °C. The pyrolysate (104.4 mg, 93.0%) was collected in a cold trap cooled with liquid nitrogen. Analysis by ^{1}H NMR revealed 2-deuterio-1,1-dimethyl-1-silaindene (**8-2D**) and 3-deuterio-1,1-dimethyl-1-silaindene (**8-3D**) in 73% and 19% yields (NMR), respectively: ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 6 H), 6.25 (s, 0.2 H), 7.1–7.34 (m, 3.8 H), 7.47–7.54 (d, 1 H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ −4.03, 124.08, 126.87, 129.67, 131.62, 132.27, 138.45, 149.11, 149.35; mass spectrum (14 eV), *m/e* (relative intensity) 161 (100), 146 (13); calcd for $C_{10}H_{11}DSi$ *m/e* 161.077 11, measd *m/e* 161.077 09. The sp^2 resonance signals at δ 132.27 (C_1) and 149.11 (C_2) showed a strong correlation with the amount of deuterium incorporation (a 65% reduction and 29% reduction in the signal intensities, respectively, compared to the undeuterated material). Assignment of these signals was made possible with the additional information gained below. (See ^{1}H and ^{13}C NMR elucidation of 1,1-dimethyl-1-silaindene (**8**).)

(ii) Acetylene **6-D** (113.5 mg) was pyrolyzed by distillation (40 °C, 2 × 10^{-5} torr), over a 40-min period, through a horizontal quartz tube packed with quartz chips heated to 600 °C. The pyrolysate (109 mg, 96%) was collected in a cold trap cooled with liquid nitrogen. Analysis of ^{1}H NMR ($CDCl_3$) revealed **8-2D**, **8-3D**, 7-deuterio-1,1-dimethyl-2-methylenebenzo-1-silacyclobutene (**12-D**), and starting material **6-D** in 17%, 2%, 27%, and 46% yields (NMR), respectively. The ^{1}H NMR of **12-D** shows singlet resonances at δ 5.29 (0.5 H) and 5.90 (0.5 H) revealing a 1:1 mixture of the *E* and *Z* isomers as expected. Additional supporting spectra of **12-D** include the following: GC/MS (70 eV), *m/e* (relative intensity) 161 (35), 146 (100), 119 (11), 105 (8), 93 (7), 67 (6), 53 (17); GC/IR (gas phase) 3063, 3009, 2974, 2908, 2233 (C-D), 1254, 1042, 852, 795 cm^{-1}.

Copyrolysis of the Mixture of (*o*-Dimethylsilylphenyl)acetylene (6), 1,1-Dimethyl-2-methylenebenzo-1-silacyclobutene (12), and 1,1-Dimethyl-1-silaindene (8). The mixture of isomers **6**, **12**, and **8** was obtained by the distillation (40 °C, 2 × 10^{-5} torr) of **6** (222 mg), over a 70-min period, through a horizontal quartz tube packed with quartz chips heated to 640 °C. The pyrolysate (215 mg, 97%) was collected in a cold trap cooled with liquid nitrogen. The pyrolysate was analyzed by ^{1}H NMR and determined to be comprised of a mixture of **6** (8%), **12** (58%), and **8** (34%). A sample (100.0 mg) of this mixture was then pyrolyzed by distillation (40 °C, 1 × 10^{-4} torr), over a 40-min period, through a horizontal quartz tube packed with quartz chips heated to 800 °C. The pyrolysate (93 mg, 93%) was collected in a cold trap cooled with liquid nitrogen. Analysis by GC and ^{1}H NMR showed only **8** (93%, NMR yield) to be present in the pyrolysate.

Pyrolysis of Dimethylsilyl(*o*-(dimethylsilyl)phenyl)acetylene (9). (i) Acetylene **9** (405.3 mg) was pyrolyzed by distillation (60 °C, 1 × 10^{-3} torr), over a 60-min period, through a horizontal quartz tube packed with quartz chips heated to 800

°C. The pyrolysate (351.5 mg, 86.7%) was collected in a cold trap cooled with liquid nitrogen. The clear, yellow pyrolysate was analyzed by GC and ^{1}H NMR and found to contain a mixture of 1,1-dimethyl-1-silaindene (**8**), 3-(dimethylsilyl)-1,1-dimethyl-1-silaindene (**16**), and 2-(dimethylsilyl)-1,1-dimethyl-1-silaindene (**18**) in 15%, 62%, and 4% yields (NMR), respectively. Components of the mixture were purified by preparative GC on a 5 ft × 0.25 in. 12% SE-30 Chromosorb W column temperature programmed from 200 to 250 °C at 5 °C per min. Compound **8** was isolated and identified by its ^{1}H NMR and mass spectrum. Isomers **16** and **18** were individually identified by GC/MS and GC/IR but were not separable by preparative GC. ^{1}H and ^{13}C NMR, high-resolution mass spectra, and elemental analysis were performed on the isomer mixture. Supportive data for **16** includes the following: ^{1}H NMR (CDCl$_3$) δ 0.38 (s, 6 H), 0.42 (d, 6 H, J = 3.8 Hz), 4.56 (h, 1 H, J = 3.8 Hz), 6.90 (s, 1 H), 7.18–7.67 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ −4.02, −3.94, 124.54, 126.52, 129.68, 131.72, 139.17, 146.73, 151.60, 163.01; GC/IR (gas phase) 3055, 2960, 2120, 1585, 1440, 1250, 1150, 1130, 945, 870, 820, 780, 750 cm^{-1}; GC/MS (70 eV), *m/e* (relative intensity) 218 (69), 203 (100), 177 (12), 159 (11), 145 (40), 105, (6), 73 (41); high-resolution mass spectrum (70 eV) calcd for $C_{12}H_{18}Si_2$ *m/e* 218.09471, measd *m/e* 218.09420. Anal. Calcd for $C_{12}H_{18}$: C, 65.98; H, 8.31. Found: C, 65.74; H, 8.47. Data for **18**: ^{1}H NMR (CDCl$_3$) δ 0.24 (d, 6 H, J = 3.8 Hz), 4.32 (h, 1 H, J = 3.8 Hz), the vinyl H is buried in the aromatic absorption, definitive analysis of the PMR spectra of **16** and **18** required the detailed analysis of the spectrum of **8** (vide infra); GC/IR (gas phase) 3055, 2960, 2120, 1520, 1440, 1250, 1130, 980, 880, 820, 780, 750 cm^{-1}; GC/MS (70 eV), *m/e* (relative intensity) 218 (17), 203 (27), 177 (3), 159 (5), 145 (31), 105 (8), 73 (100).

(ii) Acetylene **9** (409.4 mg) was pyrolyzed by distillation (60 °C, 5 × 10^{-4} torr), over a 60-min period, through a horizontal quartz tube packed with quartz chips heated to 700 °C. The pyrolysate (397.3 mg, 97.0%) was collected in a cold trap cooled with liquid nitrogen. The clear, yellow pyrolysate was analyzed by ^{1}H NMR and found to contain 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene (**12**), 1,1-dimethyl-1-silaindene (**8**), 2-(dimethylsilyl)-1,1-dimethyl-1-silaindene (**18**), and 3-(dimethylsilyl)-1,1-dimethyl-1-silaindene (**16**) in 1%, 2%, 2%, and 64% yields (NMR) based on 53% recovered starting material **9**.

Copyrolysis of 2- and 3-(Dimethylsilyl)-1,1-dimethyl-1-silaindenes (18 and 16). A mixture of **16** and **18** (114.0 mg, 96:6) was pyrolyzed by distillation (60 °C, 4 × 10^{-4} torr), over a 30-min period, through a horizontal quartz tube packed with quartz chips heated to 800 °C. The pyrolysate (95.1 mg, 83.4%) was collected in a cold trap cooled with liquid nitrogen. The pyrolysate was analyzed by ^{1}H NMR and found to contain 1,1-dimethyl-1-silaindene (**8**) and 2- and 3-(dimethylsilyl)-1,1-dimethyl-1-silaindenes (**18** and **16**) in 15%, 5%, and 63% yields (NMR), respectively.

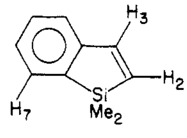
Pyrolysis of 7-(Trimethylsilyl)-1-methylenebenzocyclobutene (21). (i) Compound **21** (46 mg) was pyrolyzed by distillation (30 °C, 1 × 10^{-2} torr), over a 10-min period, through a horizontal quartz tube packed with quartz chips heated to 620 °C. The pyrolysate (40 mg, 87%) was collected in a cold trap cooled with liquid nitrogen. The pyrolysate was analyzed by NMR and GC and found to contain only *o*-tolyl(trimethylsilyl)acetylene (87%, NMR) based on comparison by ^{1}H NMR, IR, and GC/MS with an authentic sample.

(ii) Compound **21** (50 mg) was pyrolyzed by distillation (30 °C, 1 × 10^{-2} torr), over a 10-min period, through a horizontal quartz tube packed with quartz chips heated to 520 °C. The pyrolysate (32 mg, 80%) was collected in a cold trap cooled with liquid nitrogen. The pyrolysate was analyzed by NMR and GC and found to contain *o*-tolyl(trimethylsilyl)acetylene and starting material **21** in 35% and 45% yields (NMR), respectively.

Pyrolysis of (Dimethylsilyl)(dimethylphenylsilyl)acetylene (24). Acetylene **24** (187.1 mg) was pyrolyzed by distillation (60 °C, 4 × 10^{-4} torr), over a 40-min period, through a horizontal quartz tube packed with quartz chips heated to 800 °C. The pyrolysate (141.3 mg, 75.5%) was collected in a cold trap cooled with liquid nitrogen. The products were isolated by preparative GC on a 5 ft × 0.25 in. 20% SE-30 Chromosorb W column temperature programmed from 100 to 250 °C at 6 °C/min. Identified from the mixture, by comparison of their ^{1}H NMR and GC/MS spectra with authentic samples, was dimethylphenylsilane, dimethylphenylsilylacetylene, and 1,1-dimethyl-1-silaindene (**8**) in 4%, 50%, and 3% yields (GC) based on 22% recovered starting material **24**.

Pyrolysis of (Dimethylphenylsilyl)acetylene (25). Acetylene **25** (202.1 mg) was pyrolyzed by distilltion (20 °C, 1 × 10^{-4} torr), over a 60-min period, through a horizontal quartz tube packed with quartz chips heated to 850 °C. The pyrolysate (174.0 mg, 86.1%) was collected in a cold trap cooled with liquid nitrogen. The products were isolated by preparative GC on a 5 ft × 0.25 in. 20% SE-30 Chromosorb W column temperature programmed from 100 to 250 °C at 6 °C/min. Identified from the mixture, by comparison of their ^{1}H NMR and GC/MS spectra with authentic samples, were phenylacetylene, dimethylphenylsilane, and 1,1-dimethyl-1-silaindene (**8**) in 7%, 3%, and 14% yields (GC) based on 71% recovered starting material **24**.

^{1}H and ^{13}C NMR Elucidation of 1,1-Dimethyl-1-silaindene (8). To determine the assignment of the proton and carbon resonance signals of the silaindenyl ring, the structure was probed with a Nicolet NT-300, 300-MHz ^{1}H, 75.5-MHz ^{13}C NMR spectrometer. First, the normal ^{1}H NMR (CDCl$_3$) spectrum was taken: δ 0.31, (s, 6 H), 6.26 (d, 1 H$_2$, J = 10.3 Hz), 7.17–7.41 (m, 4 H), 7.51 (d, 1 H$_7$, J = 6.9 Hz). Irradiation of the doublet at δ 6.26 resulted in the collapse of a doublet at δ 7.32. These two signals were tentatively ascribed to H$_2$ and H$_3$ of the indenyl ring. This assignment was then confirmed by performing a NOE experiment. A sample of 1,1-dimethyl-1-silaindene (**8**) in CDCl$_3$ was degassed by 10 freeze–thaw cycles and then sealed under vacuum. The ^{1}H spectrum was then acquired by using a 20-s pulse delay while irradiating at the silicon methyl resonance δ 0.31. A second ^{1}H spectrum was then acquired under the same conditions while irradiating at δ 11.6. The two Fourier transformed spectra were then subtracted from each other leaving only the silicon methyl signal and two residual NOE enhanced signals at δ 6.26 and 7.51. These two signals were assigned to H$_2$ and H$_7$. Quantitatively these signals showed 8% (H$_2$) and 16% (H$_7$) enhancements by integration of the spectrum irradiated at δ 0.31. No NOE was observed for the resonance at δ 7.32 (H$_3$).



8

The ^{13}C NMR spectrum of **8** was then taken in CDCl$_3$ (broad-band-decoupled): δ −4.05, 124.06, 126.91, 129.67, 131.61, 132.38, 138.50, 149.20, 149.34. A single off-resonance-decoupled (SORD) spectrum was acquired while irradiating at δ 6.26: δ −4.01, (q, J = 28.2 Hz), 124.05, 126.87, 129.65, 131.59 (d, J = 5.7 Hz), 132.38, 138.41, 149.18 (d, J = 5.7 Hz), 149.27. The signal at δ 132.38 was strongly enhanced relative to all other sp^2 resonance signals and was assigned to the carbon bearing H$_2$. A second ^{13}C NMR SORD spectrum was then acquired while irradiating at δ 7.32 within the aromatic multiplet: δ −4.00 (q, J = 30.1 Hz), 124.07, 126.87, 129.67, 131.61, 132.39 (d, J = 3.7 Hz), 138.40, 149.18, 149.27. Even though the resonance signals at δ 131.61 and 149.18 were both enhanced and collapsed into singlets, only the signals at δ 149.18 and 132.38 showed a reduction in intensities in the labeled compounds (see pyrolysis of (*o*-(deuteriodimethylsilyl)phenyl)acetylene (**6-D**)). Therefore, the carbon atom bearing H$_3$ was assigned to the signal at δ 149.18.

Acknowledgment. The support of this work by the National Science Foundation is gratefully acknowledged.

Registry No. **6**, 94138-33-7; **6-D**, 94138-45-1; **8**, 58310-24-0; **8-2D**, 94138-46-2; **8-3D**, 94138-47-3; **9**, 94138-34-8; **10**, 94138-35-9; **11**, 94138-36-0; **12**, 94138-37-1; (*E*)-**12-D**, 94138-48-4; (*Z*)-**12-D**, 94138-49-5; **16**, 94138-38-2; **18**, 94138-39-3; **19**, 94138-40-6; (*E*)-**20**, 94138-41-7; (*Z*)-**20**, 94138-50-8; (*E*)-**21**, 94138-42-8; (*Z*)-**21**, 94138-43-9; **23**, 3989-15-9; **24**, 94138-44-0; **25**, 17156-64-8; CrO$_3$-(C$_5$H$_5$N)$_2$, 20492-50-6; Me$_2$SiHCl, 1066-35-9; Ph$_3$P, 603-35-0; CBr$_4$, 558-13-4; H(O)P(OEt)$_2$, 762-04-9; Me$_3$SiCl, 75-77-4; Me$_2$PhSiH, 766-77-8; phenylacetylene, 536-74-3; benzocyclobutanone, 3469-06-5; benzocyclobutanyl, 3469-03-2; benzocyclobutanol, 35447-99-5.