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Radical-Induced Formation of Some Siloles and Diazasiloles

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The Bu_3Sn radical-induced reaction of *o*-iodobenzylvinylsilanes and *o*-iodoallylsilanes leads to cyclic products in yields of 40−60%. These regioselective cyclizations occur with high preference for a 5-exo and a 7-endo mode with a 6-exo mode being absent. An example for ring closure via a 7-exo mode is described.

Introduction

In the course of our interest in siloles, aza-siloles, and polycyclic silaalkanes, we considered intramolecular, radical-induced cyclizations as an attractive method for their preparation. Intramolecular free-radical-mediated formation of C−C bonds has been studied for a long time and is one of the important methods for the synthesis of carbocyclic compounds.[1] This synthetic potential is further underlined by tandem radical cyclizations, useful for the preparation of natural products and architectural structures.[2−8] Recently, tandem radical cyclizations have been used for the preparation of steroid analogues via acyl radical intermediates.[9−11] Intramolecular radical reactions of ortho-substituted phenyl halides induced by tributyltin radicals have been explored for the preparation of indanes, dihydroindoles, dihydrobenzofurans and tetrahydrobenzopyrans.[12−17] These reactions of ortho-substituted phenyl halides have also been initiated by samarium(II) iodide[18,19] or sodium naphthalenide.[20]

Whereas the regioselectivities of cyclization reactions of hex-5-enyl and hex-5-inyl radicals are well-established[1], the number of analogous examples in Si chemistry is much smaller.[21] Nevertheless, it is apparent that the larger Si−C bond lengths enhance a 6-endo-trig cyclization at the expense of a 5-exo-trig reaction.[22] Beyond the synthesis of silaalkanes, it was of interest to investigate the regioselectivity in the cyclization of *o*-iodobenzylvinyl- and *o*-iodobenzylallylsilanes. In addition, we explored radical-induced cyclization reactions of some spirotetraazasilanes.[1]

The *o*-iodobenzylvinyl- and *o*-iodobenzylallylsilanes **4a**−**d** and the trimethylsilylethinylsilane **4e** were prepared from *o*-bromobenzyl bromide **1** in two steps (Scheme 1).[23] When the *o*-bromobenzylvinylsilane **3b** was treated with tributyltin hydride and AIBN in reflux benzene, no radical cleavage of the C−Br bond was observed. Addition of tributyltin hydride to the vinylic groups rather than ring closure products was observed. Apparently, the cleavage of the aromatic C−Br bond is slower than the addition of the tributyltin radical to the vinyl groups attached to silicon. Subsequently *o*-iodobenzylsilanes **4a**−**e** were submitted to the radical conditions to attempt ring closure via a 5-exo cyclization.[24−29]

Results and Discussion

When the *o*-iodobenzyldimethylvinylsilane **4a** was treated with tributyltin hydride and AIBN, the siloles **8a** and **9a** were formed in 72% and 3% yield, respectively (Scheme 2). 5-Exo-trig cyclization also took place in preference to the 6-endo reaction with **4b** and gave 60% **8b** and 5% **9b**. When **4b** was placed in a 90 °C oil bath

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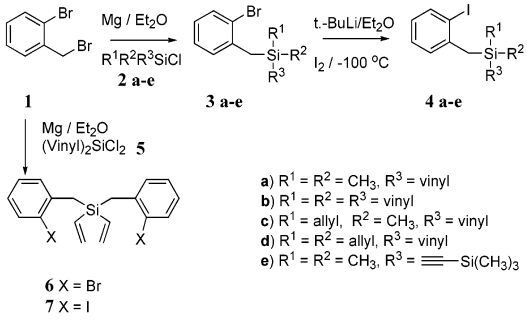
SCHEME 1



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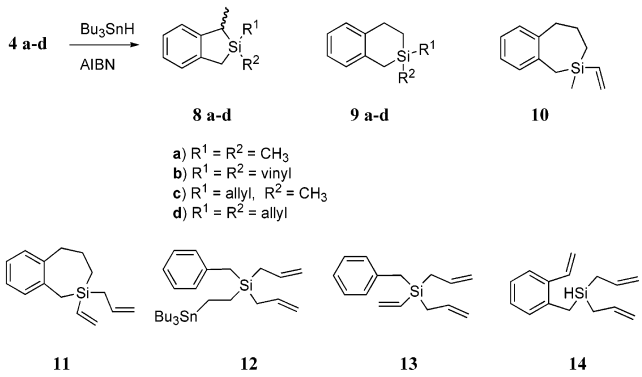


and a solution of tributyltin hydride and AIBN in benzene was injected very slowly, the yield of the 6-endo product **9b** increased to 25%, while the 5-exo product **8d** was still formed preferentially (Scheme 2).

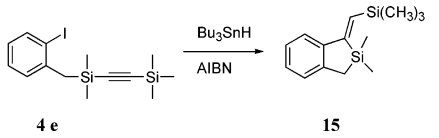
Treatment of the *o*-iodobenzylallylvinylmethylsilane **4c** with Bu_3SnH and AIBN gave products **8c** (mixture of diastereomers) and **9c** as well as **10** in 40%, 8%, and 25% isolated yield, respectively. In this case, the 7-endo cyclization is competitive with the 5-exo cyclization, while the 6-endo reaction appears to be rather slow. Neither products arising from a 6-exo cyclization nor from a cascade reaction were observed (Scheme 2).

When **4d** was treated with Bu_3SnH and AIBN in reflux benzene, the siloles **8d** and **9d** were formed via a 5-exo and 6-endo cyclization in 29% and 6% yield, respectively. The 7-endo product **11** was obtained in 18% yield, whereas the three noncyclic products **12**, **13,** and **14** are formed in rather low yields (2%, 5%, and 4%) (Scheme 2). Again, a cascade product has not been detected. Since the *o*-iodobenzylvinylsilanes **4a**−**d** are converted preferentially to the siloles **8a**−**d**, it was tempting to attempt to prepare a spirosilane from **7** by a double 5-endo cyclization. When **7** was submitted to the standard reaction conditions, a complex mixture of compounds was obtained. GC−MS data did not allow us to assign a structure to any of these compounds. When **4e** was treated with Bu_3SnH, the reaction was highly selective and gave exclusively the cis-5-exo product **15** in 90% yield (Scheme 3). The configuration of **15** was determined by NOE.

In a further attempt to prepare diazasiloles containing a N−Si−N group, we prepared the spirotetraazasilane **18a** and investigated radical-induced cyclizations (Scheme 4).

When **18a** was refluxed in toluene with Bu_3SnH and AIBN, the monoadduct **19** was obtained in 42% yield. At

SCHEME 3



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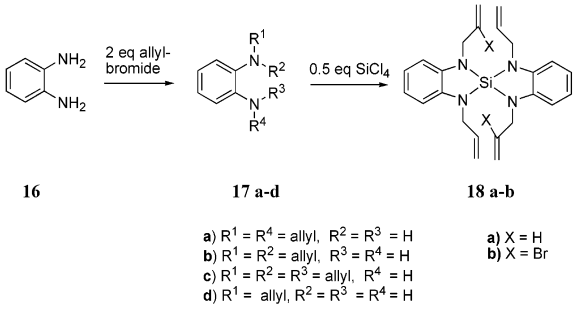

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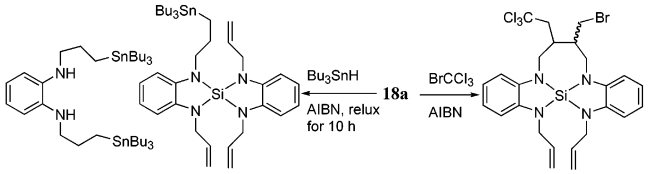
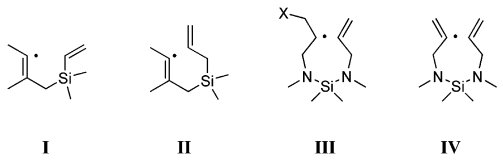


SCHEME 6



a 10-fold higher dilution with a reaction time of 7 days, the bis-tributylstannyl adduct **20** was isolated 36% yield. No cyclization products were observed. However, when **18a** was treated with bromotrichloromethane and AIBN, the monocyclization product **21** could be isolated in low yield as a mixture of stereoisomers (Scheme 5).

It is apparent from the intramolecular, radical-induced reactions of the *o*-iodobenzylalkenylsilanes investigated that both 5-exo and 6-endo cyclizations occur with a preference for the *o*-iodobenzylethynylsilane **4e**, and a highly selective 5-exo-digonal cyclization is observed. The results with **4c,d** clearly indicate that the vinyl group reacts in preference to the allyl group (Scheme 2). The small amount of siloles **10** and **11** obtained from the reactions of **4c** and **4d**, respectively, and the absence of any silamethylcyclohexane products suggest that radicals of type **II** cyclize preferentially via a 7-endo pathway rather than a 6-exo route (Scheme 6). It is quite different from the cyclization reactions of 5-hexenyl and 6-heptenyl radicals, which are exothermic and irreversible reactions with a preference for formation of the smaller ring size by cyclization in the exo mode.[21,30] While in the case of **18a** a Bu_3Sn radical-induced cyclization has not been found, a 7-exo cyclization has been observed with $BrCCl_3$ in the presence of AIBN, giving **21**. In view of the selec-

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tive reaction of **18b** via a double 8-endo cyclization, leading to a tetraazasilafenestrane,[31] the formation of the tricyclic diazasilaheptane **21** in the case of **18a** is remarkable. However, it is certainly premature to draw conclusions from this result concerning the stereoelectronic requirements of the preferred pathway of cyclizations leading to larger rings involving Si and N−Si−N groups.

Conclusions

A variety of siloles have been prepared from *o*-iodobenzylalkenylsilanes via radical reactions induced by Bu_3SnH in the presence of AIBN. The precursors are readily prepared in two steps. These radical-induced cylizations with silicon compounds have been explored with respect to the impact of Si on the chemo- and regioselectivity. It is apparent that vinyl groups bonded to the Si atom react in preference to allyl groups. No cascade cyclization reactions have been observed for **4b**−**c**. Furthermore, products arising from 6-exo cyclizations have not been observed.

Experimental Section

General. All reactions are performed under an Ar or N_2 atmosphere. Chemicals were purchased from commercial suppliers and used without further purification. *tert*-Butyllithium was used as a 1.7 M solution in pentane. After workup by pouring the reaction mixture onto ice and extraction of the aqueous phase with ether, the solutions were dried over $MgSO_4$ and the residue purified by flash chromatography or column chromatography. Thin-layer chromatography was performed on silica gel plates SIL G/UV_{254} with hexane as eluent, if not stated otherwise. GC analyses were used with a HP-5 Ultra capillary column (length 10 m, i.d. 0.2 mm) with a temperature program 40−220 °C (3°/min), and t_R are reported in minutes. Preparative HPLC was performed with a 715004 ET, 250/10, Nuc. 50−7 column (flow: 12 mL/min. NMR spectra (^{1}H, 300 MHz; ^{13}C, 75 MHz, ^{29}Si, 99.325 MHz) were measured in $CHCl_3$ and $CDCl_3$ respectively. Chemical shifts are given relative to $Si(CH_3)_4$ in δ (ppm) for ^{1}H NMR, $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR, and $Si(CH_3)_4$ (δ = 0.0 ppm) for ^{29}Si NMR. Coupling constants are given in hertz and multiplicities are indicated as s (singlet), d (doublet) t (triplet), q (quartet), m (multiplet), and st (stack). Mass spectra (MS) are reported in units of *m*/*z* and in relative intensities to the base peak (100%).

Diallylvinylchlorosilane 2d. To a solution of 8.07 g (0.05 mol) of vinyltrichlorosilane in dry THF was added dropwise 50 mL of 2 M allylmagnesiumchloride (0.1 mol) in THF at 0 °C.[32] The mixture was slowly warmed to room temperature and stirred for another 1 h. Distillation at 135−140 °C/200 mmHg gave 3.4 g (40%) **2d**.

The preparation of the compounds **4a**−**e** from **1** via **3** is described elsewhere.[29]

Bis(*o*-bromobenzyl)divinylsilane (**6**) To 0.24 g (0.01 mol) of Mg in 40 mL of dried diethyl ether was added a solution of 2.5 g (0.01 mol) 2-bromobenzyl bromide **(1)** in 10 mL of diethyl ether at −5 °C.[33] The mixture was stirred at this temperature until the Mg disappeared completely. The chlorosilane **(5)** (0.4 mol equiv) was added and the mixture refluxed for 24 h. After workup with NH_4Cl (aq), and extraction of the water phase twice with diethyl ether, the combined organic phases were dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by flash chromatography with hexane to give **6** as colorless oil. Yield: 0.69 g (41%). R_f (hexane): 0.30. IR: 1470 (s), 1435 (s), 1404 (s), 1160 (s), 1020 (s), 1005 (s), 960 (s), ^{1}H NMR: 2.58 (s, 4 H), 5.69−5.83 (m, 2 H), 6.06−6.20 (m, 4 H), 6.95−7.00 (m, 2 H), 7.08−7.20 (m, 4 H), 7.52−7.55 (m, 2 H). ^{13}C NMR: 23.12 (t), 124.07 (s), 126.01 (d), 127.05 (d), 130.11 (d), 132.72 (d), 133.57 (d), 135.01 (t), 139.06 (s). ^{29}Si NMR: −15.020. MS: 422 (M + 2^+, 5), 420 (M, 4), 395 (8), 252 (100), 225 (22), 180 (37), 171 (80), 161 (27), 145 (56), 137 (48), 129 (25), 115 (40), 109 (35). HR-MS: found 419.9742, calcd $C_{18}H_{18}Br_2Si$ 419.9545.

Bis(*o*-iodobenzyl)divinylsilane 7. To an ethereal solution of the *o*-bromobenzylsilane **6** (1 mmol) in 10 mL of dried diethyl ether was added 2 equiv of *t*-BuLi at −100 °C.[34] The reaction was followed by TLC. When the starting material had disappeared (ca. 10 min), 2.4 equiv of I_2 in 5 mL of diethyl ether was added and the mixture slowly warmed to room temperature. After workup with 5% Na_2SO_3 (aq) the residue was purified by chromatography with hexane to give **7** as colorless oil. Yield: 0.39 g (75%). R_f (hexane): 0.23. IR: 1460 (m), 1430 (m), 1405 (m), 1160 (m), 1010 (s), 960 (m). ^{1}H NMR: 2.62 (s, 2 H), 5.72−5.79 (m, 2 H), 6.06−6.21 (m, 4 H), 6.76−6.82 (m, 2 H), 7.08−7.11 (m, 2 H), 7.17−7.23 (m, 2 H), 7.79−7.82 (m, 2 H). ^{13}C NMR: 28.27 (t), 101.22 (s), 126.20 (d), 127.99 (d), 129.00 (d), 133.62 (d), 135.24 (t), 139.45 (d), 142.58 (s). ^{29}Si NMR: −15.020. MS: 515 ([M + 1]$^+$, 4), 489 (4), 300 (22), 299 (88), 298 (100), 183 (14), 171 (11), 145 (20), 119 (10). HR-MS: found 515.9302, calcd $C_{18}H_{18}I_2Si$ 515.9367.

General Procedure for the Reactions of 4a−e with Tributyltin Hydride. A solution of the precursor (1 mmol), 1.2 mmol of Bu_3SnH, and 0.1 mmol of AIBN in benzene (20 mL) was degassed by bubbling Ar into the solution under ultrasound for 30 min, placed in an oil bath, preheated to 90 °C, and refluxed for 14 h. The solvent was removed, and after addition of diethyl ether (30 mL) and 10% KF (aq) (20 mL), the mixture was stirred for 4 h. The white precipitate was filtered off, and the filtrate was separated. The aqueous phase was extracted with diethyl ether. Drying combined organic extraction over anhydrous $MgSO_4$ and evaporating the solvent gave the crude product, which was purified by flash chromatography and preparative GC.

Radical Reaction of 4a: 1,2,2-Trimethyl-2,3-dihydro-1*H*-benzo[*c*]silole 8a. GC-purified. Yield: 127 mg (72%) as colorless oil. R_f (hexane): 0.45. IR: 2960 (w), 1676 (s), 1358 (m), 1256 (s), 1154 (m). ^{1}H NMR: 0.13 (s, 3 H), 0.23 (s, 3 H), 1.30 (d, *J* = 7.7 Hz, 3 H), 1.99 (d, *J* = 17.3 Hz, 1 H), 2.07 (d, *J* = 17.3 Hz, 1 H), 2.18 (q, *J* = 7.7 Hz, 1 H), 7.06−7.18 (m, 2 H), 7.22−7.28 (m, 2 H). ^{13}C NMR: −5.68 (q), −3.03 (q), 15.26 (q), 19.73 (t), 25.55 (d), 125.52 (d), 125.77 (d), 126.74 (d), 129.06 (d), 141.32 (s), 147.83 (s). ^{29}Si NMR: 21.801. MS: 177 (M + 1^+, 40), 176 (M$^+$, 100), 162 (38), 161 (94), 159 (94), 145 (74), 133 (68), 131 (24), 115 (20). HR-MS: found 176.1022, calcd $C_{11}H_{16}Si$ 176.1021.

2,2-Dimethyl-1,2,3,4-tetrahydro-2-silanaphthalene 9a.[35] Yield: 5 mg (3%). R_f (hexane): 0.45. ^{1}H NMR: 0.044 (s, 6 H), 0.72−0.77 (m, 2 H), 1.96 (s, 2 H), 2.72−2.76 (m, 2 H), 7.03−7.14 (m, 4 H).

Radical Reaction of 4b: 1-Methyl-2,2-divinyl-2,3-dihydro-1*H*-benzo[*c*]silole 8b. GC-purified. Yield: 120 mg (60%). R_f (hexane): 0.41. IR: 3050 (m), 2950 (s), 2870 (m), 1590 (m), 1460 (m), 1400 (s), 1120 (m), 1000 (m), 960 (s). ^{1}H NMR: 1.33 (d, *J* = 7.4 Hz, 3 H), 2.17 (d, *J* = 17.3 Hz, 1 H), 2.27(d, *J* = 17.3 Hz, 1 H), 2.42 (q, *J* = 7.7 Hz, 1 H), 5.83−5.95 (m, 2 H), 6.10−6.34 (m, 4 H), 7.09−7.20 (m, 2 H), 7.25−7.28 (m, 2 H). ^{13}C NMR: 15.74 (q), 17.12 (t), 24.58 (d), 125.77 (d), 126.06 (d), 126.70 (d), 128.92 (d), 132.27 (d), 133.73 (d), 134.94 (t), 135.78 (t), 140.53 (s), 147.30 (s). ^{29}Si NMR: 5.193. MS: 201 (M + 1^+, 60), 200 (M$^+$, 174), 185 (25), 173 (34), 172 (100), 159 (41), 158 (55), 157 (72), 145 (93), 131 (55), 128 (52), 115 (30), 105 (30). HR-MS: found 200.1021, calcd $C_{13}H_{16}Si$ 200.1021.

2,2-Divinyl-1,2,3,4-tetrahydro-2-silanaphthalene 9b. Yield: 10 mg (5%). R_f (hexane): 0.38. IR: 2920 (s), 2854 (m), 1592 (w), 1456 (m), 1406 (m), 1152 (w), 1008 (w), 960 (m). ^{1}H NMR: 0.95 (t, *J* = 7.0 Hz, 2 H), 2.14 (s, 2 H), 2.80 (t, *J* = 7.0

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Hz, 2 H), 5.74 (dd, J = 19.1, 4.4 Hz, 2 H), 6.03 (dd, J = 14.7, 4.4 Hz, 2 H), 6.14 (dd, J = 19.1, 14.3 Hz, 2 H), 7.07−7.13 (m, 4 H). ^{13}C NMR: 8.91 (t), 18.12 (t), 29.33 (t), 125.06 (d), 126.48 (d), 127.94 (d), 129.75 (d), 133.92 (t), 135.32 (d), 137.14 (s), 141.57 (s). ^{29}Si NMR: −15.30. MS: 201 (M + 1$^+$, 19), 200 (38), 173 (19), 172 (100), 159 (48), 158 (21), 146 (25), 145 (42), 144 (32), 131 (22). HR-MS: found 200.1025, calcd $C_{13}H_{16}Si$ 200.1021.

Alternative Method. A solution of 1.2 mmol of Bu_3SnH and 0.1 mmol of AIBN in benzene (10 mL) was slowly added to a boiling solution of 1 mmol of **4b** in 30 mL of benzene via a syringe pump over 7 h under Ar with stirring. The resulting mixture was stirred for another 2 h after completion of the addition. The solvent was removed completely. The residue was dissolved in diethyl ether (30 mL) and stirred with 10% KF (aq) (20 mL) for 4 h. After filtering off the white precipitate, the filtrate was extracted with diethyl ether, and the combined organic phases were dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude product was purified by flash chromatography and preparative GC [**8b**, 100 mg (50%); **9b**, 50 mg (25%)].

Radical Reaction of 4c: 2-Allyl-1,2-dimethyl-2,3-dihydro-1*H*-benzo[*c*]silole 8c. Purified by GC. Yield: 81 mg (40%) as colorless oil (6:1 mixture of stereoisomers). R_f (hexane): 0.36. IR: 3060 (w), 3005 (w), 2960 (w), 1660 (m), 1630 (m), 1470 (w), 1250 (m), 1200 (s), 1150 (m), 990 (m). ^{1}H NMR: 0.15 (s, 3 H), 1.30 (d, J = 7.7 Hz, 3 H), 1.74 (d, J = 8.1 Hz, 2 H), 2.00 (d, J = 17.6 Hz, 1 H), 2.08 (d, J = 17.3 Hz, 1 H), 2.28 (q, J = 7.7 Hz, 1 H), 4.85−4.96 (m, 2 H), 5.76−5.90 (m, 1 H), 7.07−7.18 (m, 2 H), 7.18−7.25 (m, 2 H). ^{13}C NMR: −7.61 (q), 15.57 (q), 17.96 (t), 21.69 (t), 23.74 (d), 113.53 (t), 125.65 (d), 125.91 (d), 126.82 (d), 129.12 (d), 134.22 (d), 140.90 (s), 147.61 (s). ^{29}Si NMR: 21.259. MS: 202 (M$^+$, 13), 162 (12), 161 (60), 160 (100), 159 (18), 145 (33), 133 (24), 115 (10), HR-MS: found 202.1180, calcd $C_{13}H_{18}Si$ 202.1178.

2-Allyl-2-methyl-1,2,3,4-tetrahydro-2-silanaphthalene 9c. Purified by GC. Yield: 6 mg (8%) as colorless oil. R_f (hexane): 0.36. IR: 2930 (m), 2850 (m), 1630 (m), 1485 (m), 1465 (m), 1250 (m), 1150 (s), 1070 (m), 1035 (s). ^{1}H NMR: 0.049 (s, 3 H), 0.65−0.75 (m, 1 H), 0.80−0.90 (m, 1 H), 1.56 (d, J = 8.0 Hz, 2 H), 1.93 (d, J = 14.3 Hz, 1 H), 2.06 (d, J = 14.3 Hz, 1 H), 2.75 (t, J = 6.6 Hz, 2 H), 4.82−4.91 (m, 2 H), 5.70−5.85 (m, 1 H), 7.05−7.13 (m, 4 H). ^{13}C NMR: −4.14 (q), 9.87 (t), 18.82 (t), 22.48 (t), 29.57 (t), 113.29 (t), 124.90 (d), 126.36 (d), 127.89 (d), 129.65 (d), 134.39 (d), 137.78 (s), 141.57 (s). MS: 202 (M$^+$, 84), 188 (25), 162 (44), 161 (100), 160 (82), 159 (40), 145 (63), 133 (44), 131 (22), 115 (18). HR-MS: found 202.1176, calcd $C_{13}H_{18}Si$ 202.1178.

6-Methyl-6-vinyl-6,7,8,9-tetrahydro-5*H*-6-silabenzocycloheptane 10. Yield: 51 mg (25%). R_f (hexane): 0.42. IR: 3050 (w), 2930 (s), 2860 (s), 1630 (w), 1590 (w), 1450 (m), 1405 (s), 1250 (m), 1150 (s), 1065 (m), 1005 (m), 955 (m). ^{1}H NMR: −0.0078 (s, 3 H), 0.72−0.90 (m, 2 H), 1.69−1.82 (m, 1 H), 1.85−1.98 (m, 1 H), 2.19 (d, J = 14.0 Hz, 1 H), 2.36 (d, J = 14.0 Hz, 1 H), 2.71−2.75 (m, 2 H), 5.70 (dd, J = 19.5, 4.8 Hz, 1 H), 5.96 (dd, J = 14.7, 4.8 Hz, 1 H), 6.09 (dd, J = 19.5, 14.7 Hz, 1 H), 7.00−7.11 (m, 4 H). ^{13}C NMR: −5.03 (q), 15.18 (t), 23.90 (t), 24.08 (t), 35.24 (t), 124.90 (d), 126.22 (d), 128.94 (d), 129.55 (d), 132.27 (t), 137.52 (d), 139.13 (s), 141.32 (s). ^{29}Si NMR: −12.367. MS: 203 (M + 1$^+$, 14), 202 (M$^+$, 63), 187 (15), 174 (20), 162 (21), 161 (100), 159 (52), 146 (33), 145 (30), 131 (21). HR-MS: found 202.1176, calcd $C_{13}H_{18}Si$ 202.1178.

Radical Reaction of 4d: 1,2-Diallyl-2,3-dihydro-1*H*-benzo[*c*]silole 8d. Yield: 66 mg (29%). R_f (hexane): 0.23. IR: 3080 (m), 2958 (m), 1672 (m), 1630 (s), 1472 (m), 1392 (m), 1260 (w), 1160 (s), 992 (m), 902 (s). ^{1}H NMR: 1.35 (d, J = 7.7 Hz, 3 H), 1.70−1.81 (m, 4 H), 2.06 (d, J = 5.2 Hz, 2 H), 2.35 (d, J = 7.7 Hz, 1 H), 4.86−4.98 (m, 4 H), 5.76−5.88 (m, 2 H), 7.07−7.24 (m, 4 H). ^{13}C NMR: 15.44 (q), 16.22 (t), 17.56 (t), 19.60 (t), 23.65 (d), 113.97 (t), 114.11 (t), 125.74 (d), 125.98 (d), 126.59 (d), 129.08 (d), 133.80 (d), 133.87 (d), 140.51 (s), 147.31 (s). MS: 229 (M + 1$^+$, 14), 187 (22), 186 (40), 160 (22), 159 (100), 145 (31), 131 (27), 119 (10), 105 (12). HR-MS: found 228.1335, calcd $C_{15}H_{20}Si$ 228.1334.

2-Allyl-2-methyl-1,2,3,4-tetrahydro-2-silanaphthalene 9d. Yield: 14 mg (6%). R_f (hexane): 0.23. IR: 3078 (w), 2928 (m), 1628 (s), 1484 (m), 1460 (m), 1156 (m), 992 (m), 902 (s). ^{1}H NMR: 0.78−0.83 (m, 2H), 1.59 (dt, J = 8.1, 1.1 Hz, 4 H), 2.03 (s, 2 H), 2.72−2.77 (m, 2 H), 4.83−4.92 (m, 4 H), 5.66−5.83 (m, 2 H), 7.04−7.15 (m, 4 H). ^{13}C NMR: 8.09 (t), 16.84 (t), 20.60 (t), 29.60 (t), 113.72 (t), 125.01 (d), 126.48 (d), 127.95 (d), 133.99 (d), 137.36 (s), 141.99 (s). MS: 229 (M + 1$^+$, 20), 187 (36), 186 (18), 160 (22), 159 (53), 146 (19), 145 (100), 133 (13), 131 (25), 119 (10), 105 (12). HR-MS: found 228.1317, calcd $C_{15}H_{20}Si$ 228.1334.

6-Allyl-6-vinyl-6,7,8,9-tetrahydro-5*H*-6-silabenzocycloheptane 11. Yield: 41 mg (18%). R_f (hexane): 0.23. IR: 3060 (w), 3005 (m), 2920 (s), 2860 (m), 1660 (m), 1600 (w), 1490 (m), 1455 (m), 1405 (m), 1200 (s), 1180 (m), 1150 (s), 1005 (m), 955 (m). ^{1}H NMR: 0.82 (t, J = 7.0 Hz, 2 H), 1.53 (dt, J = 3.7, 1.1 Hz, 1 H), 1.56 (dt, J = 3.7, 1.1 Hz, 1 H), 1.73−1.95 (m, 2 H), 2.27 (d, J = 14.0 Hz, 1 H), 2.34 (d, J = 14.0 Hz, 1 H), 2.72-(t, J = 5.9 Hz, 2 H), 4.83−4.90 (m, 2 H), 5.66−5.81 (m, 2 H), 5.98−6.11 (m, 2 H), 7.02−7.08 (m, 4 H). ^{13}C NMR: 12.81 (t), 20.56 (t), 21.93 (t), 23.84 (t), 35.06 (t), 113.52 (t), 125.07 (d), 126.27 (d), 129.13 (d), 129.55 (d), 133.29 (t), 134.13 (d), 135.56 (d), 138.60 (s), 141.17 (s). ^{29}Si NMR: −13.861. MS: 228 (M$^+$, 25), 188 (25), 187 (100), 160 (12), 159 (54), 145 (24), 131 (25), 105 (11). HR-MS: found 228.1333, calcd $C_{15}H_{20}Si$ 228.1334.

Benzyldiallyl-(2-tributylstannylethyl)silane 12. Yield: 10 mg (2%). R_f (hexane): 0.31. IR: 3060 (w), 2920 (m), 1640 (w), 1600 (m), 1155 (s), 1010 (m), 990 (m), 900 (s). ^{1}H NMR: 0.79−0.84 (m, 5 H), 0.88−0.93 (m, 12 H), 1.25−1.37 (m, 8 H), 1.42−1.53 (m, 6 H), 1.59 (d, J = 8.1 Hz, 4 H), 2.17 (s, 2 H), 4.85−4.93 (m, 4 H), 5.70−5.84 (m, 2 H), 7.03−7.11 (m, 3 H), 7.19−7.25 (m, 2 H). ^{13}C NMR: 0.065 (t), 7.34 (t), 8.61 (t), 13.74 (q), 19.07 (t), 21.20 (t), 27.42 (t), 29.27 (t), 113.55 (t), 124.09 (d), 128.24 (d), 128.27 (d), 134.50 (d), 139.78 (s). MS: 520 (M + 1$^+$, 5), 518 (M − 1$^+$, 4), 468 (20), 466 (33), 464 (100), 462 (90), 460 (49), 235 (10), 177 (12), 119 (9).

Benzyldiallylvinylsilane 13. Yield: 11 mg (5%). R_f (hexane): 0.28. IR: 3080 (m), 3028 (s), 2924 (m), 1630 (s), 1600 (m), 1494 (s), 1452 (m), 1460 (s), 1262 (m), 1160 (s), 1008 (m), 958 (m), 932 (m). ^{1}H NMR: 1.62−1.66 (m, 4 H), 2.23 (s, 2 H), 4.89−4.95 (m, 4 H), 5.67−5.84 (m, 3 H), 6.04−6.09 (m, 2 H), 7.04−7.12 (m, 3 H), 7.21−7.26 (m, 2 H). ^{13}C NMR: 19.37 (t), 21.80 (t), 114.18 (t), 124.29 (d), 128.24 (d), 128.51 (d), 133.87 (d), 134.17 (t), 134.32 (d), 139.01 (s). MS: 228 (M$^+$, 15), 188 (32), 187 (100), 159 (30), 146 (25), 145 (98), 137 (55), 132 (24), 119 (20), 109 (27).

***o*-Vinylbenzyldiallylsilane 14.** Yield: 9 mg (4%). R_f (hexane): 0.23. IR: 3080 (m), 2924 (m), 2130 (s), 1630 (s), 1482 (m), 1448 (w), 1418 (m), 1262 (w), 1160 (s), 992 (m), 902 (s). ^{1}H NMR: 1.62−1.66 (m, 4 H), 2.29 (d, J = 3.7 Hz, 2 H), 3.84 (m, 1 H), 4.89−4.97 (m, 4 H), 5.29 (dd, J = 10.7, 1.5 Hz, 1 H), 5.63 (dd, J = 17.3, 1.5 Hz, 1 H), 5.69−5.84 (m, 2 H), 6.93 (dd, J = 17.3, 10.7 Hz, 1 H), 7.03−7.19 (m, 3 H), 7.46−7.49 (m, 1 H). ^{13}C NMR: 17.69 (t), 18.23 (t), 114.30 (t), 115.22 (t), 125.02 (d), 125.96 (d), 127.77 (d), 129.44 (d), 133.98 (d), 135.12 (d), 135.65 (s), 137.04 (s). MS: 229 (M + 1$^+$, 12), 187 (18), 186 (20), 159 (65), 146 (30), 145 (100), 143 (19), 131 (30), 119 (12), 105 (10). HR-MS: found 228.1334, calcd $C_{15}H_{20}Si^+$ 228.1334.

Radical Reaction of 4e: 2,2-Dimethyl-1-trimethylsilylmethylene-2,3-dihydro-1*H*-benzo[*c*]silole 15. Yield: 221 mg (90%). R_f (hexane): 0.38. IR: 3060 (m), 3005 (m), 2960 (s), 2900 (m), 1690 (m), 1550 (m), 1470 (s), 1450 (m), 1395 (m), 1295 (m), 1250 (s), 1205 (s), 1150 (m), 1130 (s), 1065 (m), 940 (m). ^{1}H NMR: 0.27 (s, 9 H), 0.41 (s, 6 H), 2.10 (s, 2 H), 7.14 (s, 1 H), 7.18−7.23 (m, 2 H), 7.29−7.32 (m, 1 H), 7.59−7.65 (m, 1 H). ^{13}C NMR: −1.12 (q), 0.32 (q), 19.76 (t), 120.91 (d), 125.89 (d), 128.05 (d), 130.36 (d), 137.37 (d), 142.34 (s), 145.02 (s), 158.72 (s). NOE: irradiation of the vinylic H led to an enhanced signal of the adjacent aromatic (ortho) C−H and vice versa. ^{29}Si NMR: −8.313, 5.941. MS: 247 (M + 1$^+$, 28), 246

(M^+, 100), 232 (25), 231 (85), 215 (18), 173 (59), 172 (90), 158 (27), 145 (33), 73 (48). HR-MS: found 246.1253, calcd $C_{14}H_{22}Si_2^+$ 246.1260.

***N,N′*-Diallyl-1,2-phenylenediamine 17a**. To a solution of 32.4 g (0.3 mol) of 1,2-phenylenediamine in 40 mL of DMF (distilled over P_2O_5) was added dropwise 72.5 g (0.6 mol) of allyl bromide at 0 °C during 1.5 h. The mixture was warmed to 40 °C overnight, treated with 100 mL of H_2O and 24 g of NaOH, and stirred for 1 h. The organic phase was extracted by ethyl acetate and the extract dried over $MgSO_4$. The crude product was purified by column chromatography to give 9.4 g (17%) of **17a** as a pale yellow oil, 3.2 g (5.6%) of **17b** as a pale yellow oil, 5.5 g (8%) of **17c** as a pale yellow oil, and 14.5 g (33%) of **17d** as a pale yellow oil.

***N,N′*-Diallyl-1,2-phenylenediamine 17a**. R_f (hexane:ethyl acetate = 5:1): 0.69. IR: 3348 (m), 3010 (vs), 2926 (m), 2842 (m), 1646 (m), 1600 (vs), 1512 (vs), 1448 (vs), 1446 (vs), 1418 (w), 1310 (m), 1256 (s), 1222 (vs), 1142 (m), 1054 (m), 994 (s), 926 (s), 788 (vs), 758 (vs). ^{1}H NMR: 6.89−7.06 (m, 4 H), 6.18−6.27 (m, 2 H), 5.39−5.55 (m, 4 H), 3.94 (s, 4 H), 3.63 (s, 2 H). ^{13}C NMR: 46.82 (t), 111.91 (d), 116.01 (t), 119.15 (d), 135.64 (d), 136.88 (s). MS: 188 (M^+, 100), 159 (92), 147 (72), 130 (81), 119 (72), 9 2(19), 65 (15). Anal. Calcd for $C_{12}H_{16}N_2$: C 76.54, H 8.57; N 14.89. Found: C 76.42; H 8.52; N 14.87.

***N,N*-Diallyl-1,2-phenylenediamine 17b**. R_f (hexane:ethyl acetate = 5:1): 0.60. IR: 3460 (m), 3360 (m), 3020 (vs), 1608 (vs), 1500 (vs), 1458 (m), 1418 (m), 1270 (m), 1210 (vs), 1200 (vs), 1136 (w), 1108 (w), 992 (s). ^{1}H NMR: 6.98−7.05 (m, 2 H), 6.76−6.79 (m, 2 H), 5.82−5.88 (m, 2 H), 5.15−5.26 (m, 4 H), 4.08 (s, 2 H), 3.61−3.63 (m, 4 H). ^{13}C NMR: 55.15 (t), 112.02 (d), 117.07 (t), 117.84 (d), 122.54 (d), 124.56 (d), 135.12 (d), 137.09 (s), 142.50 (s). MS: 188 (M^+, 100), 173 (15), 159 (35), 147 (92), 130 (81), 119 (86), 103 (11), 92 (19), 65 (24). HR-MS: found 188.1312, calcd $C_{12}H_{16}N_2$ 188.1313.

***N,N,N′*-triallyl-1,2-phenylenediamine 17c**. R_f (hexane: ethyl acetate = 5:1): 0.87. IR: 3382 (s), 3080 (m), 3020 (vs), 2982 (m), 2926 (m), 2834 (s), 1642 (m), 1598 (vs), 1510 (vs), 1460 (s), 1434 (s), 1418 (s), 1322 (s), 1224 (s), 1200 (s), 1160 (m), 1110 (m), 992 (s), 924 (vs). ^{1}H NMR: 7.07−7.27 (m, 2 H), 6.79−6.82 (m, 2 H), 6.09−6.15 (m, 1 H), 5.95−6.01 (m, 2 H), 5.28−5.47 (m, 6 H), 5.25 (t, 1 H), 3.99−4.01 (m, 2 H), 3.70−3.72 (d, 4H). ^{13}C NMR: 46.27 (t), 53.11 (t), 55.53 (t), 110.34 (d), 115.49 (t), 116.17 (d), 117.22 (t), 121.50 (d), 122.28 (d), 125.04 (d), 135.22 (d), 135.49 (d), 135.78 (d), 136.72 (s), 144.02 (s). MS: 228 (M^+, 100), 199 (79), 187 (80), 172 (19), 159 (82), 146 (76), 130 (40), 119 (86), 92 (21), 65 (19). HR-MS: found 228.1626, calcd $C_{15}H_{20}N_2$ 228.1626.

***N*-Allyl-1,2-diphenylenediamine 17d**.[36] ^{1}H NMR: 6.88−6.91 (m, 1 H), 6.75−6.78 (m, 3 H), 6.02−6.15 (m, 1 H), 5.24−5.41 (m, 2 H), 3.81−3.83 (d, 2 H), 3.45 (s, 2 H).

2,2′-Spirobis(1,3-bisallyl)-2-silabenzimidazoline 18a. To a solution of 3.77 g (20 mmol) of **17a** and 4.04 g (40 mmol) of triethylamine in 70 mL of CH_2Cl_2 was dropped 1.70 g (10 mmol) of $SiCl_4$ at 0 °C under N_2 during 1 h, and the mixture was kept at room temperature overnight. Workup and flash chromatography gave 2.93 g (73.3%) as white solid (mp: 37−38 °C) **18a**. R_f (diethyl ether:hexane = 40:1): 0.65. IR: 3014 (s), 2908 (m), 2854 (m), 1596 (s), 1486 (vs), 1462 (m), 1418 (m), 1378 (s), 1276 (vs), 1162 (vs), 1060 (m), 1038 (m), 1002 (m), 926 (s), 888 (m). ^{1}H NMR ($DCCl_3$): 6.70−6.81 (m, 8 H), 5.77−5.86 (m, 4 H), 5.06−5.20 (m, 8 H), 3.92−3.94 (m, 8 H). ^{13}C NMR: 136.24 (s), 134.82 (d), 118.00 (d), 116.33 (t), 108.33 (d), 44.90 (t). ^{29}Si NMR: −32.17. MS: 400 (M^+, 100), 371 (6), 359 (10), 331 (4), 317 (18), 277 (6), 188 (14), 159 (12), 149 (8), 130 (6), 119 (10). Anal. Calcd $C_{24}H_{28}N_4Si$: C 71.96; H 7.05; N 14.00. Found: C 71.67; H 6.93; N 13.85.

Reactions of 18a with Bu_3SnH. A solution of 80 mg (0.2 mmol) of **18a**, 197.9 mg (0.68 mmol) of Bu_3SnH, and 10 mg of AIBN in 100 mL of degassed toluene was refluxed for 20 h. After removal of the solvent and column chromatography, 29.7 mg (42.9%) of **19** as a colorless oil and 39 mg of **18a** were obtained. R_f (diethyl ether:hexane = 40:1): 0.76. IR: 3014 (m), 2958 (vs), 2852 (m), 1596 (m), 1508 (m), 1486 (s), 1462 (m), 1378 (m), 1272 (vs), 1154 (m), 1072 (m), 926 (s). ^{1}H NMR: 6.69−6.82 (m, 8 H), 5.75−5.84 (m, 3 H), 5.07−5.20 (m, 6 H), 3.90−3.93 (m, 6 H), 3.18−3.24 (t, J = 8.09 Hz, 2 H), 2.21−2.30 (m, 1 H), 1.67−1.78 (m, 3 H), 1.24−1.38 (m, 12 H), 0.0.87−0.92 (t, J = 6.99 Hz, 9 H), 0.073−0.79 (t, J = 8.09 Hz, 6 H). ^{13}C NMR: 137.04 (s), 137.03 (s), 136.66 (s), 136.64 (s), 136.15 (d), 135.33 (d), 135.24 (d), 119.90 (d), 119.77 (d), 118.45 (d), 118.03 (d), 116.73 (t), 116.70 (t), 116.64 (t), 112.54 (d), 112.03 (d), 108.72 (d), 107.87 (d), 47.47 (t), 45.35 (t), 45.30 (t), 31.05 (t), 30.28 (t), 30.13 (t), 29.65 (t), 29.63 (t), 14.15 (q), 9.26 (t). ^{29}Si NMR: −32.49. MS: 693 (M^+ + 1, 21), 635 (20), 578 (17), 523 (71), 467 (100), 411 (100), 355 (64), 295 (24), 239 (28), 177 (36).

20: A solution of 80 mg (0.2 mmol) of **18a**, 1979 mg (6.8 mmol) of Bu_3SnH, and 98.95 mg (5wt % of Bu_3SnH) of AIBN in 1 L of absolute toluene was degassed and refluxed for 1 week. Column chromatography gave 52 mg (36%) of **20** as a colorless oil. R_f (diethyl ether:hexane = 40:1): 0.49. IR: 3684 (w), 3020 (vs), 2926 (m), 1600 (w), 1518 (s), 1422 (m), 1376 (w), 1220 (vs), 1018 (w), 928 (m), 774 (vs), 666 (s). ^{1}H NMR: 6.78−6.81 (m, 2 H), 6.66−6.69 (m, 2 H), 3.27 (s, 2 H), 3.05−3.10 (t, J = 7.35 Hz, 4 H), 1.82−1.92 (m, 4 H), 1.46−1.52 (m, 12 H), 1.27−1.35 (m, 12 H), 0.88−0.92 (m, 34 H). ^{13}C NMR: 137.41 (s), 118.92 (d), 111.50 (d), 48.56 (t), 31.92 (t), 29.26 (t), 27.40 (t), 13.71 (q), 8.82 (t), 6.07 (t). MS: 769 (M^+ − 1, 0.2) (cluster), 739 (0.1), 713 (M^+ − Bu, 100), 663 (5), 647 (7), 599 (4), 505 (3), 457 (6), 423 (12), 365 (22), 291 (23), 269 (15), 235 (33), 179 (16).

Reaction of 18a with $BrCCl_3$. A solution of 80 mg (0.2 mmol) of **18a**, 171 mg (0.86 mmol) of $BrCCl_3$, and 16 mg of AIBN in 60 mL of degassed CCl_4 was refluxed for 6 h. After 2 and 4 h the same amount of $BrCCl_3$ and AIBN as above was added. After removal of the solvent, the residue was purified by column chromatography to give 11.6 mg (9.7%) (yellow oil) of **21** as a mixture of two stereoisomers (HPLC: 10:1) and 4.6 mg of **18a**. R_f (diethyl ether:hexane = 1:40): 0.41. IR: 3028 (s), 1596 (w), 1522 (m), 1486 (vs), 1376 (m), 1272 (vs), 1228 (s), 1202 (s), 1162 (s), 1038 (w), 932 (m), 908 (m). ^{1}H NMR: 6.74−6.89 (m, 8 H), 5.74−5.84 (m, 2 H), 5.03−5.20 (m, 4 H), 3.90−3.93 (m, 5 H), 3.59−3.75 (m, 2 H), 3.14−3.30 (m, 1 H), 2.51−2.78 (m, 4 H), 2.12−2.22 (m, 2 H). ^{13}C NMR: 136.23 (s), 135.68 (s), 134.80 (d), 134.33 (d), 133.78 (s), 133.53 (s), 118.76 (d), 118.63 (d), 118.51 (d), 118.27 (d), 116.56 (t), 116.32 (t), 108.94 (d), 108.74 (d), 108.35 (d), 107.39 (d), 98.96 (s), 58.30 (t), 50.54 (t), 49.22 (t), 48.06 (d), 46.37 (t), 44.89 (t), 44.51 (t), 34.37 (d). Minor isomer: 135.82 (s), 135.74 (s), 134.42 (d), 134.10 (d), 133.75 (s), 133.31 (s), 118.74 (d), 118.61 (d), 118.42 (d), 118.03 (d), 116.36 (t), 116.27 (t), 108.91 (d), 108.72 (d), 108.33 (d), 107.37 (d), 101.00 (s), 58.37 (t), 57.11 (d), 49.98 (t), 48.51 (t), 46.19 (t), 44.68 (t), 44.47 (t), 34.17 (d). ^{29}Si: −32.72; MS: 597 (M^+-1, 29), 554 (55), 519 (35), 477 (20), 400 (100), 359 (27), 331 (22), 317 (41), 303 (21), 293 (22), 277 (29), 185 (21), 173 (26), 122 (38), 82 (34), 41 (80). HR-MS: found 596.0315, calcd $C_{25}H_{28}BrCl_3N_4Si$: 596.0332.

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Supporting Information Available: ^{13}C spectra of compounds **8a−d, 9b−d, 10, 11, 12, 13, 14, 15, 17a−c, 18a, 19, 20, 21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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