Photochemical [1,3-C] Migration of a Bridgehead Silanorbornene

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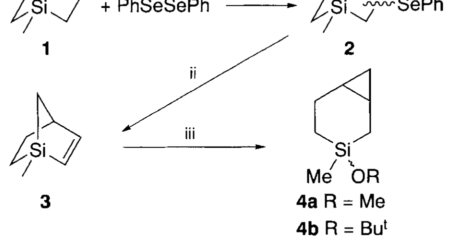
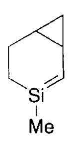
Direct photolysis (214 nm) of 1-methyl-1-silabicyclo[2.2.1]hept-2-ene in alcohols results in [1,3-C_7] migration to produce 3-alkoxy-3-methyl-3-silabicyclo[4.1.0]heptanes.

Direct photolyses of cyclopentenes produce carbene-derived products of [1,2-C] migration across the double bond in addition to free radical products of hydrogen abstraction from the solvent.[1,2] The π,3s (Rydberg) state is known to be the reactive excited state in these [1,2-C] shifts, and nucleophilic trapping of this state by alcohol has been observed among heavily alkylated derivatives.[2] In contrast, mono-[3] and di-silacyclopentenes[4] more closely resemble medium-ring cycloalkenes by undergoing protonation of the double bond to give carbocation-derived alcohol addition products. While the high reactivity towards protonation has been ascribed to the intermediacy of strained *trans*-mono- and di-silacycloalkenes,[3–5] an alternate mechanism can be envisioned whereby photoprotonation occurs directly in the σ,π* excited state, which is the lowest energy singlet excited state[4,6–8] of polysilylethylenes. Since twisting about the double bond is not necessarily prerequisite for this latter process, we have explored the possibility of photoprotonation of a rigid ring system, 1-methyl-1-silabicyclo-[2.2.1]hept-2-ene **3**.

Limited quantities (*ca.* 100 mg) of silanorbornene **3**† were obtained in 27% yield by chloramine-T (*N*-chloro-*p*-toluenesulfonamide sodium salt) oxidation[9] of phenylselenides **2** in THF followed by preparative GC purification (Scheme 1). The mixture of isomeric phenylselenides **2** in turn were produced in 8% yield upon mild Gif^{III} (Fe, AcOH, py, air, H_2O) oxidation of 1-methyl-1-silabicyclo[2.2.1]heptane **1**[10] utilizing the procedure of Barton and coworkers.[11,12]



Scheme 1 *Reagents and conditions*: i, Fe, AcOH, py, air, H_2O; ii, chloramine-T, THF; iii, *hν*, 214 nm, MeOH or Bu^{t}OH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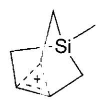
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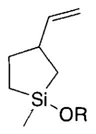
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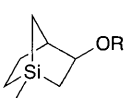
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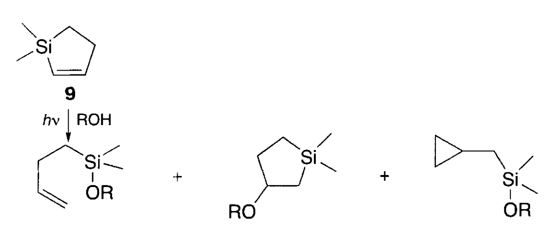

10a R = Me Φ = 0.066 **11a** R = Me Φ = 0.006 **12a** R = Me Φ = 0.013
10b R = Bu^t Φ = 0.022 **11b** R = Bu^t Φ = 0.008 **12b** R = Bu^t Φ = 0.010

Direct photolysis of 10^{-2} mol dm^{-3} silanorbornene **3** in acid-free (distilled from Mg) deoxygenated methanol at 214 nm with a 15 W Philips zinc lamp produced a 57:43 ratio (by NMR analysis) of epimeric alcohol adducts **4a** in 37% yield (Scheme 1). In addition, there was 57% unreacted **3**, and GC and GC–MS analyses revealed the presence of a minor product in *ca.* 4% yield, which was isomeric with **4a**. Epimers **4a** proved inseparable and thus were isolated by preparative GC as a mixture that was identified by comparison of GC retention times and spectral data to an independently synthesized epimeric sample.‡ With *tert*-butyl alcohol as the solvent bicyclic adduct **4b** (Scheme 1) was exclusively formed in 24% yield as a 65:35 ratio of epimers along with 73% unreacted **3**. The earlier eluting, minor epimer was obtained pure by preparative GC on a 16 ft × 1/4 in column of 10% Carbowax 20 M at 100 °C. Both the pure minor epimer and the enriched major epimer of **4b** were identified by comparison of spectral data to independently synthesized samples,‡§ although the relative stereochemistry could not be assigned. With the pure epimer NMR assignments were made utilizing ^{13}C APT, ^1H, ^{13}C HETCOR, and ^1H, ^1H COSY techniques.

The formation of adducts **4a,b** (Scheme 1) can be attributed to excited state [1,3-C] migration followed by trapping of silene **5** by alcohol. An alternate mechanism is 1,3-rearrangement of carbonium ion **6**, produced upon photoprotonation of silanorbornene **3**. Evidence for a silene intermediate analogous to **5** in the formation of **12** was obtained in our previous study[3] of silacyclopentene **9** through trapping by methoxytrimethylsilane and acetone. In this case the [1,3-C] shift was less efficient than photoalcoholysis to form **10** and **11**. In contrast, quantum yields for formation of **4a** and **4b**, determined at low conversions (1–3%) utilizing uranyl oxalate actinometry,[13,14] are 0.053 and 0.062, respectively, while the total quantum yield for **7** plus **8** is negligible in *tert*-butyl alcohol and < 0.01 in methanol. Exclusive cleavage to form **7** (R = CF_3CH_2) is observed in the dark with 2,2,2-trifluoroethanol as the solvent, as shown by ^1H, ^{13}C NMR spectroscopy after preparative GC isolation. Otherwise controls show silanorbornene **3** to be stable in methanol or *tert*-butyl alcohol for at least several days.

Financial support of this work by a Research Opportunity Award from Research Corporation and the College of Arts and Sciences, Marquette University, is gratefully acknowledged. We thank Yan Zheng and Torrey Adams (Marquette University) for technical assistance.

Received, 17th August 1994; Com. 4/05049E

Footnotes

† ^1H NMR (300 MHz, $CDCl_3$) δ 0.08–0.18 (m, 1 H, CH_2), 0.35–0.62 (m, 3 H, CH_2), 0.48 (s, 3 H, CH_3), 1.20–1.30 (m, 1 H, CH_2), 1.61–1.72 (m, 1 H, CH_2), 3.09 (br s, 1 H, CH), 6.04 (d, J = 10.5 Hz, 1 H, CH=CH), 6.91 (dd, J = 10.5, 4.7 Hz, 1 H, CH=CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ −7.93, 1.41, 24.79, 28.68, 39.18, 130.80, 153.66; GC–MS (70 eV) m/z (relative intensity) 124 (3), 109 (1), 96 (100), 83 (2), 81 (10), 68 (6), 55 (13), 43 (19). Analysis. Calc. for $C_7H_{12}Si$: C, 67.66; H, 9.73. Found: C, 67.50; H, 10.20%.

‡ The epimeric photoproducts **4a,b** gave satisfactory elemental analyses.

§ Pure minor epimer of **4b**: ^1H NMR (300 MHz, $CDCl_3$) δ −0.09 (ddd, J_{gem} = J_{vic} = 4.9 Hz, 1 H, cyclopropyl CH_2), 0.10 (s, 3 H, CH_3), 0.42–0.72 (m, 4 H, CH_2, CH and cyclopropyl CH_2), 0.78–0.94 (m, 2 H,

CH_2 and CH), 1.11–1.19 (m, 1 H, CH_2), 1.26 [s, 9 H, $C(CH_3)_3$], 1.28–1.40 (m, 1 H, CH_2), 2.10–2.22 (m, 1 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.33 (CH_3), 7.87 (CH), 11.33 (CH_2), 12.64 (CH_2), 13.27 (CH_2), 13.31 (CH), 21.57 (CH_2), 32.09 (CH_3), 72.09 (C); GC–MS (70 eV) *m/z* (relative intensity) 198 (6), 183 (7), 170 (34), 155 (17), 141 (12), 115 (11), 114 (73), 99 (100), 97 (50), 96 (58), 87 (20), 75 (50), 74 (71), 61 (86), 45 (98), 43 (44). Major epimer of **4b** after subtraction of minor epimer: ^1H NMR δ 0.09 (ddd, $J_{gem} = J_{vic} = 4.9$ Hz, 1 H), 0.17 (s, 3 H), 0.56–1.15 (m, 7 H), 1.23 (s, 9 H), 1.38–1.50 (m, 1 H), 1.98–2.09 (m, 1 H); ^{13}C NMR δ 1.44, 8.00, 12.05, 12.77, 13.15, 13.23, 22.12, 32.09, 72.19.

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