Supporting Information

β-Effects of Silicon in Directing Fragmentation of β-Silylcycloalkanone Radical Cations

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Experimental Section

General Procedure. Acetonitrile, ethyl acetate, and hexanes were purchased from Mallinckrodt Chemical Co. Ethyl acetate and hexanes were dried and distilled from CaH₂. Diethyl ether and THF from Mallinckrodt Chemicals Co. were dried by distillation from sodium and benzophenone under an atmosphere of nitrogen. Unless stated otherwise, reagents were purchased from Aldrich. Compounds prepared by literature methods include 3-(trimethylsilyl)cyclohexan-1-one, 3-(trimethylsilyl)cyclopentan-1-one, 2-[(trimethylsilyl)methyl)cyclohexan-1-one, and 2-[(trimethylsilyl)methyl)cyclopentan-1-one. Separation by analytical thin layer chromatography (TLC) was performed on precoated plates (silica gel 60 F-254), purchased from Merck Inc. Mixtures of ethyl acetate and hexanes were used as eluants. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument equipped with a 25-m cross-linked methyl silicone gum capillary column (0.32 mm i.d.). Nitrogen was used as carrier gas and the flow rate was kept constant at 14.0 mL/min. The retention time \( t_R \) was
measured under the following conditions: injector temperature 260 °C, the initial
temperature for column 70 °C, duration 2.00 min, increment rate 10 °C/min, and
the final temperature for column 250 °C. Gas chromatography and low
resolution mass spectral analyses were performed on a Hewlett-Packard 5890
Series II instrument equipped with a Hewlett-Packard 5971A Mass Selective
Detector and a capillary HP-1 column. Separations by medium-pressure liquid
chromatography (MPLC) were performed at a flow rate of 60 mL/h by use of a
Jasco Model 880-PU intelligent HPLC pump. Purification by radial thin-layer
chromatography was performed on a Model 7924T Chromatotron from Harrison
Research, Palo Alto. The plate (2-mm thickness) was coated with EM Reagents
silica gel 60 PF254 containing gypsum. Infrared (IR) spectra were measured on a
Bomem Michelson Series FT–IR spectrometer. The wavenumbers reported are
referenced to the polystyrene 1601 cm⁻¹ absorption. Absorption intensities are
recorded by the following abbreviations: s, strong; m, medium; w, weak. Proton
NMR spectra were obtained on a Varian Unity-400 (400 MHz) spectrometer or a
Varian Gemini-300 (300 MHz) spectrometer by use of chloroform-d as solvent and
tetramethylsilane as internal standard. Carbon-13 NMR spectra were obtained
on a Varian Unity-400 (100 MHz) spectrometer or Varian Gemini-300 (75 MHz)
spectrometer by use of chloroform-d as solvent. Carbon-13 chemical shifts are
referenced to the center of the CDCl₃ triplet (δ 77.0 ppm). Multiplicities are
recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet;
m, multiplet; J, coupling constant (hertz).

**Standard Procedure for the Conversions of β-Silylcycloalkanones to ω-
Alkenylcarboxylic Acids.** To a solution of β-silylcycloalkanone in 50% aqueous
acetonitrile (20 mL) was added CAN (2.4 equiv). The mixture was placed in a pre-
heated oil bath (60 °C) for 0.50–12 h until the orange color faded. Ether (25 mL)
was added to the solution after it was cooled to room temperature. The solution
was extracted with 10% aqueous Na$_2$CO$_3$ (3 × 10 mL), and the combined aqueous layers were acidified with 10% aqueous HCl. After the solution was extracted with ether (4 × 50 mL), the combined ether solutions were washed with brine (25 mL), dried over MgSO$_4$ (s), filtered, and concentrated under reduced pressure. The residue was chromatographed through a column packed with silica gel to give the desired product.

4-Penten-1-oic Acid (5). The standard procedure was followed by use of 1 (317 mg, 2.03 mmol, 1.0 equiv) and CAN (2.68 g, 4.89 mmol, 2.4 equiv). The solution was stirred for 1.5 h and then the orange color faded. After the reaction mixture was worked up, the residue was purified by column chromatography on silica gel (2.2 cm × 0.5 cm column, 60% EtOAc in hexanes as eluant) to give pure 5 (166 mg, 1.66 mmol) as a pale yellow oil in 82% yield: GC $t_R$ 4.09 min; $^1$H NMR (CDCl$_3$, 300 MHz) δ 2.13–2.29 (m, 4 H), 4.92–5.16 (m, 2 H, =CH$_2$), 5.74–5.87 (m, 1 H, CH=), 11.57 (br, 1 H, COOH); IR (neat) 3446 (br, s, OH), 2918 (s, C–H), 1716 (s, C=O), 1637 (m, C=C), 1558 (w), 1419 (s), 839 (w), 839 (m) cm$^{-1}$; MS m/z (relative intensity) 100 (M$^+$, 24), 82 (14), 73 (9), 60 (17), 58 (26), 57 (16), 56 (20), 55 (100), 54 (38), 53 (15). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.

5-Hexen-1-oic Acid (6). Method 1: The standard procedure was followed by use of 2 (342 mg, 2.01 mmol, 1.0 equiv) and CAN (2.61 g, 4.76 mmol, 2.4 equiv). The solution was stirred for 0.50 h and then the orange color faded. After the reaction mixture was worked up, the residue was purified by column chromatography on silica gel (2.2 cm × 0.5 cm column, 60% EtOAc in hexanes as eluant) to give pure 6 (225 mg, 1.97 mmol) as a pale yellow oil in 98% yield: GC $t_R$ 5.29 min; $^1$H NMR (CDCl$_3$, 300 MHz) δ 1.63–1.82 (m, 2 H), 2.05–2.17 (m, 2 H, CH$_2$C=), 2.36 (t, $J = 7.5$ Hz, 2 H, COCH$_2$), 4.92–5.07 (m, 2 H, =CH$_2$), 5.65–5.81 (m, 1 H, CH=), 11.07 (br, 1 H, COOH); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 23.68, 32.85, 33.19, 115.47, 137.44, 179.64 (CO);
IR (neat) 3419 (br, s, OH), 2933 (s, C–H), 1716 (s, C=O), 1637 (m, C=C), 1558 (w), 1508 (w), 1417 (s), 839 (w), 816 (w) cm⁻¹; MS m/z (relative intensity) 114 (M⁺, 9), 99 (6), 96 (13), 69 (13), 68 (34), 67 (7), 60 (100), 55 (68), 54 (18), 53 (8). Its physical properties and spectroscopic characteristics are consistent with those reported.⁵

**Method 2:** The standard procedure was followed by use of 3 (349 mg, 2.06 mmol, 1.0 equiv) and CAN (2.71 g, 4.95 mmol, 2.4 equiv). The solution was stirred for 2.0 h and then the orange color faded. After the reaction mixture was worked up, the residue was purified by column chromatography on silica gel (2.2 cm × 0.5 cm column, 60% EtOAc in hexanes as eluant) to give pure 6 (169 mg, 1.48 mmol) in 72% yield.

**6-Hepten-1-oic Acid** (7). The standard procedure was followed by use of 4 (376 mg, 2.04 mmol, 1.0 equiv) and CAN (2.62 g, 4.78 mmol, 2.4 equiv). The solution was stirred for 2.0 h and then the orange color faded. After the reaction mixture was worked up, the residue was purified by column chromatography on silica gel (2.2 cm × 0.5 cm column, 60% EtOAc in hexanes as eluant) to give pure 7 (214 mg, 1.67 mmol) as a pale yellow oil in 82% yield: GC tᵣ 8.35 min; ¹H NMR (CDCl₃, 300 MHz) δ 1.38–1.54 (m, 2 H), 1.56–1.77 (m, 2 H), 2.05–2.09 (m, 2 H, CH₂C=), 2.37 (t, J = 7.3 Hz, 2 H, COCH₂), 4.95–5.07 (m, 2 H, =CH₂), 5.75–5.83 (m, 1 H, CH=), 9.43 (br, 1 H, COOH); IR (neat) 3408 (br, s, OH), 2929 (s, C–H), 1730 (s, C=O), 1636 (m, C=C), 1579 (m), 1459 (w), 1338 (s), 1276 (s), 1124 (s), 744 (s) cm⁻¹; MS m/z (relative intensity) 110 (M⁺ – 18, 36), 99 (8), 87 (10), 82 (21), 69 (65), 68 (100), 60 (48), 57 (9), 56 (15), 55 (53). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.⁴

**7-anti-(Trimethylsilyl)bicyclo[2.2.1]heptan-2-one** (8).⁶ Potassium hydride (35% in mineral oil, 10.3 mg, 0.257 mmol, 1.5 equiv) was added to a dry, round-bottomed flask equipped with a stirring bar and a rubber septum. The mineral oil was washed away with hexanes and the remainder was dried under reduced pressure to give pure KH as a white powder. This flask was cooled to 0 °C, to
which was added a solution of 7-anti-(trimethylsilyl)-2-nitrobicyclo[2.2.1]heptane\(^7\) (36.4 mg, 0.171 mmol, 1.0 equiv) in THF (2.5 mL). The mixture was stirred at 0 °C for 30 min and then at room temperature for 2.5 h. The reaction was quenched with 3.5% aqueous HCl (25 mL) and the solution was extracted with ether (4 × 25 mL). The combined etheral solution was washed with brine (25 mL), dried over MgSO\(_4\) (s), filtered, and concentrated to give the crude product as an oil. Separation of the oil by use of a Chromatotron (2-mm plate, 2% ether in pentane as eluant) afforded ketone 8 (28.2 mg, 0.155 mmol) as a colorless oil in 91% yield: TLC \(R_f\) 0.25 (5% EtOAc in hexanes); GC \(t_R\) 10.57 min; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 0.07 (s, 9 H, Si(CH\(_3\))\(_3\)), 0.77–1.93 (m, 7 H), 2.60–2.72 (m, 2 H, 2 × CH); \(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) –1.18 (SiCH\(_3\)), 23.31, 27.20, 37.79, 39.39, 47.83, 51.50, 221.56 (CO); IR (neat) 2954 (s, C–H), 1749 (s, C=O), 1255 (s, Si–CH\(_3\)), 860 (m) cm\(^{-1}\); MS \(m/z\) (relative intensity) 182 (M\(^+\), 6), 167 (3), 154 (3), 140 (17), 101 (4), 80 (20), 75 (7), 73 (100), 67 (5), 59 (10).

**Cyclopent-2-enyl)acetic Acid** (9).\(^8\) The standard procedure was followed by use of 8 (384 mg, 2.11 mmol, 1.0 equiv) and CAN (2.68 g, 4.89 mmol, 2.4 equiv). The solution was stirred for 0.50 h and then the orange color faded. After the reaction mixture was worked up, the residue was purified by column chromatography on silica gel (2.2 cm × 0.5 cm column, 60% EtOAc in hexanes as eluant) to give pure 9 (156 mg, 1.31 mmol) as a pale yellow oil in 62% yield: GC \(t_R\) 8.56 min; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 1.41–1.53 (m, 2 H), 2.07–2.46 (m, 5 H), 5.63–5.69 (m, 1 H, CH=), 5.71–5.78 (m, 1 H, CH=), 10.36 (br, 1 H, COOH); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 29.66, 31.81, 40.25, 41.72, 131.69, 133.36, 179.48 (CO); IR (neat) 3444 (s, OH), 2925 (s, C–H), 1707 (s, C=O), 1645 (m, C=C), 1406 (s), 1361 (s), 1290 (m), 914 (m) cm\(^{-1}\); MS \(m/z\) (relative intensity) 126 (M\(^+\), 5), 108 (16), 81 (7), 80 (10), 79 (15), 67 (100), 66 (49), 65 (9), 60 (8), 53 (8).

**exo-3-[(Trimethylsilyl)methyl)bicyclo[2.2.1]heptan-2-one** (10).\(^9\) The procedure of Fleming\(^3\) was followed. Freshly prepared \(N\)-bicyclo[2.2.1]hept-2-
ylidenecyclohexylamine (965 mg, 5.05 mmol, 1.0 equiv) in THF (25 mL) was added slowly to a stirred solution of LiN(i-Pr)_2 (2.0 M, 2.7 mL, 5.4 mmol, 1.1 equiv) in THF (25 mL) at −78 °C. After 30 min at −78 °C, (iodomethyl)trimethylsilane (1.25 g, 5.84 mmol, 1.2 equiv) was added to the reaction mixture and the solution was stirred at 0–5 °C for 1.0 h. The solution was added brine and the aqueous layer was extracted with ether (2 × 20 mL). The combined organic layers were shaken with a buffered acetic acid solution [sodium acetate trihydrate (2.5 g), acetic acid (5.0 mL), and water (5.0 mL)] for 5.0 min. The solution was neutralized by aqueous NaHCO_3 and extracted with ether (4 × 25 mL). The combined ethereal solutions were washed with brine and dried over MgSO_4 (s). After the solvents were removed under reduced pressure, the residue was purified by MPLC (1% EtOAc in hexanes as eluant) to give ketone 10 (713 mg, 3.64 mmol) as a colorless oil in 72% yield: TLC $R_f$ 0.48 (5% EtOAc in hexanes); GC $t_R$ 12.18 min; $^1$H NMR (CDCl₃, 300 MHz) δ −0.03 (s, 9 H, (Si(CH₃)₃), 0.54 (dd, $J = 19.2, 15.2$ Hz, 1 H, SiCH), 0.87 (dd, $J = 19.2, 5.3$ Hz, 1 H, SiCH), 1.33–1.95 (m, 7 H), 2.22–2.58 (m, 2 H); $^{13}$C NMR (CDCl₃, 75 MHz) δ −1.08 (SiCH₃), 16.55, 23.79, 27.90, 34.22, 41.31, 49.15, 49.64, 221.71 (CO); IR (neat) 2954 (s), 2877 (s), 1747 (s, C=O), 1455 (w), 1248 (s, Si–CH₃), 1172 (m), 1076 (w), 862 (s), 841 (s, Si–CH₃), 692 (w) cm⁻¹; MS m/z (relative intensity) 196 (M⁺, 7), 181 (33), 168 (14), 155 (14), 142 (6), 127 (15), 75 (24), 73 (100), 67 (5), 59 (6).

cis-3-Vinylcyclopentane-1-carboxylic Acid (11). The standard procedure was followed by use of 9 (381 mg, 1.94 mmol, 1.0 equiv) and CAN (2.57 g, 4.68 mmol, 2.4 equiv). The solution was stirred for 0.50 h and then the orange color faded. After the reaction mixture was worked up, the residue was purified by column chromatography on silica gel (2.2 cm × 0.5 cm column, 60% EtOAc in hexanes as eluant) to give pure 11 (179 mg, 1.28 mmol) as a pale yellow oil in 66% yield: GC $t_R$ 8.24 min; $^1$H NMR (CDCl₃, 400 MHz) δ 1.17–2.16 (m, 6 H), 2.42–2.55 (m, 1 H, CHC=), 2.73–2.86 (m, 1 H, COCH), 4.84–5.05 (m, 2 H, =CH₂), 5.65–5.77 (m, 1 H,
CH=), 10.31 (br, 1 H, COOH); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 28.87, 32.18, 36.51, 43.46, 44.67, 113.44, 141.68, 182.82 (CO); IR (neat) 3419 (br, s, OH), 2931 (s, C–H), 1703 (s, C=O), 1641 (m, C=C), 1419 (s), 1338 (s), 1227 (s), 912 (s) cm$^{-1}$; MS m/z (relative intensity) 140 (M$^+$, 0.4), 111 (9), 97 (7), 95 (100), 94 (23), 79 (33), 68 (14), 67 (33), 55 (11), 53 (8). Its physical properties and spectroscopic characteristics are consistent with those reported.$^{10}$

2-Cyclopenten-1-one (23). To a solution of 21 (742 mg, 1.99 mmol, 1.0 equiv) in 50% aqueous acetonitrile (20 mL) was added CAN (2.68 g, 4.89 mmol, 2.4 equiv). The mixture was placed in a pre-heated oil bath (60 °C) for 1.5 h until the orange color faded and then allowed to cool to room temperature. The reaction mixture was poured into water and then extracted with ether (3 × 25 mL). The combined ethereal extracts were dried over MgSO$_4$ (s) and concentrated under reduced pressure. The residue was purified by column chromatography (2.2 cm × 10 cm column, 10% EtOAc in hexanes as eluant) to give pure 23 (132 mg, 1.61 mmol) as a pale yellow oil in 81% yield: GC $t_R$ 3.81 min; TLC $R_f$ 0.36 (40% EtOAc in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.23–2.36 (m, 2 H), 2.61–2.74 (m, 2 H), 6.16 (d, $J$ = 6.0 Hz), 1 H, CH=), 7.63–7.71 (m, 1 H, =CH); IR (neat) 2923 (s), 1713 (s, C=O), 1586 (m), 1438 (m), 1347 (s), 1182(s), 915 (m), 754 (m) cm$^{-1}$; MS m/z (relative intensity) 82 (M$^+$, 100), 54 (40), 53 (37), 51 (16), 50 (19), 39 (73), 28 (28), 27 (35), 26 (25). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.$^4$

2-Cyclohexen-1-one (24). The above procedure was followed by use of 22 (828 mg, 2.14 mmol, 1.0 equiv) and CAN (2.72 g, 4.96 mmol, 2.4 equiv). The solution was stirred for 1.0 h and then the orange color faded. After workup, the residue was purified by column chromatography (2.2 cm × 11 cm column, 10% EtOAc in hexanes as eluant) to give pure 24 (175 mg, 1.82 mmol) as a pale yellow oil in 85% yield: GC $t_R$ 4.29 min; TLC $R_f$ 0.37 (40% EtOAc in hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 1.92–2.06 (m, 2 H), 2.27–2.48 (m, 4 H), 5.99 (d, $J$ = 10.4 Hz, 1 H, CH=), 6.92–
7.05 (m, 1 H, =CH); IR (neat) 2950 (s), 2896 (s), 1682 (s, C=O), 1454 (m), 1427 (m), 1322 (s), 1255 (m), 1122 (s), 876 (m) cm⁻¹; MS m/z (relative intensity) 96 (M⁺, 31), 68 (100), 55 (9), 53 (9), 42 (14), 40 (17), 39 (43), 28 (9), 27 (20), 26 (13). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.

References

(4) Compounds are available from Aldrich Chemical Co.