Supporting information

Novel DMAP-catalyzed skeletal rearrangement of 5-*exo*-(2-hydroxy-ethylene)oxasilacyclopentanes

Dominique Bonafoux and Iwao Ojima*

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400
iojima@notes.cc.sunysb.edu

Experimental section

General methods and material: the ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-250 or Gemini 2300 using $CDCl_3$ as the internal standard. The IR spectra were measured with a Perkin-Elmer 1600 FT-IR spectrometer. Mass spectra and high-resolution mass spectra were recorded at the Mass Spectrometry Facility, University of Illinois at Urbana-Champaign. Acetylacetonatorhodium dicarbonyl was obtained from the Mitsubishi Chemical Corporation and use as received. X-ray data was collected with a Bruker AXS Smart 1000 system. Compounds **2b**,[1] **3b**,**d-f**,[1] and **7**[2] were synthesized by the literature methods.[1,2]

General procedure for the rhodium-catalyzed intramolecular silylformylation of terminal akynes 1: In a 10 mL round bottomed flask under CO atmosphere, $Rh(acac)(CO)_2$ (0.48 mg, 0.0018 mmol) was dissolved in 2 mL of toluene and a solution of alkyne **1** (0.36 mmol) in toluene (3mL) was added. The flask was placed in a 500 mL stainless steel autoclave, pressurized with 10 atm of CO, and the reaction mixture stirred at room temperature for 16 h. The solvent was removed under vacuum to afford **2** quantitatively.

3-Methyl-5-*exo*-(formylmethylene)-1,1-dimethyl-2-oxa-1-silacyclopentane (2a): yellow oil; ^{1}HNMR ($CDCl_3$) δ 0.34 (s, 1H), 0.4 (s, 1H), 1.32 (d, 3H, J = 6 Hz), 2.36-2.43 (m, 1H), 2.82-2.90 (m, 1H), 4.19 (m, 1H), 6.71-6.3 (m, 1H), 9.54 (d, 1H, J = 4.6 Hz); ^{13}CNMR ($CDCl_3$) δ -1.1, -0.5, 23.6, 45.2, 71.3, 134.6, 172.5, 190.8; IR (neat) 1688 (ν_{CO}), 1592 ($\nu_{C=C}$); HRMS (EI) calcd for $C_8H_{15}O_2Si$ (MH^+) 171.0832, found 171.0841 (Δ = 0.9 ppm)

3-Phenyl-5-*exo*-(formylmethylene)-1,1-dimethyl-2-oxa-1-silacyclopentane (2c): dark yellow oil; ^{1}HNMR ($CDCl_3$) δ 0.33 (s, 1H), 0.39 (s, 1H), 2.5-2.62 (m, 2H), 2.96-3.05 (m, 2H), 4.9-4.96 (m, 1H), 6.66 (m, 1H), 7.14-7.27 (m, 5H), 9.45 (d, 1H, J = 3.9 Hz); ^{13}CNMR ($CDCl_3$) δ -1.1, -0.9, 46.2, 76.4, 125.3, 127.5, 128.5, 134.1, 143.6, 171.3, 190.8; IR (neat) 1688 (ν_{CO}), 1591 ($\nu_{C=C}$); HRMS (EI) calcd for $C_{13}H_{15}O_2Si$ (M^+-H) 231.0838, found 231.0841 (Δ= 0.3 ppm)

General procedure of the reduction of α,β-unsaturated aldehydes 2 or 7 obtained by silylformylation: To a solution of **2** or **7** (0.36 mmol) in 5 mL of MeOH cooled to 0 ºC, was added $NaBH_4$ (13 mg, 0.36 mmol) at 0 ºC. The reaction mixture was stirred for 45 min at 0

°C, quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with EtOAc. The organic layer was dried over $MgSO_4$ and the solvent evaporated. The residue was subjected to column chromatography on silica gel (CH_2Cl_2/MeOH = 30/1, for **3a**) or precipitated by treating with Et_2O (for **3c** and **8**). Slow recrystallization of **8** in ether at room temperature for 3 weeks gave colorless crystals, which were suitable for single crystal X-ray crystallographic analysis. After the X-ray analysis, the obtained crystalline compound was found to be the rearranged product **9**.

3-Methyl-5-*exo*-(2-hydroxyethylene)-1,1-dimethyl-2-oxa-1-silacyclopentane (**3a**): colorless oil; 70%; ^{1}HNMR ($CDCl_3$) δ 0.24 (s, 3H), 0.26 (s, 3H), 1.19 (d, 3H, J = 6.16 Hz), 2.36-2.5 (m, 2H), 3.84 (m, 1H), 4.52 (d, 2H, J = 1.7 Hz), 6.51 (s, 1H); ^{13}CNMR ($CDCl_3$) δ 0.4, 0.5, 23.4, 41.4, 67.3, 71.4, 138.5, 144.1; HRMS (EI) calcd for $C_8H_{15}O_2Si$ (M^+-H) 171.0845, found 171.0841 (Δ = -0.4 ppm)

3-Phenyl-5-*exo*-(2-hydroxyethylene)-1,1-dimethyl-2-oxa-1-silacyclopentane (**3c**): off-white solid; 82% yield; ^{1}HNMR ($CDCl_3$) δ 0.26 (s, 6H), 0.26, 3.9 (s, 1H), 2.67-2.70 (m, 2H), 4.53 (d, 2H, J = 1.69 Hz), 4.69 (t, 1H, J = 5.7 Hz), 6.53 (s, 1H), 7.27-7.36 (m, 5H); ^{13}CNMR ($CDCl_3$) δ 0.3, 0.5, 41.5, 71.3, 73.8, 125.8, 127.6, 128.5, 138.4, 144.2; HRMS (EI) calcd for $C_{13}H_{17}O_2Si$ (M^+-H) 233.0998, found 233.0997 (Δ = -0.1 ppm)

***Trans*-4-*exo*-(2-hydroxyethylene)-2-oxa-3-silacyclo[4.3.0]nonane** (**8**): white solid, 90%; ^{1}HNMR ($CDCl_3$) δ 0.27 (s, 3H), 0.29 (s, 3H), 1.17-1.29 (m, 4H), 1.6-1.1.83 (m, 4H), 2.02-2.04 (m, 1H), 3.21-3.24 (m, 1H), 4.55 (s, 2H), 6.57 (s, 1H); ^{13}CNMR ($CDCl_3$) δ 1.2, 1.6, 24.8, 25.4, 32.2, 34.4, 49.6, 71.4, 73.5, 117.5, 143.6

***Trans*-5-(2-hydroxycyclopropyl)-1,1-dimethyl-2-oxa-1-silacyclopent-4-ene** (**9**): colorless crystals; ^{1}HNMR ($CDCl_3$) δ 0.26 (s, 3H), 0.29 (s, 3H), 1.16-1.29 (m, 4H), 1.66-1.83 (m, 4H), 1.99-2.04 (m, 1H), 2.17-2.24 (m, 1H), 3.19-3.28 (m, 1H), 4.55 (s, 2H), 6.57 (s, 1H); ^{13}CNMR ($CDCl_3$) δ 1.3, 1.7, 24.8, 25.5, 32.2, 34.5, 49.6, 71.4, 73.5, 87.4, 143.6; HRMS (EI) calcd for $C_{11}H_{20}O_2Si$ (M^+) 212.1226, found 212.1232 (Δ = -0.7 ppm)

General procedure for the DMAP-catalyzed skeletal rearrangement: To a solution of **3** (0.23 mmol) in THF (5 mL) were added at room temperature Ac_2O [(28 mg, 0.27 mmol) for **3a,b,c** or (56 mg, 0.54 mmol) for **3d,e,f**], Et_3N [(27 mg, 0.27 mmol) for **3** or (54 mg, 0.54 mmol) for **3d,e,f**] and DMAP (1.4 mg, 5 mol%). The mixture was stirred overnight at room temperature, quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc. After evaporation of the solvent the resulting alcohol **4** was purified by column chromatography on silica gel (hexane/EtOAc = 3/1).

5-(2-Acetoxypropyl)-1,1-dimethyl-2-oxa-1-silacyclopent-4-ene (**4a**): colorless oil, 78 %; ^{1}HNMR ($CDCl_3$) δ 0.21(s, 3H), 0.25 (s, 3H), 1.18 (d, 3H, J = 6.2 Hz), 2.01 (s, 3H), 2.43-2.58 (m, 2H), 4.51 (d, 2H, J = 1.6), 4.93 (m, 1H), 6.40 (s, 1H)); ^{13}CNMR ($CDCl_3$) δ 0.1, 0.3, 19.5, 21.4, 37.8, 70.5, 71.4, 137.0, 144.6, 170.4; HRMS (CI) calcd for $C_{10}H_{19}O_3Si$ (MH^+) 215.1099 found 215.1103 (Δ = 0.4 ppm)

5-(2-Acetoxypent-4-ynyl)-1,1-dimethyl-2-oxa-1-silacyclopent-4-ene (**4b**): light yellow oil; 65% yield; ^{1}HNMR ($CDCl_3$) δ 0.23 (s, 3H), 0.27 (s, 3H), 2.02 (m, 1H), 2.05 (s, 3H), 2.49 (CH_2, dd, J = 2.47 Hz, J = 5 Hz), 2.66 (d, 2H, J = 5 Hz), 4.53 (s, 2H), 4.96 (m, 1H), 6.57 (s,

1H) ; ^{13}CNMR ($CDCl_3$) δ 0.2, 0.3, 21, 23.1, 34.5, 70.7, 71.4, 79.4, 135, 136.2, 145.5, 170.2; HRMS (CI) calcd for $C_{12}H_{19}O_3Si$ (MH^+) 239.1100, found 239.1103 (Δ = 0.3 ppm)

5-(2-Acetoxy-2-phenylethyl)-1,1-dimethyl-2-oxa-1-silacyclopent-4-ene (**4c**): colorless oil; 76 %; ^{1}HNMR ($CDCl_3$) δ 0.13(s, 3H), 0.17 (s, 3H), 1.99 (s, 3H), 2.63-2.88 (m, 2H), 4.44 (d, 2H, J = 1.63 Hz), 5.69 (dd, 1H, J = 7.95 Hz, J = 7.95 Hz), 6.38 (s, 1H), 7.2-7.27 (m, 5H); ^{13}CNMR ($CDCl_3$) δ 0.1, 0.3, 21.3, 37.9, 71.5, 75.9, 126.6, 128.0, 128.4, 136.7, 140.3, 145.0, 170.4; HRMS (EI) calcd for $C_{15}H_{19}O_3Si$ (M^+-H) 275.1107, found 275.1103 (Δ = -0.4 ppm)

5-(2-Acetoxy-4-acetoxymethyl-5-phenyldimethylsilylpent-4-enyl)-1,1-dimethyl-2-oxa-1-silacyclopent-4-ene (**4d**): light yellow oil; 62% ^{1}HNMR ($CDCl_3$) δ 0.23 (s, 3H), 0.29 (s, 3H), 0.38 (s, 6H), 1.95 (s, 3H), 1.97 (s, 3H), 2.39 (m, 2H), 2.54 (d, 2H, J = 5.2 Hz), 4.9 (m, 4H), 5.11 (m, 1H), 5.72 (s, 1H), 6.48 (s, 1H), 7.33-7.34 (m, 3H), 7.47-7.50 (m, 2H); ^{13}CNMR ($CDCl_3$) δ -1.0, 0.1, 0.5, 20.7, 21.1, 29.6, 36.0, 42.2, 65.7, 71.4, 71.7, 127.8, 129.1, 132.0, 133.5, 136.7, 138.6, 145.0, 149.5, 170.2, 170.5; HRMS (CI) calcd for $C_{23}H_{35}O_5Si_2$ (MH^+) 447.2025, found 447.2023 (Δ = - 0.2 ppm).

5-(2-Acetoxy-4-acetoxymethyl-5-triethylsilylpent-4-enyl)-1,1-dimethyl-2-oxa-1-silacyclopent-4-ene (**4e**): light yellow oil; 74%; ^{1}HNMR ($CDCl_3$) δ 0.22 (s, 3H), 0.29 (s, 3H), 0.61 (q, 6H, J = 7.8 Hz), 0.91 (t, 9H, ^{3}J = 7.8 Hz), 1.99 (s, 3H), 2.06 (s, 3H), 2.38 (d, 2H, J = 6.6 Hz), 2.53 (m, 2H), 4.52-4.61 (m, 4H), 5.11 (m, 1H), 5.50 (s, 1H), 6.49 (s, 1H);^{13}CNMR ($CDCl_3$) δ 0.1, 0.5, 4.5, 7.3, 20.8, 21.2, 35.9, 41.9, 66.2, 71.4, 71.8, 130.8, 136.8, 144.9, 148.9, 170.1, 170.7; HRMS (CI) calcd for $C_{21}H_{37}0_5Si_2$ (M^+-H) 425.2156, found 425.217956 (Δ = 2.4 ppm)

5-(2-Acetoxy-4-acetoxymethyl-5-*tert*-butyldimethylsilylpent-4-enyl)-1,1-dimethyl-2-oxa-1-silacyclopent-4-ene (**4f**): light yellow oil; 64%; ^{1}HNMR ($CDCl_3$) δ 0.08 (s, 3H), 0.09 (s, 3H), 0.23 (s, 3H), 0.30 (s, 3H), 0.87 (s, 9H), 1.99 (s, 3H), 2.07 (s, 3H), 2.37 (m, 2H), 2.54 (m, 2H), 4.53-4.63 (m, 2H), 5.12 (m, 1H), 5.59 (s, 1H), 6.5 (s, 1H); ^{13}CNMR ($CDCl_3$) δ -4.3, 0.1, 0.5, 20.9, 21.2, 26.2, 36.0, 42.2, 65.8, 71.4, 71.7, 131.7, 136.8, 145.0, 148.8, 170.1, 170.7; HRMS (CI) calcd for $C_{21}H_{39}O_5Si_2$ (M^+-1) 425.2154, found 425.2180 (Δ = 2.6 ppm)

Reaction of 3e with acetyl chloride and NEt_3: To a solution of **3e** (0.153 g, 0.44 mmol) in freshly distilled THF (7 mL) were added at room temperature AcCl (0.105 g, 1.34 mmol.) and Et_3N (0.13g, 1.34 mmol). The reaction mixture was stirred overnight at room temperature, quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with EtOAc. The solvent was removed under reduced pressure and the crude product purified by column chromatography on silica gel (hexane/EtOAc = 4/1) afforded 3-(3-triethylsilyl-2-acetoxymethylprop-2-enyl)-5-*exo*-hydroxyethylidene-1,1-dimethyl-2-oxa-1-silacyclopentane (**5**) as a light yellow oil (0.116 g, 0.30 mmol) in 67% yield: ^{1}HNMR ($CDCl_3$) δ 0.23 (s, 3H), 0.26 (s, 3H), 0.60 (q, 6H, J = 7.8 Hz), 0.91 (t, 9H, J = 7.8 Hz), 2.05 (s, 3H), 2.19-2.54 (m, 4H), 3.79 (m, 1H), 4.52 (m, 4H), 5.59 (s, 1H), 6.50 (s, 1H);^{13}CNMR ($CDCl_3$) δ 0.4, 0.5, 4.5, 7.4, 20.9, 39.2, 46.2, 66.5, 69.1, 71.3, 131.7, 138.2, 143.9, 149.7, 170.7; HRMS (CI) calcd for $C_{19}H_{35}O_4Si_2$ (M^+-1) 383.2078, found 383.2073 (Δ = -0.4 ppm).

Reaction of 9 with acetic anhydride, Et_3N and DMAP: To a solution of **9** (87 mg, 0.41 mmol) in freshly distilled THF (5 mL) were added at room temperature Ac_2O (62 mg, 0.61

mmol), Et_3N (62 mg, 0.61 mmol) and DMAP (2.4 mg, 0.02 mmol). The reaction mixture was stirred at room temperature for 5h, quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with EtOAc. The solvent was removed under reduced pressure and the crude product purified by column chromatography on silica gel (hexane/EtOAc = 5/1) afforded **10** as a colorless oil (79 mg, 0.31 mmol) in 76% yield.

***trans*-5-(2-Acetoxycyclopropyl)-1,1-dimethyl-2-oxa-1-silacyclopent-4-ene (10)**: ^{1}HNMR ($CDCl_3$) δ 0.22 (s, 6H), 1.20-1.38 (m, 4H), 1.69-1.86 (m, 3H), 1.95 (s, 3H), 2.03-2.09 (m, 1H), 2.40-2.49 (m, 1H), 4.49 (d, 2H, J = 0.7 Hz), 4.48-4.56 (m, 1H), 6.46 (s, 1H); ^{13}CNMR ($CDCl_3$) δ 1.0, 1.5, 21.3, 24.5, 25.2, 31.7, 33.2, 45.8, 71.4, 76.2, 87.3, 142.8; 170.3; HRMS (EI) calcd for $C_{13}H_{22}O_4Si$ (M^+) 254.1331, found 254.1338 (Δ = -0.7 ppm).

Table 1. Crystal data and structure refinement for **9**

Empirical formula	$C_{11}H_{22}O_2Si$	
Formula weight	214.37	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.561(19) Å	α = 90 °
	b = 18.30(5) Å	β = 90.23(5) °
	c = 8.81(2) Å	γ = 90 °
Volume	1220(5)^3 Å	
Z	4	
Density (calculated)	1.162.10 mg/m^3	
Absorption coefficient	0.169 mm^{-1}	
F(000)	468	
θ range for data collection	2.23 to 23.32°	
Index ranges	-7<=h<=8, -20<=k<=19, -9<=l<=6	
Reflections collected	3192	
Independent reflections	1713 [R(int) = 0.0541]	
Completeness to	θ = 23.32 97.3 %	
Absorption correction	none	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1713 / 0 / 135	
Goodness-of-fit on F^2	1.029	
Final R indices[I>2σ(I)]	R1 = 0.0574, wR2 = 0.1913	
R indices (all data)	R1 = 0.0772, wR2 = 0.2199	
Largest diff. peak and hole	0.331 and -0.480 e/Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	1795(2)	2147(1)	-1054(1)	53(1)
O(1)	4440(4)	1596(2)	790(4)	62(1)
C(2)	736(6)	1546(2)	404(5)	52(1)
O(2)	-174(4)	2391(2)	-1814(4)	67(1)
C(4)	1654(6)	1126(2)	1686(5)	54(1)
C(5)	-984(6)	1547(2)	120(5)	59(1)
C(6)	3537(6)	946(2)	1265(5)	57(1)
C(7)	647(6)	433(2)	2198(5)	60(1)
C(8)	3021(8)	1653(3)	-2568(6)	78(2)
C(9)	-1648(6)	2029(3)	-1151(6)	66(1)
C(10)	1692(8)	32(3)	3468(6)	79(2)
C(11)	4533(7)	543(3)	2531(6)	67(1)
C(12)	2878(7)	3025(3)	-517(6)	70(1)
C(13)	3554(7)	-143(3)	3009(7)	77(2)

Table 3. Bond lengths [Å] and angles [°] for **9**

Si(1)-O(2)	1.690(5)
Si(1)-C(8)	1.862(6)
Si(1)-C(12)	1.864(6)
Si(1)-C(2)	1.873(5)
O(1)-C(6)	1.436(6)
C(2)-C(5)	1.324(7)
C(2)-C(4)	1.531(6)
O(2)-C(9)	1.425(6)
C(4)-C(6)	1.510(7)
C(4)-C(7)	1.547(7)
C(5)-C(9)	1.510(7)
C(6)-C(11)	1.532(7)
C(7)-C(10)	1.553(7)
C(10)-C(13)	1.501(8)
C(11)-C(13)	1.518(7)
O(2)-Si(1)-C(8)	106.5(3)
O(2)-Si(1)-C(12)	104.9(2)
C(8)-Si(1)-C(12)	112.4(3)
O(2)-Si(1)-C(2)	92.8(2)
C(8)-Si(1)-C(2)	115.0(3)
C(12)-Si(1)-C(2)	121.4(2)
C(5)-C(2)-C(4)	125.6(4)
C(5)-C(2)-Si(1)	107.0(3)
C(4)-C(2)-Si(1)	127.4(4)
C(9)-O(2)-Si(1)	113.8(3)
C(6)-C(4)-C(2)	110.7(4)
C(6)-C(4)-C(7)	111.0(4)
C(2)-C(4)-C(7)	113.9(4)
C(2)-C(5)-C(9)	117.6(4)
O(1)-C(6)-C(4)	109.9(4)
O(1)-C(6)-C(11)	112.2(4)
C(4)-C(6)-C(11)	112.8(4)
C(4)-C(7)-C(10)	110.4(4)
O(2)-C(9)-C(5)	108.6(4)
C(13)-C(10)-C(7)	112.4(4)
C(13)-C(11)-C(6)	111.2(4)
C(10)-C(13)-C(11)	111.0(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **9**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + \ + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	61(1)	44(1)	53(1)	5(1)	4(1)
O(1)	56(2)	54(2)	75(2)	9(2)	5(2)
C(2)	61(3)	38(2)	57(3)	0(2)	6(2)
O(2)	73(2)	63(2)	64(2)	21(2)	-8(2)
C(4)	66(3)	42(2)	52(3)	1(2)	4(2)
C(5)	56(3)	54(3)	68(3)	5(2)	8(2)
C(6)	66(3)	44(2)	62(3)	4(2)	-2(2)
C(7)	70(3)	44(2)	67(3)	4(2)	11(2)
C(8)	91(4)	86(4)	58(3)	-3(3)	10(3)
C(9)	58(3)	65(3)	75(3)	1(2)	-3(2)
C(10)	104(5)	57(3)	77(3)	21(3)	5(3)
C(11)	72(3)	52(3)	77(3)	7(2)	-9(2)
C(12)	88(4)	48(3)	75(3)	10(2)	0(3)
C(13)	88(4)	51(3)	91(4)	16(3)	-8(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **9**

	x	y	z	U(eq)
H(1)	5462	1495	564	92
H(2)	-284	2731	-2594	80
H(4)	1710(60)	1450(20)	2560(50)	64
H(5)	-1757	1260	683	71
H(6)	3490(60)	620(30)	390(50)	69
H(7A)	486	109	1338	72
H(7B)	-513	569	2571	72
H(8A)	2535	1172	-2689	117
H(8B)	4247	1617	-2290	117
H(8C)	2913	1916	-3506	117
H(9A)	-2252	1736	-1909	79
H(9B)	-2477	2385	-757	79
H(10A)	1717	335	4370	95
H(10B)	1084	-419	3721	95
H(11A)	5705	412	2178	80
H(11B)	4669	864	3399	80
H(12A)	2825	3358	-1359	106
H(12B)	4091	2936	-251	106
H(12C)	2274	3235	335	106
H(13A)	3535	-488	2173	92
H(13B)	4171	-369	3853	92

References

1: Bonafoux, D.; Ojima, I., *Org. Lett.,* **2001**, *3*, 1303
2: Ojima, I.; Vidal, E.; Tzamarioudaki, M.; Matsuda, I. *J. Am. Chem. Soc.*, **1995**, *117*, 6797.