Vinyl Anion Equivalents. Part IV.[1] Efficient Synthesis of 2-(1-Hydroxyalkyl)-2-cyclopenten-1-ones

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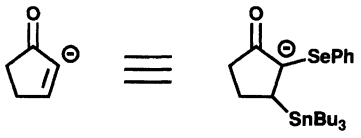
Aldol reactions of lithium enolates resulted from conjugate additions of tributylstannyllithium to 2-(phenylseleno)-2-cyclopenten-1-one provides 2-(1-hydroxyalkyl)-2-cyclopenten-1-ones in high yields. Significantly good 1,4-asymmetric induction took place in analogous aldol reactions starting with chiral 4-[(*t*-butyldimethylsilyl)oxy]-2-(phenylseleno)-2-cyclopenten-1-one.

We have recently reported on an efficient synthesis of 2-alkyl-2-cycloalkenones via a novel vinyl anion equivalent bearing the adjacent phenylseleno and tributylstannyl groups, which work together as an excellent olefin masking group.[2] This procedure led to a successful and convenient synthesis of the prostaglandin intermediate,[3] which carries the 4-hydroxyl group on the cyclopentenone ring, known to be very labile under basic conditions.[4] Although several reports concerning 2-(1-hydroxyalkyl)-2-cyclopenten-1-ones have been reported, in which organoaluminium reagents R_2AlX (X=SPh,[5] SeMe,[5] TePh[6]) or an organoborane reagent R_2BSePh were employed,[7] there have been no reports concerning the synthesis of hydroxyalkylcylopentenones having a 4-hydroxyl group, which could be potential intermediates for the synthesis of prostaglandins[8] and punaglandins.[9] We report herein an aldol reaction of the vinyl anion equivalent which resulted from the conjugate addition of tributylstannyllithium to 2-(phenylseleno)-2-cyclopenten-1-one, giving 2-(1-hydroxyalkyl)-2-cyclopenten-1-ones by spontaneous β-elimination of the phenylseleno and tributylstannyl groups (Scheme 1). We also describe 1,4-asymmetric induction in an aldol reaction starting with chiral 4-[(*t*-butyldimethylsilyl)oxy]-2-(phenylseleno)-2-cyclopenten-1-one.

Results and Discussion

A tetrahydrofuran (THF) solution of readily available 2-(phenylseleno)-2-cyclopenten-1-one[10] (**1**) was treated with tributylstannyllithium[11] (1.1 molar amount, −78 °C, 5 min), generated in situ from hexabutyldistannane and butyllithium; the resulting lithium enolate **2** was reacted with benzaldehyde in THF at −78 to −50 °C for 3 h to give 2-(α-hydroxybenzyl)-2-cyclopenten-1-one (**4a**) in 69% yield (Table 1, Entry 1). It is noted that spontaneous β-eliminations of the phenylseleno and tributylstannyl groups took place during the reaction without the addition of any β-elimination-inducing reagent, such as tetrabutylammonium fluoride, providing the enone **4a** where the aldol product **3a** was not obtained (Scheme 2). In attempts to improve the yield of the aldol reaction we found that it should be carried out below −50 °C; otherwise once **4a** was formed it gradually decomposed in the reaction mixture upon standing above −50 °C. **4a** was not obtained when the reaction mixture was allowed to warm to room temperature. The reaction using hexane or dichloromethane as a solvent gave neither **3a** nor **4a**. We finally found that the addition of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) or hexamethylphosphoric triamide (HMPA) to a THF solution of the enolate **2a** remarkably improved the yield of **4a** upto 76 or 89%, respectively (Entries 2 and 3). The aldol reaction using a variety of aldehydes, such as hexanal, acetaldehyde, or isobutyraldehyde, also afforded the corresponding 2-(1-hydoxyalkyl)cyclopentenones **4b**—**d** in high yields (Entries 4—6).

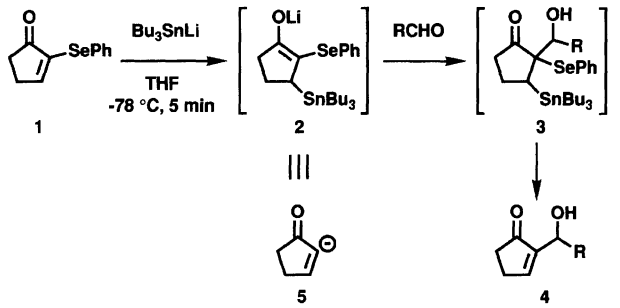


Scheme 1.

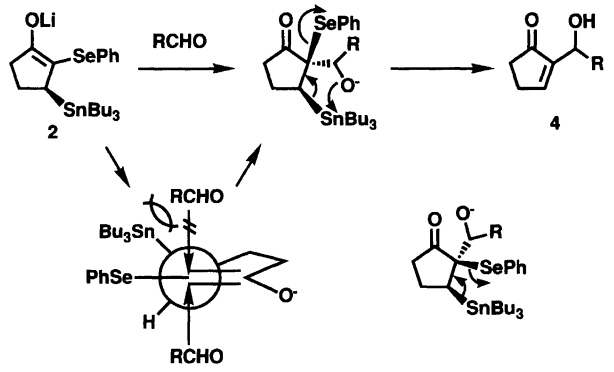
In allylation reactions of the enolate **2**, 2-allylated 3-(tributylstannyl)-2-(phenylseleno)cyclopentanones, once formed, are stable under the reaction conditions and can be isolated by column chromatography. The destannylselenenylation of the selenostannylcyclopentanones can be achieved under a variety of conditions involving the basic conditions.[2] A catalytic amount of lithium benzeneselenolate or tributylstannyllithium is highly effective for the elimination. Potassium *t*-butoxide does effect β-elimination, though it is not so effective as the above-mentioned lithium reagents. In the present reaction we could not avoid a β-elimination of the phenylseleno and tributylstannyl groups under the aldol reaction conditions. This is presumably because destannylselenenylation from the initially formed aldol product is effected intermolecularly or, more likely, intramolecularly by the lithium alkoxide formed during the aldol reaction (depicted in Scheme 3), giving the enone **4**. This assumption is supported by the fact that the enone **4** is formed very rapidly even under high diluted conditions. We also isolated *n*-$Bu_3SnSePh$ (92%), which would be formed by the reaction between the stannyl alkoxide and lithium selenolate generated through intramolecu-

Table 1. Aldol Reaction of the Lithium Enolate Resulted from Conjugate Addition of Tributylstannyllithium to 2-(Phenylseleno)-2-cyclopenten-1-one **1**

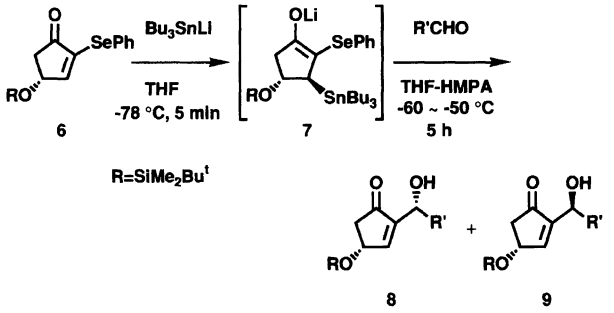
Entry	RCHO	Solvent	Temp/°C	Time/h	Product	Yield/%
1	PhCHO	THF	−78→−50	3.0	**4a**	69
2	PhCHO	THF–TMEDA	−60—−50	3.0	**4a**	76
3	PhCHO	THF–HMPA	−60—−50	3.0	**4a**	89
4	$CH_3(CH_2)_4CHO$	THF–HMPA	−60—−50	5.0	**4b**	87
5	CH_3CHO	THF–HMPA	−60—−50	4.0	**4c**	84
6	*i*-PrCHO	THF–HMPA	−60—−50	5.0	**4d**	81



Scheme 2.



Scheme 3.



Scheme 4.

lar destannylselenenylation, although a direct *syn* elimination could not be excluded. As conventionally shown in Scheme 3, the selective formation of the aldols, which have a *cis*-configuration between the phenylseleno and the tributylstannyl groups, is reasonably assumed because a preferential attack of the electrophile from the side opposite to the bulky stannyl group has been well demonstrated in the allylation reaction of the enolate **2**.[1,2]

We next examined 1,4-asymmetric induction in an aldol reaction starting with chiral (4*R*)-4-[(*t*-butyldimethylsilyl)oxy]-2-(phenylseleno)-2-cyclopenten-1-one[12] (**6**). After completing a conjugate addition of tributylstannyllithium (2.0 molar amounts) to the selenocyclopentenone **6**, benzaldehyde was added to the resulting enolate **7** in THF–HMPA at −78 °C, and the mixture was allowed to warm to −50°C for over 5 h. Again, spontaneous destannylselenenylation afforded a 70/30 diastereomeric mixture of (4*R*)-4-[(*t*-butyldimethylsilyl)oxy]-2-[(*R*)-α-hydroxybenzyl]-2-cyclopenten-1-one (**8a**) and (4*R*)-4-[(*t*-butyldimethylsilyl)oxy]-2-[(*S*)-α-hydroxybenzyl]-2-cyclopenten-1-one (**9a**) in 91% yield (Scheme 4 and Table 2). The reaction with other aldehydes also gave hydroxyalkylcyclopentenones **8** and **9** with good diastereoselectivity (Entries 2 and 3). It is noteworthy that the 4-siloxyl group on the cyclopentenone ring remained intact under these reaction conditions.

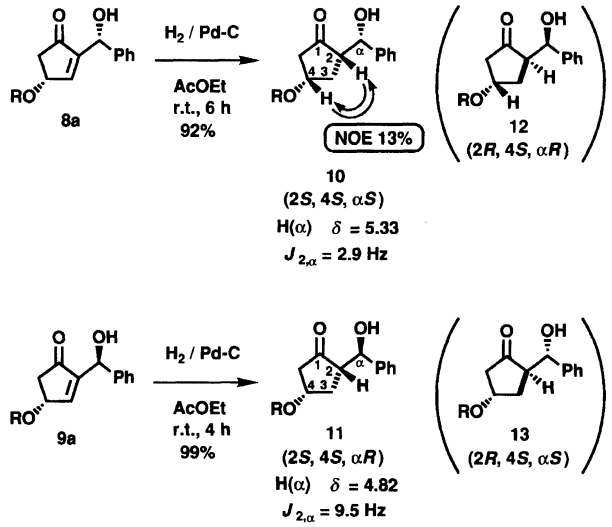
The stereochemistry of the 2-(1-hydroxyalkyl)-2-cyclopenten-1-ones **8** and **9** was determined by a chemical correlation. As shown in Scheme 5, the major and minor benzaldehyde adducts, **8a** and **9a**, were separately subjected to catalytic hydrogenation to give the corresponding keto alcohols. The hydrogenation products obtained from **8a** and **9a** showed the H(α) proton at δ=5.33 ($J_{H(\alpha)-H(2)}$=2.9 Hz) and 4.82 ($J_{H(\alpha)-H(2)}$=9.5 Hz), respectively, in their ^{1}H NMR spectra, suggesting that the former is either the (2*S*, 4*S*, α*S*) (**10**) or (2*R*, 4*S*, α*R*) (**12**) isomer and the latter either the (2*S*, 4*S*, α*R*) (**11**) or (2*R*, 4*S*, α*S*) (**13**) isomer.[13] The significant NOE (13%) between H(2) and H(4) of the product obtained from **8a** allowed us to assign the configuration to (2*S*, 4*S*, α*S*) (**10**); thus, the compound obtained from **9a** should have the (2*S*, 4*S*, α*R*) (**11**) configuration. The configuration of the major product **8a** was therefore deduced to be (4*R*,α*R*) and the minor **9a** to be (4*R*,α*S*).

In summary, the present aldol reaction of the enolates derived from 2-(phenylseleno)-2-cyclopenten-1-one by a conjugate addition of tributylstannyllithium involving the spontaneous destannylselenenylation provides a short and efficient synthetic method for 2-(1-hydroxyalkyl)-2-cyclopenten-1-ones. The reaction starting with (4*R*)-4-[(*t*-butyldimethylsilyl)oxy]-2-(phenylseleno)-2-cyclopenten-1-one gives, without any elimination of the 4-siloxyl group, chiral 4-[(*t*-butyldimethyl-

Table 2. Aldol Reaction of the Lithium Enolate Resulted from Conjugate Addition of Tributylstannyllithium to (4*R*)-4-[(*t*-Butyldimethylsilyl)oxy]-2-(phenylseleno)-2-cyclopenten-1-one **6**

Entry	R′CHO	Product	Yield/%	Ratio[a] **8** : **9**
1	PhCHO	**8a**+**9a**	91	70 : 30
2	CH_3CHO	**8b**+**9b**	81	87 : 13
3	$MeO_2C(CH_2)_5CHO$	**8c**+**9c**	51	81 : 19

a) Isolated ratio.



Scheme 5.

silyl)oxy]-2-(1-hydroxyalkyl)-2-cyclopenten-1-ones with good 1,4-asymmetric induction.

Experimental

General. The melting points were measured on a Yanaco micro melting-point apparatus and were uncorrected. The ^{1}H NMR spectra were recorded on either a Varian XL-200 (200 MHz) or a Varian Gemini-200BB (200 MHz) spectrometer, and are reported in δ from Me_4Si. The IR spectra were recorded on a JASCO A-102 spectrometer, and the reported IR figures are ν_{max} in cm^{-1}. The mass spectra were recorded on a Hitachi M-2000 spectrometer, and optical rotations were measured on a JASCO DIP-4 polarimeter.

All reactions were performed in an oven- and flame-dried glassware under a positive pressure of argon. Air- and moisture-sensitive reagents and solvents were transferred via syringe or cannula, and were introduced into the reaction vessels through a rubber septa. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25-mm E. Merck silica gel plates (60F-254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid in ethanol/heat. Column chromatography was carried out with a Michel Miller column packed with Fuji Davison silica gel (BM-200) equipped with an FMI Lab Pump (RP-G150) and an FMI Pulse Dampener (PD-60-LF), normally at a pressure of 1—2 $kg\,cm^{-2}$.

Materials. Unless otherwise noted, the materials were obtained from commercial suppliers and were used without purification. Tetrahydrofuran (THF) was freshly distilled from sodium diphenylketyl under argon before use. Hexamethylphosphoric triamide (HMPA) was freshly distilled from calcium hydride before use. The aldehydes were freshly distilled before use. Methyl 6-formylhexanoate was prepared according to procedures described in the literature.[14]

Representative Procedure for the Preparation of 2-(1-Hydroxyalkyl)-2-cyclopenten-1-ones. 2-(α-Hydroxybenzyl)-2-cyclopenten-1-one (4a): To a solution of hexabutyldistannane (282 mg, 0.49 mmol) in THF (1.0 ml) was added butyllithium (1.49 $mol\,dm^{-3}$ in hexane, 0.31 ml, 0.46 mmol) at −20 °C; the mixture was stirred for 15 min, during which time it was warmed to −10 °C. After the reaction mixture was cooled to −78 °C, a solution of 2-(phenylseleno)-2-cyclopenten-1-one (**1**) (85 mg, 0.36 mmol) in THF (1.3 ml) was added. After the mixture was stirred for 5 min HMPA (0.2 ml, 1.16 mmol) and benzaldehyde (76 mg, 0.72 mmol) were added. The reaction mixture was stirred for 3 h at a temperature of between −60 and −50 °C. Saturated aq NH_4Cl (5 ml) was added under vigorous stirring and the organic layer was separated. The water layer was extracted with CH_2Cl_2 (3×5 ml) and the combined organic extracts were washed successively with water (5 ml) and brine (5 ml), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residual oil was purified by column chromatography (silica gel 15 g, 60 : 40 hexane/ethyl acetate) to give 60 mg (89%) of **4a** as a white solid and 147 mg (92%) of tributyl(phenylseleno)stannane.[15] **4a**: mp 88—89 °C (hexane/ethyl acetate); TLC R_f=0.55 (40 : 60 hexane/ethyl acetate); IR (KBr) 3200 (OH), 1670 (C=O), 1630 (C=C), and 700 cm^{-1} (phenyl); ^{1}H NMR ($CDCl_3$) δ=2.44—2.51 (2H, m, H-5), 2.56—2.64 (2H, m, H-4), 3.38 (1H, d, J=3.9 Hz, OH), 5.54—5.60 (1H, m, C<u>H</u>OH), 7.22—7.26 (1H, m, CH=C), and 7.27—7.42 (5H, m, arom); MS m/z (rel intensity) 188 (M^+; 75), 170 (5), 128 (100), and 77 (46). Found: m/z 188.0843. Calcd for $C_{12}H_{12}O_2$: M, 188.0837.

The following compounds were prepared according to the representative procedure described above. The selenoenone **1** (amount), aldehyde (amount), reaction time, eluent for column chromatography, product yield, and product property are given in this abbreviated format.

2-(1-Hydroxyhexyl)-2-cyclopenten-1-one (4b): **1** (100 mg, 0.42 mmol), hexanal (84 mg, 0.84 mmol), 5 h, 60 : 40 hexane/ethyl acetate, 67 mg (87%), a colorless oil; TLC R_f = 0.33 (40 : 60 hexane/ethyl acetate); IR (neat) 3400 (OH), 1685 (C=O), and 1625 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=0.89 (3H, t, J=6.6 Hz, CH_3), 1.19—1.53 (6H, m, ($C\underline{H}_2$)$_3CH_3$), 1.60—1.74 (2H, m, CH(OH)$C\underline{H}_2$), 2.41—2.48 (2H, m, H-5), 2.58—2.66 (2H, m, H-4), 2.79 (1H, d, J=5.8 Hz, OH), 4.44 (1H, ddd, J=1.2, 5.8 and 5.8 Hz, C<u>H</u>OH), and 7.45 (1H, dt J=1.2 and 2.7 Hz, CH=C); MS m/z (rel intensity) 182 (M^+; 0.7), 164 (46), 149 (5), 135 (21), 121 (26), and 111 (100). Found: m/z 182.1322. Calcd for $C_{11}H_{18}O_2$: M, 182.1307.

2-(1-Hydroxyethyl)-2-cyclopenten-1-one (4c): **1** (104 mg, 0.44 mmol), acetaldehyde (39 mg, 0.89 mmol), 4 h, 40 : 60 hexane/ethyl acetate, 46 mg (83%), a pale yellow oil; TLC R_f=0.26 (30 : 70 hexane/ethyl acetate); IR (neat) 3400 (OH), 1680 (C=O), and 1625 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=1.40 (3H, d, J=6.5 Hz, CH_3), 2.42—2.49 (2H,

m, H-5), 2.58—2.66 (2H, m, H-4), 3.02 (1H, d, J=4.3 Hz, OH), 4.56—4.72 (1H, m, CHOH), and 7.46 (1H, dt, J=1.2 and 2.8 Hz, CH=C); MS m/z (rel intensity) 126 (M^+; 30), 111 (100), 108 (99), and 83 (98). Found: m/z 126.0688. Calcd for $C_{17}H_{10}O_2$: M, 126.0681.

2-(1-Hydroxy-2-methylpropyl)-2-cyclopenten-1-one (4d): **1** (164 mg, 0.69 mmol), isobutyraldehyde (103 mg, 1.43 mmol), 5 h, 60:40 hexane/ethyl acetate, 86 mg (81%), a colorless oil; TLC R_f=0.36 (50:50 hexane/ethyl acetate); IR (neat) 3430 (OH), 1680 (C=O), and 1625 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=0.91 (6H, t, J=6.7 Hz, 2×CH_3), 1.96 (1H, dqq, J=6.3, 6.7, and 6.7 Hz, CH(CH_3)$_2$), 2.42—2.49 (2H, m, H-5), 2.60—2.68 (2H, m, H-4), 2.78 (1H, d, J=6.4 Hz, OH), 4.19 (1H, ddd, J=1.1, 6.3, and 6.4 Hz, CHOH), and 7.44 (1H, dt, J=1.1 and 2.6 Hz, CH=C); MS m/z (rel intensity) 154 (M^+, 3.5), 136 (70), and 111 (100). Found: m/z 154.1005. Calcd for $C_9H_{14}O_2$: M, 154.0994.

Representative Procedure for the Preparation of (4*R*)-4-[(*t*-Butyldimethylsilyl)oxy]-2-(1-hydroxyalkyl)-2-cyclopenten-1-ones. (4*R*)-4-[(*t*-Butyldimethylsilyl)oxy]-2-[(*R*)-α-hydroxybenzyl]-2-cyclopenten-1-one (8a) and (4*R*)-4-[(*t*-Butyldimethylsilyl)oxy]-2-[(*S*)-α-hydroxybenzyl]-2-cyclopenten-1-one (9a): To the reaction mixture obtained from hexabutyldistannane (1.17 g, 2.02 mmol) and butyllithium (1.57 mol dm^{-3} in hexane, 1.22 ml, 1.92 mmol), as described above, was added a solution of (4*R*)-4-[(*t*-butyldimethylsilyl)oxy]-2-(phenylseleno)-2-cyclopenten-1-one (**6**) (352 mg, 0.96 mmol) in THF (3.5 ml) at −78 °C. The mixture was stirred for 5 min at the same temperature; then, HMPA (0.50 ml, 2.87 mmol) and benzaldehyde (204 mg, 1.92 mmol) were added. The reaction mixture was stirred for 5 h at a temperature of between −60 and −50 °C. The same workup as mentioned above gave a residual oil which was purified by column chromatography (silica gel 80 g, 83:17:0.1, 80:20:0.1, and 70:30:0.1 hexane/ethyl acetate/triethylamine) to give 182 mg (60%) of **8a** as a white solid and 96 mg (31%) of **9a** as a colorless viscous oil.

8a: Mp 38—39 °C (hexane/ethyl acetate); TLC R_f= 0.54 (70:30 hexane/ethyl acetate); $[\alpha]_D^{19}$ −25.3° (*c* 1.3, CH_3OH); IR (Nujol) 3400 (OH), 1700 (C=O), 1600 (C=C), 1250 ($SiCH_3$), 1080 (SiO), 830 (SiC), and 695 cm^{-1} (phenyl); ^1H NMR ($CDCl_3$) δ=0.09 (6H, s, Si(CH_3)$_2$), 0.89 (9H, s, *t*-Bu), 2.35 (1H, dd, J=2.1 and 18.2 Hz, H-5), 2.77 (1H, dd, J=5.9 and 18.2 Hz, H-5), 2.99 (1H, d, J=4.3 Hz, OH), 4.86—4.94 (1H, m, CHOSi), 5.52—5.57 (1H, m, CHOH), 7.11 (1H, dd, J=1.1 and 2.2 Hz, CH=C), and 7.29—7.43 (5H, m, arom); MS m/z (rel intensity) 318 (M^+; 7), 303 (3), 285 (3), 216 (100), 243 (8), and 105 (47). Found: m/z 318.1673. Calcd for $C_{18}H_{26}O_3Si$: M, 318.1651.

9a: TLC R_f=0.44 (70:30 hexane/ethyl acetate); $[\alpha]_D^{19}$ +92.0° (*c* 1.7 CH_3OH); IR (neat) 3400 (OH), 1700 (C=O), 1600 (C=C), 1250 ($SiCH_3$), 1080 (SiO), 830 (SiC), and 695 cm^{-1} (phenyl); ^1H NMR ($CDCl_3$) δ=0.09 (6H, s, Si(CH_3)$_2$), 0.88 (9H, s, *t*-Bu), 2.33 (1H, dd, J=2.2 and 18.5 Hz, H-5), 2.81 (1H, dd, J=6.0 and 18.5 Hz, H-5), 3.30 (1H, br s, OH), 4.86—4.93 (1H, m, CHOSi), 5.58 (1H, br s, CHOH), 6.99 (1H, dd, J=1.2 and 2.1 Hz, CH=C), and 7.30—7.42 (5H, m, arom); MS m/z (rel intensity) 318 (M^+; 7), 303 (2), 285 (2), 261 (92), 243 (10), 105 (100), and 75 (86). Found: m/z 318.1647. Calcd for $C_{18}H_{26}O_3Si$: M, 318.1651.

The following compounds were prepared according to the representative procedure described above. The selenoenone **6** (amount), aldehyde (amount), eluent(s) for column chromatography, product yield, and product property are given in this abbreviated format.

4-[(*t*-Butyldimethylsilyl)oxy]-2-(1-hydroxyethyl)-2-cyclopenten-1-ones (8b and 9b): **6** (173 mg, 0.47 mmol), acetaldehyde (42 mg, 0.95 mmol), 80:20:0.1 hexane/ethyl acetate/triethylamine, 85 mg (70%) of **8b** as a white solid and 13 mg (11%) of **9b** as a colorless viscous oil.

8b: Mp 41—42 °C (hexane/ethyl acetate); TLC R_f= 0.44 (70:30 hexane/ethyl acetate); IR (KBr) 3520 (OH), 1685 (C=O), 1630 (C=C), 1250 ($SiCH_3$), 1075 (SiO), and 830 cm^{-1} (SiC); ^1H NMR ($CDCl_3$) δ=0.12 (3H, s, $SiCH_3$), 0.13 (3H, s, $SiCH_3$), 0.91 (9H, s, *t*-Bu), 1.40 (3H, d, J=6.6 Hz, CH_3), 2.34 (1H, dd, J=2.1 and 18.3 Hz, H-5), 2.61 (1H, d, J=4.8 Hz, OH), 2.78 (1H, dd J=5.9 and 18.3 Hz, H-5), 4.62 (1H, ddq, J=1.2, 4.8, and 6.6 Hz, CHOH), 4.92 (1H, ddd, J=2.1, 2.6, and 5.9 Hz, CHOSi), and 7.18 (1H, dd, J=1.2 and 2.6 Hz, CH=C); MS m/z (rel intensity) 256 (M^+; 0.6), 241 (12), 223 (8), 199 (97), 181 (48), 171 (23), 157 (45), and 75 (100). Found: m/z 256.1491. Calcd for $C_{13}H_{24}O_3Si$: M, 256.1495.

9b: TLC R_f=0.35 (70:30 hexane/ethyl acetate); IR (neat) 3440 (OH), 1695 (C=O), 1630 (C=C), 1250 ($SiCH_3$), 1075 (SiO), and 830 cm^{-1} (SiC); ^1H NMR ($CDCl_3$) δ=0.12 (3H, s, $SiCH_3$), 0.13 (3H, s, $SiCH_3$), 0.91 (9H, s, *t*-Bu), 1.41 (3H, d, J=6.3 Hz, CH_3), 2.33 (1H, dd, J=2.1 and 18.2 Hz, H-5), 2.80 (1H, dd, J=5.8 and 18.2 Hz, H-5), 2.81 (1H, br s, OH), 4.59—4.72 (1H, m, CHOH), 4.91 (1H, ddd, J=2.1, 2.7, and 5.8 Hz, CHOSi), and 7.17 (1H, dd, J=1.2 and 2.7 Hz, CH=C); MS m/z (rel intensity) 241 (M^+−15; 5), 223 (4), 199 (92), 181 (47), 171 (10), 157 (23), and 75 (100). Found: m/z 241.1224. Calcd for $C_{12}H_{21}O_3Si$: M−15, 241.1260.

4-[(*t*-Butyldimethylsilyl)oxy]-2-(1-hydroxy-6-methoxycarbonylhexyl)-2-cyclopenten-1-ones (8c and 9c): **6** (200 mg, 0.54 mmol), methyl 6-formylhexanoate (172 mg, 1.09 mmol), 80:20:0.1, and 70:30:0.1, and 60:40:0.1 hexane/ethyl acetate/triethylamine, 83 mg (41%) of **8c** and 13 mg (11%) of **9c** as pale yellow viscous oils.

8c: TLC R_f=0.52 (60:40 hexane/ethyl acetate); IR (neat) 3450 (OH), 1725 (ester C=O), 1700 (C=O), 1635 (C=C), 1250 ($SiCH_3$), 1070 (SiO), and 830 cm^{-1} (SiC); ^1H NMR ($CDCl_3$) δ=0.11 (3H, s, $SiCH_3$), 0.12 (3H, s, $SiCH_3$), 0.89 (9H, s, *t*-Bu), 1.19—1.77 (8H, m, (CH_2)$_4$$CH_2CO_2CH_3$), 2.29 (2H, t, J=7.0 Hz, $CH_2CO_2CH_3$), 2.31 (1H, dd, J=3.0 and 18.0 Hz, H-5), 2.51 (1H, d, J=6.0 Hz, OH), 2.77 (1H, dd, J=6.0 and 18.0 Hz, H-5), 3.65 (3H, s, CO_2CH_3), 4.36—4.48 (1H, m, CHOH), 4.86—4.94 (1H, m, CHOSi), and 7.17 (1H, dd, J=1.3 and 2.6 Hz, CH=C); MS m/z (rel intensity) 355 (M^+−15; 3), 339 (11), 321 (5), 313 (100), 295 (12), 281 (22), 263 (17), 241 (34), 221 (8), 213 (7), 189 (61), 161 (27), and 75 (96). Found: m/z 355.1930. Calcd for $C_{18}H_{31}O_5Si$: M−15, 355.1941.

9c: TLC R_f=0.42 (60:40 hexane/ethyl acetate); IR (neat) 3450 (OH), 1725 (ester C=O), 1700 (C=O), 1630 (C=C), 1250 ($SiCH_3$), 1080 (SiO), and 830 cm^{-1} (SiC); ^1H NMR ($CDCl_3$) δ=0.11 (3H, s, $SiCH_3$), 0.12 (3H, s, $SiCH_3$), 0.90 (9H, s, *t*-Bu), 1.23—1.74 (8H, m, (CH_2)$_4$$CH_2CO_2CH_3$), 2.30 (2H, t, J=7.0 Hz, $CH_2CO_2CH_3$), 2.31 (1H, dd, J=2.2 and 19.2 Hz, H-5), 2.62 (1H, br s, OH), 2.78 (1H, dd, J=6.0 and 19.2 Hz, H-5), 3.65 (3H, s, CO_2CH_3), 4.38—4.49 (1H, m, CHOH), 4.89

(1H, ddd, J=2.2, 2.6, and 6.0 Hz, CHOSi), and 7.16 (1H, dd, J=1.2 and 2.6 Hz, CH=C); MS m/z (rel intensity) 355 (M^+-15; 2.2), 339 (11), 321 (4), 313 (100), 295 (9), 281 (15), 263 (15), 241 (18), 221 (6), 213 (8), 189 (40), 161 (19), and 75 (87). Found: m/z 355.1955. Calcd for $C_{18}H_{31}O_5Si$: M−15, 355.1941.

Catalytic Hydrogenation of (4*R*)-4-[(*t*-Butyldimethylsilyl)oxy]-2-(α-hydroxybenzyl)-2-cyclopenten-1-ones. (2*S*,4*S*)-4-[(*t*-Butyldimethylsilyl)oxy]-2-[(*S*)-α-hydroxybenzyl]-1-cyclopentanone (10): To a solution of hydroxybenzylcyclopentenone **8a** (56 mg, 0.18 mmol) in ethyl acetate (6 ml) was added a catalytic amount (8 mg) of 10% Pd–C. The mixture was stirred under a hydrogen atmosphere for 6 h. The reaction mixture was filtered and concentrated under reduced pressure and the residue was purified by column chromatography (silica gel 3 g, 85 : 15 hexane/ethyl acetate) to give 52 mg (92%) of **10** as a white solid: Mp 114—116 °C (hexane/ethyl acetate); TLC R_f=0.53 (70 : 30 hexane/ethyl acetate); $[\alpha]_D^{19}$ −167.5° (c 0.7, CH_3OH); IR (KBr) 3400 (OH), 1730 (C=O), 1250 ($SiCH_3$), 1110 (SiO), and 840 cm^{-1} (SiC); ^1H NMR ($CDCl_3$) δ=0.11 (3H, s, SiMe), 0.13 (3H, s, $SiCH_3$), 0.93 (9H, s, t-Bu), 2.00—2.13 (2H, m, H-3), 2.32 (1H, ddd, J=0.8, 4.6, and 18.6 Hz, H-5), 2.53 (1H, dd, J=5.6 and 18.6 Hz, H-5), 2.62—2.73 (1H, m, H-5), 2.53 91H, dd, J=5.6 and 18.6 Hz, H-5), 2.62—2.73 (1H, m, H-2, 13% NOE on irradiation at 4.48 ppm), 3.76 (1H, d, J=6.2 Hz, OH), 4.42—4.54 (1H, m, CHOSi, 13% NOE on irradiation at 2.68 ppm), 5.33 (1H, dd, J=2.9 and 6.2 Hz, CHOH), and 7.32—7.37 (5H, m, arom); MS m/z (rel intensity) 320 (M^+; 0.6), 287 (1.6), 263 (15), 245 (29), 185 (3), 171 (5), 157 (93), 143 (21), 129 (78), 127 (23), 115 (15), 106 (33), 105 (36), 77 (36), and 75 (100). Found: m/z 320.1804. Calcd for $C_{18}H_{28}O_3Si$: M, 320.1808.

(2*S*,4*S*)-4-[(*t*-Butyldimethylsilyl)oxy]-2-[(*R*)-α-hydroxybenzyl]-1-cyclopentanone (11): The hydroxybenzylcyclopentenone **9a** (45 mg, 0.14 mmol) was hydrogenated as above to afford 45 mg (99%) of **11** as a white solid: Mp 63—65 °C (hexane/ethyl acetate); TLC R_f=0.61 (70 : 30 hexane/ethyl acetate); $[\alpha]_D^{19}$ −69.8° (c 1.4, CH_3OH); IR (KBr) 3460 (OH), 1715 (C=O), 1250 ($SiCH_3$), 1040 (SiO), and 830 cm^{-1} (SiC); ^1H NMR ($CDCl_3$) δ=0.05 (6H, s, Si(CH_3)$_2$), 0.88 (9H, s, t-Bu), 1.60 (1H, dddd, J=1.2, 6.0, 8.6, and 14.8 Hz, H-3), 1.99 (1H, dddd, J=1.2, 5.2, 9.0, and 14.8 Hz, H-3), 2.34 (1H, dd, J=5.8, and 18.4 Hz, H-5), 2.52 (1H, q, J=9.0 Hz, H-2), 2.64 (1H, ddt, J=1.2, 5.8, and 18.4 Hz, H-5), 4.39 (1H, quintet, J=5.8 Hz, CHOSi), 4.50 (1H, d, J=1.1 Hz, OH), 4.82 (1H, dd, J=1.1 and 9.5 Hz, CHOH), and 7.35 (5H, s, arom); MS m/z (rel intensity) 320(M^+; 0.6), 287 (0.9), 263 (13), 245 (24), 185 (4), 171 (3), 157 (98), 143 (23), 129 (48), 127 (33), 115 (20), 106 (47), 105 (50), 77 (47), and 75 (100). Found: m/z 320.1825. Calcd for $C_{18}H_{28}O_3Si$: M, 320.1825.

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