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Conversion of Phenyldimethylsilyl to the Hydroxyl in the Presence of a Carbon-Carbon Double Bond

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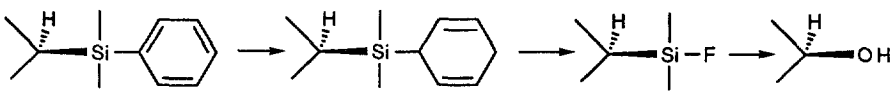
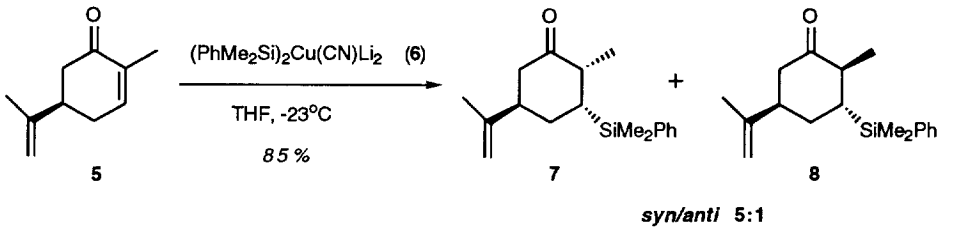
Abstract: A simple procedure for the conversion of the phenyldimethylsilyl group to the alcohol in the presence of an alkene has been established.

Fleming has shown that the bis(phenyldimethylsilyl)cuprate reagent[1] is a versatile tool for introduction of the phenyldimethylsilyl group into a series of organic structures. The phenyldimethylsilyl group can then be converted to the alcohol with retention of absolute configuration.[2] A serious difficulty with the reagents that have been used for this transformation is incompatibility with the carbon-carbon double bond.[2,3] A recent report by Fleming[4] on the conversion of the 2-methylbut-2-enyl(diphenyl)silyl group to the alcohol in the presence of a 1,2-disubstituted carbon-carbon double bond and work by Tamao[5] prompts us to disclose our recent results. Based on the work of Rabideau[6], we envisioned reduction of the phenyldimethylsilyl group of **1** to the 1,4-cyclohexadiene **2**. Conversion to silyl fluoride **3** followed by oxidation should then provide alcohol **4** with retention of configuration.

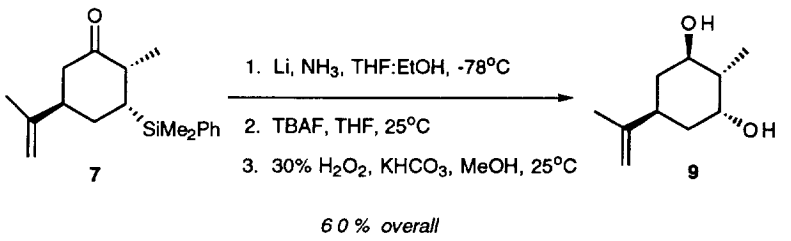


1 **2** **3** **4**

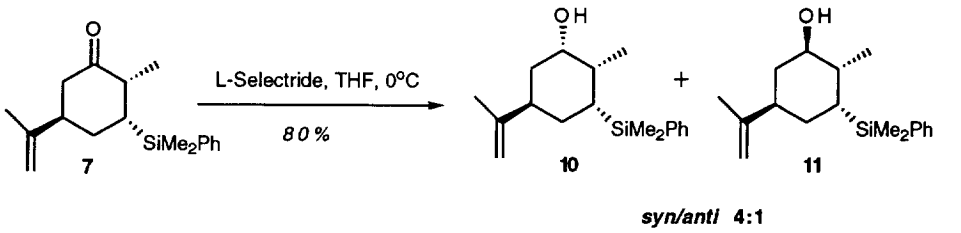
In our model study, bis(phenyldimethylsilyl)cuprate **6** was added to R-(-)-carvone (**5**)[1a] to give diastereomeric silyl ketones **7** and **8** (syn/anti 5:1), which could be separated by TLC mesh column chromatography.[7] ***Syn*** silyl ketone **7** was reduced with lithium/ammonia in THF:EtOH at -78°C with concomitant formation of the alcohol and the 1,4-cyclohexadiene. Without purification, this intermediate



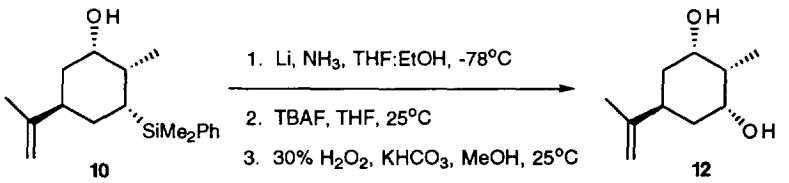
alcohol was exposed to tetrabutylammonium fluoride (TBAF) in THF at 25°C, followed by oxidation with aqueous hydrogen peroxide in the presence of potassium bicarbonate[8], to give exclusively the known 1,3-diol **9**[9] in 60% overall yield.



Alternatively, ***syn*** ketone **7** was reduced with L-Selectride in THF at 0°C to give diastereomeric silyl alcohols **10** and **11** (syn/anti 4:1) in 80% yield. Application of the same reductive protocol to ***syn*** 3-hydroxy-



silane **10**[10] afforded the previously unknown ***meso*** 1,3-diol **12**[11] in 66% overall yield.



66 % overall

In summary, the phenyldimethylsilyl group can be transformed to the hydroxyl in a procedure which is compatible with an alkene. This substantially extends the usefulness of the phenyldimethylsilyl group as an alcohol surrogate.

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References and Notes

1. (a) Ager, D.J.; Fleming, I.; Patel, S.K.J. *J. Chem. Soc., Perkin Trans. I* **1981**, 2520. (b) Fleming, I.; Newton, T.W.; Roessler, F.J. *J. Chem. Soc., Perkin Trans. I* **1981**, 2527. (c) Fleming, I.; Marchi, D. *Synthesis* **1981**, 560. (d) Fleming, I.; Rowley, M.; Cuadrado, P.; Gonzalez-Nogal, A.M.; Pulido, F.J. *Tetrahedron* **1989**, *45*, 413. (e) Fleming, I.; Higgins, D.; Lawrence, N.J.; Thomas, A.P. *J. Chem. Soc., Perkin Trans. I* **1992**, 3331.
2. (a) Fleming, I.; Hennings, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29. (b) Fleming, I.; Sanderson, P.E.J. *Tetrahedron Lett.* **1987**, *28*, 4229.
3. (a) Tamao, K.; Ishida, N. *J. Organometal. Chem.* **1984**, *269*, C37. (b) Tamao,K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, 2, 1694. (c) Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2120.
4. Fleming, I.; Winter, S.B.D. *Tetrahedron Lett.* **1993**, *34*, 7287.
5. (a) Tamao, K.; Nakajo, E.; Ito, Y. *J. Org. Chem.* **1987**, *52*, 957. (b) Tamao, K.; Kawachi, A.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 3989. (c) Tamao, K.; Ishida, N.; Ito, Y. Kumada, K. *Org. Synth.* **1990**, *69*, 96.
6. Rabideau, P.W.; Karrick, G.L. *Tetrahedron Lett.* **1987**, *28*, 2481.
7. Taber, D.F. *J. Org. Chem.* **1982**, *47*, 1351. Silica gel with particle size 10 μm from Analtech, Inc. was used in column chromatography.
8. To a solution of silyl ketone **7** (121 mg, 0.425 mmol) in dry THF:EtOH (10 mL, 1:1 v/v) and condensed ammonia (15 mL) at -78°C was added lithium metal (50 mg, 7.21 mmol) until the solution was blue with blue foam. The mixture was warmed to room temperature to evaporate the ammonia. The residue was

partitioned between water (20 mL) and EtOAc (5 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to a colorless oil. This was taken up in THF (1.0 mL) and tetrabutylammonium fluoride (0.85 mL, 0.85 mmol, 1.0 M in THF) was added. After stirring 1 h, methanol (0.5 mL), $KHCO_3$ (64 mg, 0.638 mmol), and 30% H_2O_2 (0.48 mL, 4.25 mmol) were added and stirring was continued for 4 h. The mixture was partitioned between water (20 mL) and EtOAc (5 x 10 mL). The combined extracts were dried ($MgSO_4$) and concentrated *in vacuo* to a colorless oil which was chromatographed to afford **9** (43 mg, 60%) as a viscous colorless oil: *Rf* (EtOAc: petroleum ether, 1:1) = 0.45; ^1H NMR (250 MHz, $CDCl_3$) δ 1.08 (d, *J* = 6.2 Hz, 3H), 1.10-1.14 (m,1H), 1.16-1.42 (m, 2H), 1.70 (s, 3H), 1.78-1.90 (m, 3H), 2.0-2.05 (m, 1H), 2.40-2.46 (m, 1H), 3.63 (ddd, *J* = 4.3, 6.3, 10.6 Hz, 1H), 3.95-3.98 (m, 1H), 4.69 (s, 2H); ^{13}C NMR (62 MHz,$CDCl_3$) δ u: 38.3, 40.6, 109.0, 148.8; d: 14.3, 20.8, 37.4, 43.6, 71.2, 72.0.

9. Zaitsev, V.V.; Kozhin, S.A. *J. Org. Chem. USSR* **1972**, 1889.
10. Data for **10**: ^1H NMR (250 MHz, $CDCl_3$) δ 0.32 (s, 6H), 0.88 (d, *J* = 7.2 Hz, 3H), 1.15-1.54 (m, 2H), 1.58-1.70 (m, 3H), 1.60 (s, 3H), 1.85-2.03 (m, 2H), 2.41 (s, 1H), 3.81-3.86 (m, 1H), 4.67 (s, 1H), 4.84 (s, 1H), 7.31-7.35 (m, 3H), 7.50-7.53 (m, 2H); ^{13}C NMR (62 MHz, $CDCl_3$) δ u: 22.5, 31.2, 110.7, 138.6, 146.4; d: -3.8, 9.6, 22.4, 24.4, 35.9, 40.1, 69.7, 127.6, 128.8, 133.8.
11. Data for **12**: ^1H NMR (250 MHz, $CDCl_3$) δ 1.18 (d, *J* = 7.2 Hz, 3H), 1.23-1.71 (m, 4H), 1.73 (s, 3H), 1.98-2.04 (m, 2H), 2.61-2.77 (m, 2H), 3.93 (s, 2H), 4.73 (s, 2H); ^{13}C NMR (62 MHz, $CDCl_3$) δ u: 38.9, 109.0, 149.3; d:15.0, 21.0, 31.5, 37.9, 72.6.

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