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BORON ANNULATION IN ORGANIC SYNTHESIS. 4. SILICON EFFECTS WITH TETRASUBSTITUTED OLEFINS

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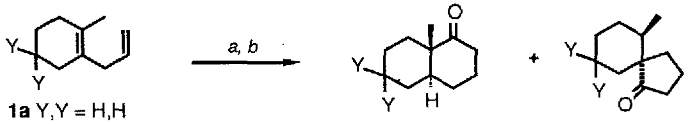
Summary: Selectivity for hydroboration and boron decalone annulation employing tetrasubstituted olefins is strongly influenced by allylic silicon.

Boron annulation utilizing tri- and tetrasubstituted olefins has proven problematic in a number of studies in these laboratories. Reported herein are new insights into successful tetrasubstituted or hindered olefin annulations that have evolved from comparison of recent results (**1a** to **2** and **3**) to earlier studies[1] with substrate **1b**.



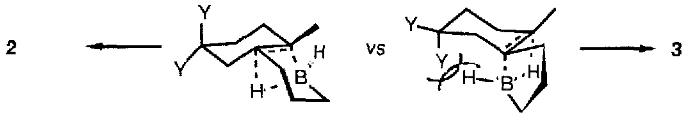
1a Y,Y = H,H
b Y,Y = $(OCH_2)_2$

2

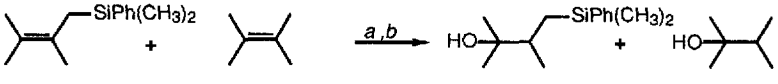
3

$^{a}BH_3\cdot THF(1eq.)$; $^{b}DCME, {}^{-}OC(Et)_3; {}^{-}OH/H_2O_2$.

It was not surprising that diene **1b** proved to be selective for *trans*-decalin formation (**2**)[1] over spiro-annulation (**3**). Steric[2] (1,3-diaxial) and weak electronic effects adding to a strained spiro-annulation, four-centered transition state seemed to proscribe the formation of **2b** from **1b**.



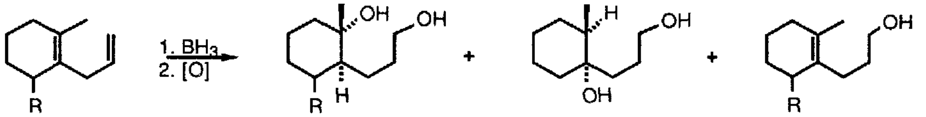
However, the hydrocarbon analog **1a** annulated, forming known systems **2** and **3**, 21% (1.3:1[3] respectively) with no strong regioselective preference for intramolecular addition to the tetrasubstituted olefin. This suggests that, even with the discord of directing (steric) and deactivating (electron withdrawal) effects, the acetal group channels boron annulation in **1b** to **2** albeit in modest yield. In looking for other groups that might more favorably influence hydroboration, we were attracted to the work of Nelson,[4] Soderquist[5] and Fleming[6] that suggests allylic silanes might have strong boron directing effects even with highly branched alkenes. To test the activating effects noted by Nelson on allyltrimethylsilane, we prepared hindered silane **4** for comparison to the formation of thexylborane from 2,3-dimethyl-2-butene. Silyl alcohol **5** is readily formed in preference to 2,3-dimethyl-2-butanol, **6** (**5**:**6**; 9:1) when a 50/50 mixture of olefins was treated with a limiting amount of BH_3.[7]



4 **5** **6**

${}^{a}BH_3$, THF, 0°; ^{b} $^{-}OH/H_2O_2$.

The regioselectivity observed with **4** could, in part, be due to steric effects of silicon but clearly the dominant effect is an electronic "β-effect" of silicon.[8] Dienes **1a**, **7a** and **7b**, prepared as outlined in Scheme 1, were next investigated in order to extend these findings to intramolecular hydroboration and boron annulation.



1a R = H
7a R =TMS
b R =SiMe₂Ph

8a R = H
b R = β-TMS
c R = α-TMS
d R = β-SiMe₂Ph
e R = α-SiMe₂Ph

9

10a R =TMS
b R = $Si(CH_3)_2Ph$

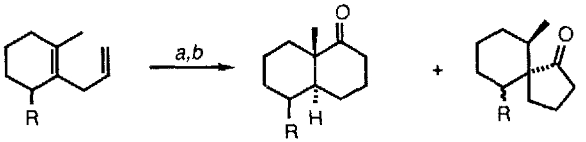
Diene **1a** and BH_3 non-selectively forms diols **8a** and **9** in good yield. This is in contrast to silane substrates **7a** that regio- but not diastereoselectively form diols **8b** and **8c** a long with varying amounts of monohydroboration product **10a**. Improvements in hydroboration yields were effected *via* use of ultrasound[9] as depicted in Table 1.

Table I

Diene	Reagents/Conditions[a]	Products(Yield)
1a	BH_3 (1 eq)/3 h, 0°, SONO	**8a**(38%), **9**(47%)
7a	BH_3 (1 eq)/18 h, RT	**8b**,**8c**(31%); **10a**(15%)
7a	BH_3 (1 eq)/0.5 h, 0°, SONO	**8b**, **8c**(18%); **10a**(72%)
7a	BH_3 (1 eq)/2 h, 0°, SONO	**8b**, **8c**(50%); **10a**(34%)
7a	BH_3 (1 eq)/4 h, 0°, SONO	**8b**, **8c**(77%); **10a**(7%)
7a	Thxy (1 eq)/4 h, 0°, SONO	**8b**, **8c**(0%); **10a**(85%)
7b	BH_3 (1 eq)/4 h, 0°, SONO	**8d**, **8e**(49%); **10b**(25%)

[a]Standard alkaline peroxide oxidation

Decoupling experiments and an alternate preparation of diol **8c**[10] confirmed the regioselectivity and stereochemical assignments of **8b** and **8c**. Phenyldimethylsilane **7b** yielded a similar product mixture, **8d**, **8e** and **10b**, with a slight loss in overall yield relative to the TMS system.



7a R =TMS
b R = $Si(CH_3)_2Ph$

11a R = β-TMS
b R = α-TMS
c R = β-$Si(CH_3)_2Ph$
d R = α-$Si(CH_3)_2Ph$

1 2

${}^{a}BH_3$, THF, 0°; ^{b}DCME, base; $^{-}OH/H_2O_2$.

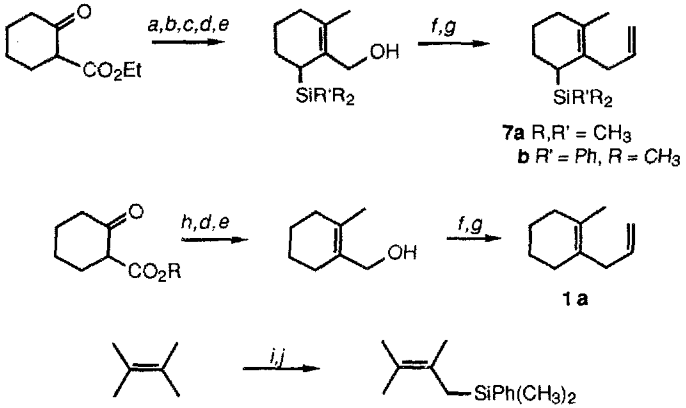
Hydroboration ($BH_3 \cdot THF$)[11] and boron replacement (dichloromethylmethylether, DCME)[12] of **7** leads exclusively to decalone diastereomers **11a**,**b** or **11c**,**d** (50% or 37%, respectively, each in approximately 1:1.2 ratio[13]) with no detectable amounts of spiro ketone **12**. The *trans*-decalin systems, **11a** and **11b**, were only separable for analysis *via* reduction to **13a** and **13b** (K-selectride) followed by repeated column chromatography with peak shaving (SiO_2).

11a R = β-TMS
b R = α-TMS

13a R = β-TMS
b R = α-TMS

In summary, it has been demonstrated that the silyl group activates and regiochemically controls tetrasubstituted olefin hydroboration and boron annulation. We are now looking at other constructs amenable to silicon influences on the boron annulation process.[14]

Scheme 1



7a R,R' = CH_3
b R' = Ph, R = CH_3

1a

4

^{a}NaH, PhSeCl; ${}^{b}H_2O_2$; ${}^{c}LiCu(SiR'R_2)_2$[15], $ClPO(OEt)_2$; ${}^{d}LiCu(CH_3)_2$; ^{e}DIBAL;
^{f}LiCl, DMF, collidine, MsCl; ^{g}CuI, vinylMgBr; ^{h}NaH, $ClPO(OEt)_2$; ^{i}NBS, $(BzO)_2$, Δ;[16] ${}^{j}LiCu(SiPhMe_2)_2$.

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[3] Ratio was determined by integration of the high field methyl groups; singlet (**2**) to doublet (**3**); see Williams, J.R.; Sarkisian, G.M. *J. Org. Chem.* **1980**, *45*, 5088-94 for spectral data on **3**; for **2** see House, H.O.; Trost, B.M. *J. Org. Chem.* **1965**, *30*, 2502-12.

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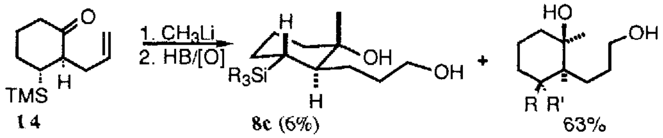
[7] One equivalent of borane was added to a mixture of one equivalent of **7** and one equivalent of 2,3-dimethyl-2-butene in THF at 0°C followed by alkaline peroxide oxidation.

[8] Lambert, J.B.; Wang, G.-t.; Finzel, R.B.; Teramura, D.H. *J. Am. Chem. Soc.* **1987**, *109*, 7838-45.

[9] Brown, H.C.; Racherla, J.S. *Tetrahedron Lett.* **1985**, *26*, 2187-90; A branson ultrasonic cleaning bath (50/60 Hz, 80 watt) was used for hydroborations utilizing ultrasound.

[10] Diol **8c** was the minor product of methyllithium addition to *trans*-ketone **14** followed by hydroboration of the monosubstituted olefin. Silane **8c** was easily distinguished form its epimer (**8b**) by the *trans*-diaxial proton coupling of the methine hydrogens.



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[13] Ratio was estimated from ^{1}H NMR intensities of overlapping methyl group singlets.

[14] NIH (GM 34896) is gratefully acknowledged for support of this work.

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