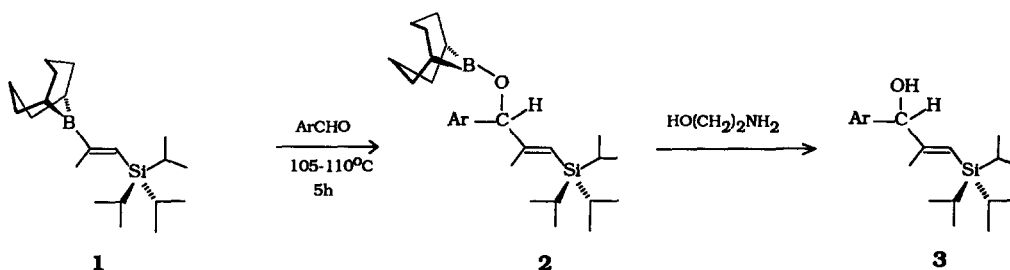


E-3-SILYL ALLYL ALCOHOLS VIA ORGANOBORANES

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Abstract. The Brown vinylation of aromatic aldehydes was developed to provide a simple, efficient route to pure *E*-1-aryl-2-methyl-3-silyl-2-propen-1-ols (**3**).

Recently, we examined the hydroboration of 1-trialkylsilyl-1-alkynes with 9-bora-bicyclo[3.3.1]nonane (9-BBN) with the finding that the triisopropylsilyl group is sufficiently large so as to force the boron atom to the internal position.² This gives *Z*-2-boryl-1-alkenylsilanes (e.g. **1**) cleanly. The traditional difficulties which are encountered with the hydroboration of alkynes with 9-BBN, namely stoichiometric control with terminal alkynes and regiochemical control with internal alkynes, are overcome with this substrate. These silyl-Markovnikov vinylboranes, **1**, undergo an extremely efficient cross-coupling reaction with complete retention of configuration *via* the Suzuki protocol³ to provide a simple entry to *E*- β,β -disubstituted vinylsilanes.⁴ We were intrigued by the possibility that **1** could provide access to *E*-3-silyl allyl alcohols (i.e. **3**) through a 1,2-addition to aldehydes. This reactivity is observed for *B*-vinyl derivatives of 9-BBN,⁵ because this system combines an accessible Lewis acid site with a rigid ring which prevents the reduction of the aldehyde through a β -hydride transfer process.^{5,6} We found this reaction of **1** with aromatic aldehydes to provide **3** cleanly. These results are summarized in Table 1.⁷



Reaction mixtures were monitored by GC for the disappearance of starting aldehyde. By ¹¹B NMR, the disappearance of **1** (δ 75 ppm) gives rise to **2** (δ 54 ppm) as a broadened signal during the reaction, suggesting that equilibrium complexation processes are occurring prior to complete conversion.⁸ With an excess of the aldehyde, we observed some oxidation of **2** to give the corresponding enone together with the reduced aldehyde product (i.e. a benzyloxy-9-BBN derivative). This probably occurs through the boron equivalent of an Oppenauer oxidation.

Unfortunately, aliphatic aldehydes failed to give significant amounts of the desired allylic alcohols under a variety of conditions, either failing to react with **1** or giving product mixtures. In some cases, we observed the partial protonolysis of **1**. Despite this limitation, the Brown vinylation of aromatic aldehydes provides a highly useful entry to stereodefined allylic alcohols which contain the silyl functionality.

Table 1. Silylvinylation of Aromatic Aldehydes.

ArCHO	3	Yield of 3 ^a
PhCHO	3a	70
<i>p</i> -MeC ₆ H ₄ CHO	3b	75
<i>p</i> -MeOC ₆ H ₄ CHO	3c	69
<i>p</i> -ClC ₆ H ₄ CHO	3d	75
<i>m</i> -ClC ₆ H ₄ CHO	3e	61

^a Analytically-pure material isolated by flash chromatography.

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- The following procedure is representative: Under a nitrogen atmosphere, a stirred mixture of **1** (1.7 g, 5.3 mmol) and *p*-chlorobenzaldehyde (0.76 g, 5.2 mmol) was heated for 5 h at 105–110°C, allowed to cool to room temperature, and dry pentane (20 mL) was added. The solution was cooled to 0°C, and ethanolamine (0.33 g, 5.3 mmol) was added dropwise. The cold bath was removed and, after 1 h at room temperature, the mixture was filtered to remove the solid *B*-(β-aminoethoxy)-9-BBN. Pure **3d** (1.32 g, 75%) was isolated by flash chromatography (230–400 mesh SiO₂, 95:5 pentane-ether). The compounds **3** gave acceptable analytical data for the structures shown and revealed the following significant spectroscopic features: **3a**: ¹H NMR (CDCl₃) δ 1.0–1.3 (m, 21H), 1.71 (s, 3H), 2.79 (s, 1H), 5.13 (s, 1H), 5.81 (s, 1H), 7.3–7.4 (m, 5H) ppm. ¹³C NMR (CDCl₃) δ 80.3 (C-1), 156.1 (C-2), 118.0 (C-3), 18.5 (Me), 12.7, 18.9 (t-Pr), 142.1, 126.3, 128.1, 127.2 (Ar: *l.o.m.p*) ppm. MS *m/z* 261 (100, M-(t-Pr)⁺). IR (neat) 3400 (OH) cm⁻¹. **3b**: ¹H NMR (CDCl₃) δ 1.0–1.2 (m, 21H), 1.62 (s, 3H), 2.15 (s, 1H), 2.33 (s, 3H), 5.06 (s, 1H), 5.74 (s, 1H), 7.18 (d, 2H, *J* = 7.9 Hz), 7.22 (d, 2H, *J* = 7.9 Hz) ppm. ¹³C NMR (CDCl₃) δ 80.3 (C-1), 156.1 (C-2); 117.7 (C-3), 18.7 (Me), 12.1, 18.8 (t-Pr), 139.2, 128.0, 126.3, 136.9, 21.0 (Ar: *l.o.m.p.Me*) ppm. MS *m/z* 275 (100, M-(t-Pr)⁺). IR (neat) 3400 (OH) cm⁻¹. **3c**: ¹H NMR (CDCl₃) δ 1.0–1.2 (m, 21H), 1.60 (s, 3H), 2.01 (s, 1H), 3.77 (s, 3H), 5.03 (s, 1H), 5.72 (s, 1H), 6.85 (d, 2H, *J* = 8.7 Hz), 7.26 (d, 2H, *J* = 8.7 Hz) ppm. ¹³C NMR (CDCl₃) δ 80.1 (C-1), 156.3 (C-2), 117.7 (C-3), 18.9 (Me), 12.3, 18.9 (t-Pr), 134.5, 127.8, 113.8, 159.1, 55.0 (Ar: *l.o.m.p.OMe*) ppm. MS *m/z* 291 (28, M-(t-Pr)⁺). IR (neat) 3440 (OH) cm⁻¹. **3d**: ¹H NMR (CDCl₃) δ 1.0–1.2 (m, 21H), 1.63 (s, 3H), 1.64 (s, 1H), 4.83 (s, 1H), 5.77 (s, 1H), 7.2–7.25 (m, 4H) ppm. ¹³C NMR (C₆D₆) δ 79.8 (C-1), 156.1 (C-2), 118.8 (C-3), 18.4 (Me), 12.1, 18.8 (t-Pr), 141.1, 128.1, 127.6, 132.7 (Ar: *l.o.m.p*) ppm. MS (³⁶Cl) *m/z* 295 (100, M-(t-Pr)⁺) IR (neat) 3400 (OH) cm⁻¹. **3e**: ¹H NMR (CDCl₃) δ 1.0–1.2 (m, 21H), 1.50 (s, 3H), 2.58 (s, 1H), 4.94 (s, 1H), 5.59 (s, 1H), 7.10 (s, 3H), 7.26 (s, 1H) ppm. ¹³C NMR (CDCl₃) δ 80.3 (C-1), 155.5 (C-2), 120.0 (C-3), 18.2 (Me), 12.2, 18.8 (t-Pr), 144.4, 126.6, 134.2, 129.4, 124.4, 127.4 (Ar: C-1 to C-6) ppm. MS *m/z* 295 (74, M-(t-Pr)⁺), 61 (100). IR (neat) 3400 (OH) cm⁻¹.
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