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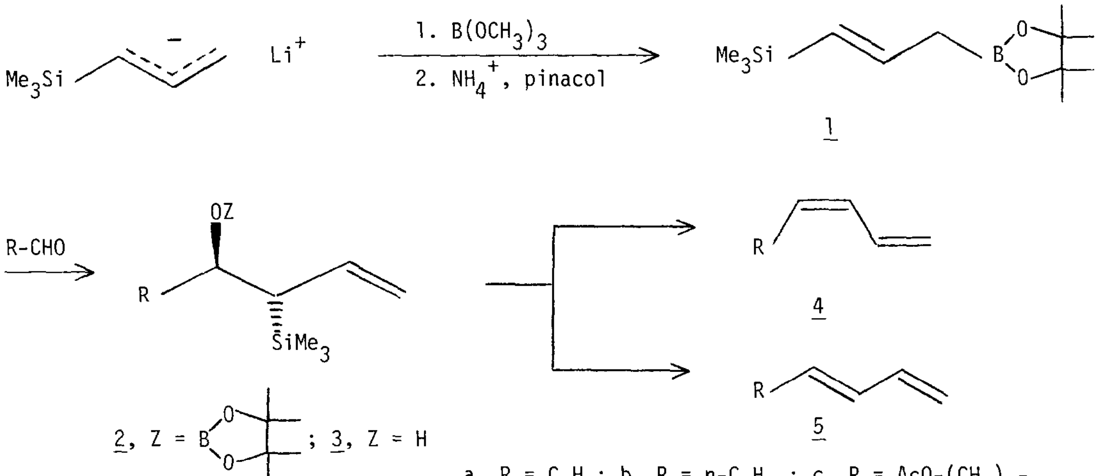
A STEREOCONTROLLED SYNTHESIS OF Z AND E TERMINAL DIENES FROM PINACOL E-1-TRIMETHYLSILYL-1-PROPENE-3-BORONATE

David Jieh Shyh Tsai and Donald S. Matteson*
Department of Chemistry, Washington State University, Pullman, Washington 99164 U.S.A.

Pinacol E-1-trimethylsilyl-1-propene-3-boronate reacts with aldehydes to form (±)-(R^*,S^*)-3-trimethylsilyl-4-hydroxy-1-alkenes, which can be deoxysilylated stereoselectively to either 98% Z or 99% E 1,3-dienes, including the separate components of the red bollworm moth pheromone.

The highly diastereoselective reaction of 2-alkene-1-boronic esters with aldehydes has been reported by Hoffmann and coworkers.[1] We have synthesized pinacol E-1-trimethylsilyl-1-propene-3-boronate (1) and found that it reacts similarly with aldehydes to yield (±)-(R^*,S^*)-3-trimethylsilyl-4-hydroxy-1-alkenes (3),[2] which are readily deoxysilylated by the methods of Hudrlik and Peterson[3] to yield either Z (4) or E (5) terminal dienes of ≥ 98% purity.



a, R = C_6H_5; b, R = n-C_7H_{15}; c, R = AcO-$(CH_2)_8$-

Trimethylsilylallyllithium[4] in THF at -78°C was treated with 1 equivalent of trimethyl borate, stirred 10 min at -78°C, and while still cold poured into saturated aqueous ammonium chloride and dichloromethane. The organic phase was concentrated and treated with one equivalent of pinacol hydrate in petroleum ether overnight. Distillation yielded 53% of 1, bp 46-50°C (0.15 torr), 60 MHz ^{1}H NMR (CDCl$_3$): δ 0.00 (s, 9, SiCH_3), 1.20 (s, 12 CCH_3), 1.73 (d, 6 Hz, 2, CH_2), 5.66 (d, 18 Hz, 1, C=CHSi), 6.20 (d of t's, 18 Hz and 6 Hz, 1, C=CH-C).[5]

Reaction of 1 (1M in ether) with an equivalent of aldehyde, RCHO, was complete in 1-3 days (by TLC) at 20°C. The borates (2) distilled (optional); 2a, R = Ph, 89%, bp 97°C (0.05 torr); 2b, R = n-C_7H_{15}, 78%, bp 107°C (0.15 torr); 2c, R = AcO$(CH_2)_8$,[6] 92%, bp 152°C (0.4 torr).[5] The pinacol borate was cleaved from 2 by triethanolamine[1] in ether 4-16 hr at 20°C. After washing with aqueous sodium bicarbonate, the β-trimethylsilyl alcohols (3) were distilled; 3a, 89%, bp 88°C (0.4 torr); 3b, 79%, bp 72-73°C (0.1 torr); 3c, 92%, bp 132-134°C (0.5 torr).[5]

Treatment of 3 with potassium hydride in THF[3] 10 min followed by aqueous sodium bicarbonate and ether, then bulb to bulb distillation, yielded the *Z*-1,3-dienes (4). With sulfuric acid in THF[3] 10 min followed by similar work-up, 3 yielded *E*-1,3-dienes (5). The geometry was verified from the IR spectra of the known phenylbutadienes 4a and 5a[7] and also by 200 MHz ^{1}H NMR spectra (Table I). By GC analysis, 4a was 98% *Z* and 5a was 99.3% *E* (and thus 3a was ≥99.3% R^*,S^*). Attempted separation of 4b/5b and 4c/5c by GC failed, but 90 or 200 MHz ^{1}H and 22.6 MHz ^{13}C NMR spectra indicated none (<3%) of the opposite isomer in each case.

The sex pheromone of the red bollworm moth (*Disparopsis castanea*) has been reported to consist of 20/80 (±5%) mixture of 4c and 5c.[8] Chemical separation of the isomers,[8] syntheses of isomer mixtures,[9,10] and a synthesis of the pure *E*-isomer[11] have been reported. The present synthesis offers advantages of efficiency and high stereochemical control.

TABLE I. Yields and 200 MHz ^{1}H NMR Data for $H^1H^2C{=}CH^3{-}CH^4{=}CH^5{-}R$ (in $CDCl_3$).[a]

Compound	Yield	δ: H^1	H^2	H^3	H^4	H^5 ;	$J^{cis}_{1,3}$	$J^{trans}_{2,3}$	$J_{3,4}$	$J^{cis}_{4,5}$	$J^{trans}_{4,5}$	J_{5,CH_2} (Hz)
4a	84%	5.18	5.33	6.87	6.22	6.42	10.1	16.8	11.3	11.3	--	--
5a	85%	5.17	5.32	6.50	6.79	6.55	10.4	16.9	10.9	--	15.9	--
4c	94%	5.08	5.17	6.63	5.99	5.45	10.1	16.8	10.9	10.9	--	7.0
5c	88%	4.95	5.08	6.30	6.05	5.69	10.1	16.8	10.1	--	15.2	7.6

[a] Diene peaks of 4b and 5b were same as 4c and 5c (±0.3 Hz) at 90 MHz. $J_{1,2}$ ∼2 for all 4 and 5.

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(2) These are "*threo*" by the convention commonly used for macrolides and related chains,[1] "*erythro*" if the carbon chain is taken as the starting point for naming.

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(5) All new compounds yielded correct elemental analyses (±0.3%) for all elements except O, as well as IR and proton NMR spectra in accord with the assigned structures.

(6) This aldehyde was made conveniently though not very efficiently from 1,9-nonanediol by acetylation with acetic anhydride, chromatographic separation of the monoacetate,[5] and oxidation with pyridinium chlorochromate in dichloromethane; bp 96°C (0.25 torr).

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