An Improved Synthesis of Trisubstituted Ethylenes (Olefins) via Organoboranes

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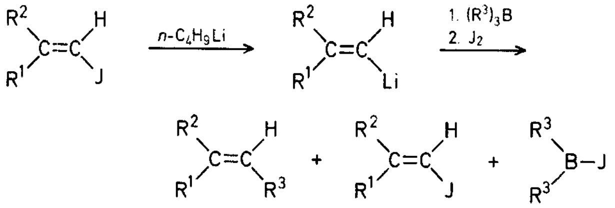
We have recently reported a new highly stereo- and regioselective synthesis[1] of trisubstituted ethylenes[2,3] (trisubstituted olefins). The reaction involves the coupling of a stereospecifically defined vinyllithium to an alkyl group via an alkenyltrialkylborate salt. The sequence is potentially quite useful since the requisite stereospecifically defined vinyl iodides are readily available[4].



However, the synthetic utility of this sequence is clearly limited by the wastage of two of the three alkyl groups on boron. A potential solution to this problem is the use of "throw-away" groups on boron, i.e. RBX_2[5]. Unfortunately, none of the reported "throw-away" groups provide a gener-

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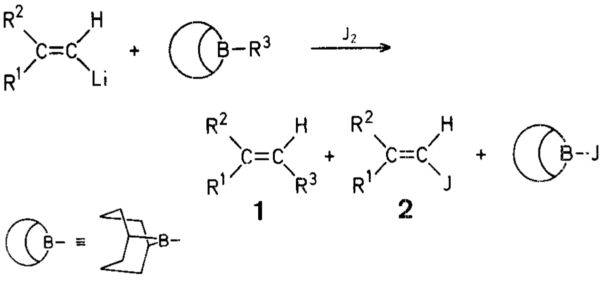
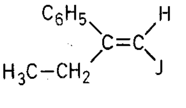
al solution for a variety of reactions[5,6]. We were therefore pleased to find that alkyl derivatives of 9-borabicyclo[3.3.1]nonane(9-BBN)[7] readily undergo this coupling reaction and selectively transfer the alkyl group in preference to the cyclooctyl ring[8]. Since these derivatives are readily available via hydroboration[5], we have investigated the utility of this sequence.



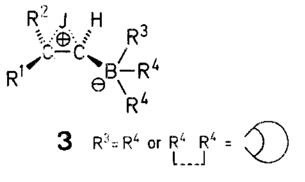
The stereochemistry of the resultant alkenes is indicated by comparison of the ^{13}C-N.M.R. spectra of compounds **1a–e** with those of alkenes previously synthesized in these laboratories.

As further corroboration, we have independently synthesized **1f** by the method of Ref.[9]. The ^{1}H- and ^{13}C-N.M.R. spectra indicated the two samples to be identical. The minimum stereochemical purity of **1f** is 97% as determined by Fourier Transform ^{1}H-N.M.R. analysis and is comparable to that obtained with trialkylboranes. In no case could we detect any of the opposite stereoisomer by ^{1}H- or ^{13}C-N.M.R. analysis.

The low yield in the synthesis of **1f** requires further explanation. Previously[1] and in the case of **1a–e**, the major side product (~10–15%) is the vinyl iodide **2**[10]. In the case of **1f**, compound **2f** represents ~50% of the reaction mixture. The problem of *ipso* substitution versus attack at the carbon β to boron has been noted previously[11,12].



2f



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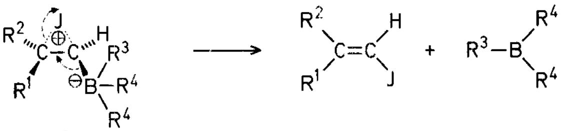
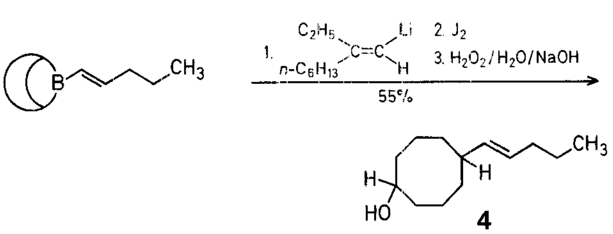
In our hands it appears to be a relatively common result of substituting the iodonium ion **3** at C-2 with groups capable of stabilizing a positive charge. When C-1 stabilizes a positive charge best the major reaction path is the desired "α-transfer"[1]. Alternatively, as C-2 is better able to support a positive charge the iodonium ion opens leaving a positive charge on C-2 an R_3B is either simultaneously or sequentially lost.



3 **2**

In addition to alkyl derivatives, 9-BBN potentially provides a synthesis of stereospecifically defined dienes via hydroboration of 1-alkynes[13]. However, hydroboration of 1-pentyne followed by treatment with a model vinyllithium leads to cyclooctyl ring migration. Only trace amounts of the desired diene could be detected by mass spectroscopy.



In summary, the use of B-alkyl-9-BBN derivatives, readily available via hydroboration allows the stereospecific syn-

Table. Trisubstituted Ethylenes (**1**) prepared

1	R^1	R^2	R^3	Yield[a] [%]	b.p. [°C]/torr	^{1}H-N.M.R. (CDCl$_3$/TMS) δ [ppm]	^{13}C-N.M.R. (CDCl$_3$/TMS) δ [ppm]
a	C_2H_5	n-C_6H_{13}	n-C_4H_9	63	61–63°/ 0.1	0.6–2.3 (m, 27H); 5.10 (t, 1H)	7.28; 8.10; 16.50; 16.75; 17.10; 21.35; 22.36; 23.23; 25.92; 26.52; 30.68; 113.19; 135.14
b	C_2H_5	n-C_6H_{13}	i-C_4H_9	66	68–71°/ 0.1	0.86 (d, 6H); 1.30 (m, 15H); 1.96 (m, 6H); 5.10 (t, 1H)	13.11; 14.10; 21.82; 21.94; 22.46; 22.72; 23.02; 28.09; 28.34; 29.06; 29.15; 31.88; 36.67; 36.91; 122.95; 141.66
c	C_2H_5	n-C_6H_{13}	s-C_4H_9	76	59–63°/ 0.1	0.5–1.6 (m, 22H); 1.9 (m, 5H); 4.81 (d, 1H)	12.04; 13.56; 14.09; 21.43; 22.73; 23.26; 28.38; 29.13; 30.70; 31.87; 33.77; 36.51; 130.84; 139.69
d	C_2H_5	n-C_6H_{13}	c-C_5H_9	82	94–96°/ 0.15	0.6–2.3 (m, 27H); 5.00 (d, 1H)	13.79; 14.05; 22.73; 23.55; 25.50; 28.39; 29.19; 31.90; 34.23; 36.65; 38.71; 129.82; 140.04
e	C_2H_5	n-C_6H_{13}	c-C_6H_{11}	74 (56)[b]	101–103°/ 0.05[c]	0.6–2.3 (m, 29H); 4.95 (d, 1H)	13.76; 14.05; 22.71; 23.39; 26.28; 28.40; 29.14; 31.90; 34.02; 36.52; 36.83; 130.65; 139.39
f	C_2H_5	C_6H_5	n-C_4H_9	39	63–65°/ 0.1	0.96 (m, 6H); 1.41 (m, 4H); 2.20 (m, 2H); 2.53 (q, 2H); 5.66 (t, 1H); 7.34 (m, 5H)	13.60; 14.02; 22.50; 22.98; 28.16; 32.19; 126.37; 128.15; 128.48; 141.58; 143.33

[a] Yield determined by G.L.C. analysis using an internal standard.

[b] Yield of isolated product.

[c] Kugelrohr distillation.

thesis of trisubstituted ethylenes in moderate to good yields. In view of the limited utility of S_N2 reactions of vinyl lithiums with alkyl halides, this methodology should be useful in the synthesis of natural products containing trisubstituted ethylene moieties.

(*E*)-1-Cyclohexyl-2-ethyl-1-octene (1e); Typical Procedure:
A dry 250 ml round bottom flask equipped with a septum-capped inlet, reflux condenser, and magnetic stirring bar is flushed with nitrogen. To this flask is added ether (25 ml) and (*E*)-2-ethyl-1-iodo-1-octene[4] (5.40 ml, 25 mmol). The flask is cooled to −80 °C and a solution of butyllithium (25 mmol) in hexane (9.25 ml) is added. The mixture is stirred at −60 °C for 30 min, then cooled to −80 °C, and a solution of 9-cyclohexyl-9-BBN (25 mmol) in tetrahydrofuran (46.25 ml) is added. Stirring is continued for 10 min, then a solution of iodine (6.35 g) in tetrahydrofuran (5 ml) is added. The mixture is stirred for 1 h at −80 °C and allowed to warm to room temperature. The organic layer is separated, washed with 3 normal aqueous sodium hydroxide (3 × 25 ml), and oxidized by the addition of 30% hydrogen peroxide (10 ml) and 3 normal aqueous sodium hydroxide (10 ml). The organic phase is separated, the solution is dried with magnesium sulfate, and the solvent removed to leave an oily solid. Trituration with hexane followed by filtration to remove cyclooctanediol and evaporation affords an oil. This product is distilled in a kugelrohr to give pure **1e**; yield: 3.08 g (56%); b.p. 61–63 °C/0.1 torr.

The remaining olefins were prepared in an analogous fashion and isolated by preparative G.L.C. All olefins were greater than 98% pure by G.L.C. analysis on 6′ columns of 10% SE-30 and XE-60 and are identical to those previously reported.

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