An Improved Method for Stereoselective Synthesis of (*E*)-Alkenes via Alkenyldialkylboranes

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Synopsis. Successive treatments of alkenyldialkylboranes, formed by the reaction of alkynes and sterically hindered dialkylboranes, with alkyllithium and benzenesulfenyl chloride afforded highly pure (*E*)-alkenes in good or excellent yields.

(*Z*)-[1] and (*E*)-[2] alkene syntheses reported by Zweifel and co-workers are some of the interesting reactions using alkenylboranes; it has a limitation that the available alkyl group is restricted to those derived from sterically hindered alkenes.[3] From a different point of view, the reactions provide a convenient method for the regio- and stereoselective synthesis of alkenes by the combination of the alkenyl group to the alkyl group on the boron moiety.

For a practical use of above (*E*)-alkene synthesis (Scheme 1), the reaction had two disadvantages: The use of very poisonous cyanogen bromide and contamination by the *Z* isomer. We wish to report here a modified method for the (*E*)-alkene synthesis using alkyllithium and benzenesulfenyl chloride instead of cyanogen bromide.

In the Zweifel's reactions, the combined yields of the (*E*)- and (*Z*)-alkenes seemed to be affected by the degree of the coordination of the anion (CN^-) to the boron atom; also, the ratio of the two isomers seemed to be affected by the ease of the elimination of the electrophile (Br^+), which once attacked the alkenyl double bond, from the carbon atom. Accordingly, we examined both nucleophilic reagents for the boron atom and electrophilic reagents for the double bond, using (*E*)-1-hexenyldicyclohexylborane. Thus, successive treatments of the 1-hexenylborane with alkyllithium and benzenesulfenyl chloride gave excellent results.

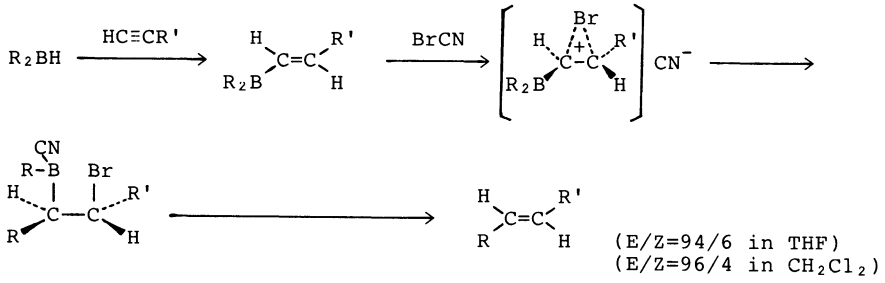
In preliminary examinations, where alkyllithium was absent, (*E*)-1-hexenyldicyclohexylborane was treated with an equimolar amount of benzenesulfenyl chloride in THF. The reaction mixture was then treated with hexane for an analysis. However, only a small amount of a mixture of (*E*)- and (*Z*)-1-cyclohexyl-1-hexene was obtained. In similar treatments of an ate-complex formed by the addition of an equimolar amount of methyllithium or butyllithium to the 1-hexenylborane, gave the mixture of the alkenes quantitatively. Essentially, the pure *E*-isomer was obtained at −78 °C. These results are shown in Table 1.

In a similar reaction, [(*E*)-1-hexenyl]bis(1,2-dimethylpropyl)borane also gave almost pure (*E*)-2,3-dimethyl-4-nonene in 92% yield. [(*E*)-1-Hexenyl]bis(*trans*-2-methylcyclohexyl)borane gave a mixture of (*E*)- and (*Z*)-(*trans*-2-methylcyclohexyl)-1-hexene (*E*/*Z*=90/10), while the *trans*-2-methylcyclohexyl group migrated with a retention of the configuration. A stereochemical consideration for the above facts suggested that the large steric hindrance between the 2-methylcyclohexyl group R, remaining on the boron atom, and the phenylthio group interfered somewhat with the favorable arrangement regarding to the cis-elimination; thus, it increased the chance for the trans-elimination which gave the *Z* isomer (Scheme 2). In a reaction of [(*E*)-3,3-dimethyl-1-butenyl]bis(*trans*-2-methylcyclohexyl)-borane or [(*E*)-2-phenylethenyl]bis(*trans*-2-methylcyclohexyl)borane, having such a bulkier group as *t*-butyl or phenyl group instead of *n*-butyl group on the β-carbon atom, exclusively gave the *E* isomer. In this case, a steric hindrance between the *trans*-2-methylcyclohexyl group R, migrated to the α-carbon, and the *t*-butyl or the phenyl group R' interfered with the arrangement favored with the trans-elimination and

Table 1. 1-Cyclohexyl-1-hexenes from 1-Hexenyldicyclohexylborane[a)]

RLi	Temp °C	Alkene ratio *E*	Alkene ratio *Z*	Total alkene yield/%
None	0			trace
	−78	14	86	5
n-C_4H_9Li	0	92	8	≒100
	−78	>99	<1	≒100
CH_3Li	−78	>99	<1	≒100

a) The isomer distribution and the yield of alkenes were determined by GLC.

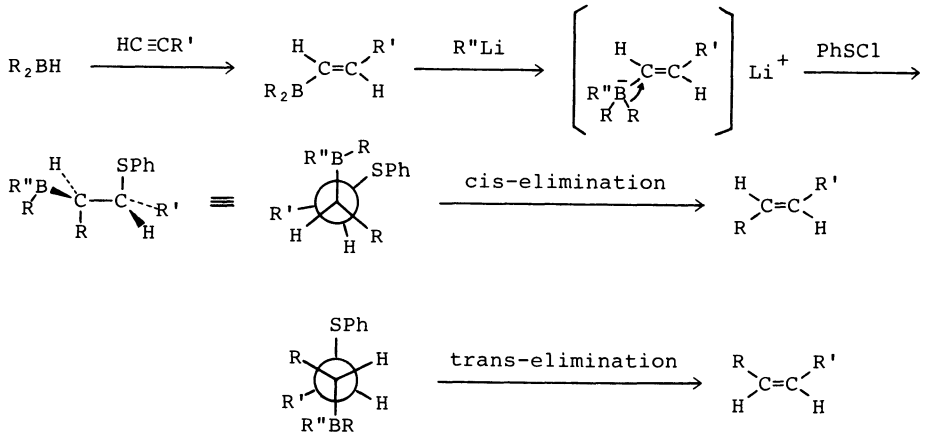


Scheme 1.

Table 2. (*E*)-1-Alkyl-1-alkenes from (*E*)-1-Alkenyldialkylboranes[a)]

R of R_2BH	Alkyne	R″ of R″Li	Yield of *E*-alkene/%	Isomeric purity/%
C_6H_{11}-*c*	HC≡CC_4H_9-*n*	*n*-C_4H_9	100[b)](91)[c)]	>99
	HC≡CC_6H_5	*n*-C_4H_9	85 (79)	≒100
	HC≡CC_4H_9-*t*	CH_3	76 (70)	≒100
$(CH_3)_2CH(CH_3)CH$	HC≡CC_4H_9-*n*	*n*-C_4H_9	92 (83)	>99
	HC≡CC_6H_5	*n*-C_4H_9	80 (75)	≒100
2-$CH_3C_6H_{10}$-*c*	HC≡CC_4H_9-*n*	CH_3	79 (72)	90
	HC≡CC_6H_5	CH_3	65 (60)	≒100
	HC≡CC_4H_9-*t*	CH_3	80 (75)	≒100

a) The alkenyldialkylborane was treated with equimolar amounts of alkyllithium (at 0°C, for 0.5 h) and benzenesulfenyl chloride (at −78°C, for 0.5 h) to the alkenyldialkylborane. b) Determined by GLC. c) The value in the parenthesis is isolated yield.



Scheme 2.

gave no chance for the formation of the *Z* isomer (Scheme 2). Similar alkenylboranes, having a *t*-butyl or a phenyl group on the β-carbon atom, gave almost pure (*E*)-alkenes. In all the cases examined, (*E*)-alkenes were isolated from the reaction mixtures by column chromatography.[4)] These results are shown in Table 2.

The high stereoselectivity and the ease of the reaction procedure, shown above, seem to make the present reaction of practically applicable to the synthesis of (*E*)-alkenes, especially having two bulky alkyl groups on the alkenyl carbon atoms.

Experimental

Instruments. IR spectra were recorded using a Hitachi 285 spectrometer. ^{1}H NMR and ^{13}C NMR (200 MHz) spectra ($CDCl_3$, TMS) were run on a JEOL FX-200 spectrometer. Mass spectra were recorded by a Hitachi M-52 mass spectrometer.

Reagents. Cyclohexene, 2-methyl-2-butene, 1-methyl-1-cyclohexene and THF were dried over lithium aluminium hydride and distilled under an argon stream. Commercial 1-hexyne and phenylacetylene were dried over Molecular Sieves-4A. 3,3-Dimethyl-1-butyne was prepared by a method described in the literature,[5)] and dried over Molecular Sieves-4A. Commercial alkyllithiums were used without any purification. Benzenesulfenyl chloride was prepared by the method described in the literature.[6)]

Reaction Procedure. A 50-ml round-bottomed flask, equipped with a gas inlet for argon, a sample inlet with a serum cap and a magnetic stirring bar, was flushed with argon. In the flask, alkenyldialkylborane was prepared by the addition of alkyne (10 mmol) to dialkylborane (10 mmol) in THF under appropriate conditions. Then, butyllithium (10 mmol) in hexane or methyllithium (10 mmol) in diethyl ether was added at 0 °C and the solution was stirred for 0.5 h, and then cooled to −78 °C. To this solution, benzenesulfenyl chloride (10 mmol) was slowly added and the reaction mixture was stirred for 0.5 h and then extracted three times with diethyl ether. The combined extracts were washed twice with NaCl-saturated water and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was put on a column packed with silica gel (Wako-gel Q-50) and eluted by pentane.

Spectral Data of the Products are as Follows. (*E*)-1-Cyclohexyl-1-hexene: ^{1}H NMR δ=0.88 (t, *J*=6.8Hz, 3H), 0.89—2.10 (m, 17H) and 5.30—5.40 (m, 2H); ^{13}C NMR δ=13.98, 22.18, 26.14 (-CH_2-, 2C), 26.27, 31.88, 32.55, 33.30 (-CH_2-, 2C), 40.69 (>CH-), 127.68 (-CH=) and 136.38 (-CH=); IR 970 cm^{-1} ($\diagdown$C=C$\diagup$); MS *m/z* 166 (M^+).

(*E*)-1-Cyclohexyl-3,3-dimethyl-1-butene: ^{1}H NMR δ=0.97 (s, 9H), 0.97—1.97 (m, 11H), 5.22 (dd, *J*=15.6 and 6.3 Hz, 1H) and 5.39 (d, *J*=15.6 Hz, 1H); ^{13}C NMR δ=26.19 (-CH_2-, 2C), 26.27, 29.87 (-CH_3, 3C), 32.54 (-C-). 33.44 (-CH_2-, 2C), 40.69 (>CH-), 130.72 (-CH=) and 138.82 (-CH=); IR 1360 and 970 ($\diagdown$C=C$\diagup$) cm^{-1}; MS *m/z* 166 (M^+).

(*E*)-1-Cyclohexyl-2-phenylethene: ^{1}H NMR δ=1.06—2.23 (m, 11H), 6.16 (dd, *J*=16.1 and 6.8 Hz, 1H), 6.34 (d, *J*=16.1 Hz, 1H) and 7.13—7.40 (m, 5H); ^{13}C NMR δ=26.02 (-CH_2-,

2C), 26.17, 32.93 (-CH_2-, 2C), 41.55 (>CH-), 125.90 (-CH=, 2C), 126.68 (-CH=), 127.19 (-CH=), 128.41(-CH=, 2C), 136.80 (-CH=) and 138.01 (>C=); IR 965 (⁀C=C⁀), 745 and 690 cm^{-1}; MS m/z 186 (M^+).

(*E*)-2,3-Dimethyl-4-nonene: ^1H NMR δ=0.82 (d, J=6.8 Hz, 3H), 0.84 (d, J=6.8 Hz, 3H), 0.89 (t, J=6.8 Hz, 3H), 0.92 (d, J=6.8 Hz, 3H), 1.22—1.60 (m, 5H), 1.78—2.10 (m, 3H) and 5.26—5.36 (m, 2H); ^{13}C NMR δ=13.96, 17.68, 19.63, 19.89, 22.18, 31.93, 32.37, 33.05, 42.98, 129.35 (-CH=) and 134.49 (-CH=); IR 970 (⁀C=C⁀) cm^{-1}; MS m/z 154 (M^+).

(*E*)-1-Phenyl-3,4-dimethyl-1-pentene: ^1H NMR δ=0.87 (d, J=7.3 Hz, 3H), 0.89 (d, J=6.8 Hz, 3H), 1.05 (d, J=6.3 Hz, 3H), 1.48—1.74 (m, 1H), 1.98—2.24 (m, 1H), 6.12 (dd, J=16.1 and 8.3 Hz, 1H), 6.23 (d, J=16.1 Hz, 1H) and 7.12—7.39 (m, 5H); ^{13}C NMR δ=17.44, 19.80, 19.97, 33.27, 43.54, 125.95 (-CH=, 2C), 126.70 (-CH=), 128.43 (-CH=, 2C), 128.82 (-CH=), 135.34 (-CH=) and 138.04 (>C=); IR 965 (⁀C=C⁀), 745 and 690 cm^{-1}; MS m/z 172 (M^+).

(*E*)-1-(*trans*-2-Methylcyclohexyl)-3,3-dimethyl-1-butene: ^1H NMR δ=0.80 (d, J=5.8 Hz, 3H), 0.85—1.80 (m, 10H), 0.98 (s, 9H), 5.07 (dd, J=15.6 and 8.3 Hz, 1H) and 5.38 (d, J=15.6 Hz, 1H); ^{13}C NMR δ=20.82, 26.29, 26.63, 29.89 (-CH_3, 3C), 32.66 (-C(-)-), 34.03, 35.31, 37.14 (>CH-), 48.91 (>CH-), 129.72 (-CH=) and 140.69 (-CH=); IR 1355 and 970 (⁀C=C⁀) cm^{-1}; MS m/z 180 (M^+).

(*E*)-1-(*trans*-2-Methylcyclohexyl)-2-phenylethene: ^1H NMR δ=0.87 (d, J=6.3 Hz, 3H), 0.90—1.90 (m, 10H), 6.03 (dd, J=15.6 and 8.3 Hz, 1H) 6.34 (d, J=15.6 Hz, 1H) and 7.07—7.43 (m, 5H); ^{13}C NMR δ=21.01, 26.10 26.46, 33.59, 35.17, 37.11 (>CH-), 49.37 (>CH-), 125.90 (-CH=, 2C), 126.65 (-CH=), 128.41 (-CH=, 2C), 128.87 (-CH=), 136.04 (-CH=) and 138.04 (>C=); IR 960 (⁀C=C⁀), 740 and 690 cm^{-1}; MS m/z 200 (M^+).

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