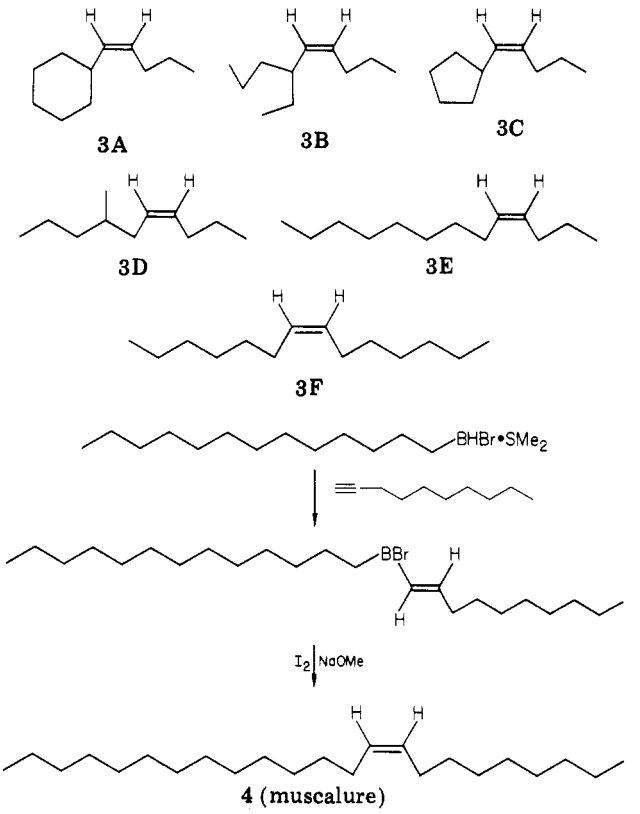

(6)

cis-3-hexene and dibromoborane–dimethyl sulfide, were added at 0 °C 3 mL of SMe_2 and 25 mL of Et_2O, followed by a slow addition of $LiAlH_4$ in Et_2O (7.5 mmol), with stirring under nitrogen. The reaction was allowed to proceed 3 h at 0 °C and 1 h at room temperature. The resulting alkylbromoborane was slowly transferred to a solution of 1-pentyne (30 mmol) in Et_2O at 0 °C. The reaction mixture was stirred 1 h at 0 °C and 1 h at room temperature. Then the resulting vinylbromoborane was added to the solution of NaOMe (150 mmol) in MeOH at 0 °C. After 0.5 h at room temperature, the solvent ether was removed under vacuum and 30 mL of MeOH was added. Iodine (30 mmol, 7.6 g) was added to this vinylborane solution in MeOH at 0 °C and the solution was stirred at room temperature for 3 h. Aqueous $Na_2S_2O_3$ solution was now added and the reaction mixture was extracted with pentane and the extract dried over anhydrous $MgSO_4$. The crude product showed ≈6% 1-pentenyl iodide. This could be separated by careful distillation to yield pure *cis*-6-ethyl-4-nonene (**3B**; 3.18 g, 69%) bp 70–71 (12 mm), n^{20}_D 1.4319 GC analysis indicated >99% chemical purity. **3B**: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.69–1.68 (m, 17 H), 1.78–2.38 (m, 3 H), 4.84–5.61 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 11.18, 13.19, 13.67, 20.14, 22.71, 28.41, 29.54, 37.86, 38.50 (alkyl C); 129.16, 134.34 (C=C).

This procedure solves the two major problems associated with the earlier procedure,[3] thus providing a general, one-pot, stereospecific synthesis of cis-disubstituted alkenes. We are presently exploring the possibilities of employing this procedure for the stereodefined synthesis of trisubstituted alkenes. The application of alkylbromoboranes for the stereospecific synthesis of trans-disubstituted alkenes has been also established.[11]

(10) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384.
(11) Brown, H. C.; Basavaiah, D.; Kulkarni, S. U. *J. Org. Chem.*; following paper in this issue.
(12) In a mixture of isomers, the vinylic carbons of cis alkenes can be distinguished from the corresponding carbons of trans alkenes. Dorman, D. E.; Jautelat, M.; Roberts, J. D.; *J. Org. Chem.* **1971**, *36*, 2757.
(13) Postdoctoral research associate on Grant GM 10937 from the National Institutes of Health.

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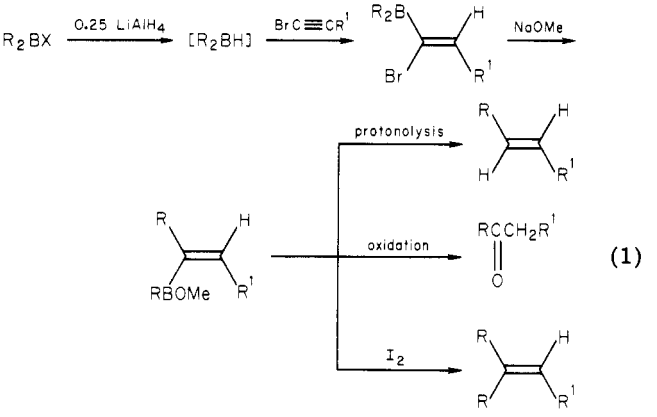
A General and Stereospecific Synthesis of Trans Alkenes and Regiospecific Synthesis of Ketones via Stepwise Hydroboration

Summary: The hydroboration of 1-bromo-1-alkynes with alkylbromoboranes ($RBHBr\cdot SMe_2$), conveniently obtained via the controlled hydridation of alkyldibromoboranes ($RBBr_2\cdot SMe_2$), followed by treatment with sodium methoxide produces *B*-(*trans*-1-alkyl-1-alkenyl)boronate esters that provide the corresponding trans alkenes on protonolysis and ketones on oxidation.

Sir: Recently we reported[1] a general synthesis of ketones, trans alkenes, and trisubstituted alkenes via the hydroboration of 1-bromo-1-alkynes, thus expanding the scope of the original Zweifel[2] procedure (eq 1).



(1)

In the preparation of trans alkenes and ketones, this procedure has a disadvantage in that one of the two alkyl groups on boron is lost, rendering it less practical for alkyl groups derived from expensive or synthesized alkenes. This difficulty was surmounted by using thexylborane[3] or thexylchloroborane.[4] These modified methods are satisfactory for the synthesis of ketones and trans alkenes, although the blocking group (thexyl moiety) does not permit application of this approach for the preparation of trisubstituted alkenes.

In order to expand further the scope of this approach, we undertook to examine the use of an easily replaceable blocking group on boron, a group such as halogen. Recently we reported the preparation of a new class of partially alkylated haloborane reagents, alkylbromoborane ($R^1BHX\cdot SMe_2$, 1), via controlled hydridation of the cor-

(1) Brown, H. C.; Basavaiah, D. *J. Org. Chem.* **1982**, *47*, 754.
(2) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 5086.
(3) Negishi, E.; Katz, J.-J.; Brown, H. C. *Synthesis* **1972**, 555.
(4) (a) Brown, H. C.; Lee, H. D.; Kulkarni, S. U. *Synthesis* **1982**, 195. (b) Kulkarni, S. U.; Lee, H. D.; Brown, H. C. *Ibid.* **1982**, 193.

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Table I. Synthesis of Trans Alkenes and Ketones from Alkyldibromoborane and 1-Bromo-1-alkyne[a]

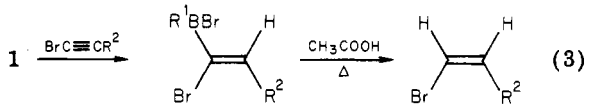
alkene for $R^1BBr_2 \cdot SMe_2$	1-bromo-1-alkyne	product[b]	% yield[c]	bp, °C/mm[e]	n^{20}_D[e]
1-hexene	1-bromo-1-hexyne	4A[d]	67	88–89/5.5 (213.5/760)[11]	1.4315 (1.4304)[1]
		5A	76	78–79/0.5 (125/12)[12]	1.4305 (1.4339)[12]
1-hexene	1-bromo-1-octyne	4B[d]	73	76–77/0.6 (69–71/0.4)[4a]	1.4382 (1.4385)[4a]
1-octene	1-bromo-1-heptyne	4C[d]	72	100–102/0.5	1.4399
2-methyl-1-pentene	1-bromo-1-octyne	4D[d]	70	74–76/0.5 (88–90/1)[1]	1.4370 (1.4365)[1]
		5B	75	100–101/0.5 (136.5/10)[10]	1.4361 (1.4358)[10]
cyclopentene	1-bromo-1-hexyne	5C	76	74–76/0.6 (77–79/0.9)[1]	1.4506 (1.4516)[1]
cis-3-hexene	1-bromo-1-hexyne	5D	78	72–73/0.5	1.4295

[a] All reactions were carried out on a 25-mmol scale. [b] Chemical purities of all compounds (4A–D, 5A–D) are >98% by GC analysis on a 6-ft SE-30 column. [c] Yields of pure products isolated by distillation based on alkene or 1-bromo-1-alkyne. [d] Isomeric purities are >96% by ^{13}C NMR analysis.[13] [e] Literature values are given in parentheses.

responding alkyldibromoborane ($R^1BBr_2 \cdot SMe_2$) for the synthesis of mixed dialkylbromoboranes and trialkylboranes (eq 2).[5]

$$R^1BBr_2 \cdot SMe_2 \xrightarrow[Et_2O]{0.25LiAlH_4} \underset{1}{R^1BHBr \cdot SMe_2} \rightarrow R^1R^2BBr \cdot SMe_2 \longrightarrow R^1R^2R^3B \quad (2)$$

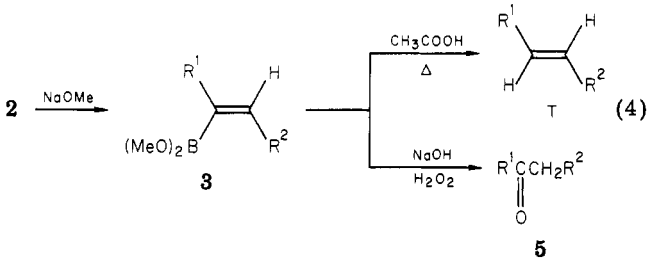
Consequently, it appeared that the hydroboration of 1-bromo-1-alkyne with **1** should provide *B*-(*cis*-1-bromo-1-alkenyl)alkylbromoborane (**2**). Indeed, this reaction was clean, proceeding to the monohydroboration stage,[6,7] as evidenced by the formation of *cis*-1-bromo-1-octene in excellent yield on protonolysis of **2** ($R^1 = n\text{-}C_6H_{13}$, $R^2 = n\text{-}C_6H_{13}$; eq 3).



(3)

2

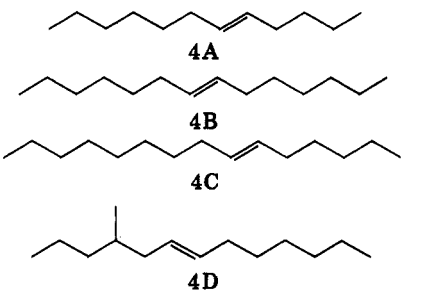
Treatment of **2** with sodium methoxide induces the migration of the alkyl group from boron to the vinylic carbon with the displacement of bromine, providing *B*-(*trans*-1-alkyl-1-alkenyl)boronate esters (**3**). Simple protonolysis of **3** affords trans alkenes (**4**), while oxidation furnishes ketones (**5**; eq 4).



(4)

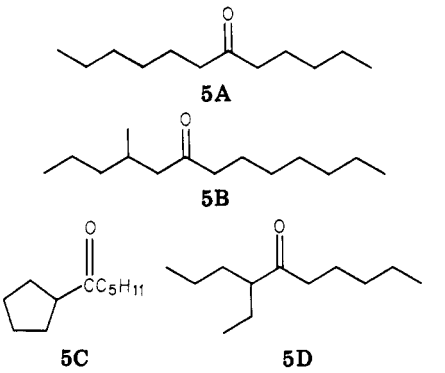
3 **5**

The protonolysis of **3** was effected by heating with acetic acid under reflux. Representative trans alkenes (**4A–D**) were prepared from the corresponding alkenes and bromoalkynes in high yields and excellent purities (>96% isomeric purity, >98% chemical purity) as shown in Table I.



4A **4B** **4C** **4D**

Oxidation of **3** with alkaline hydrogen peroxide produced the corresponding ketones (**5A–D**) in excellent yields (Table I).



5A **5B** **5C** **5D**

The following procedure for the synthesis of 4-methyl-6-tridecene (**4D**) is representative. To 25 mmol of 2-methyl-1-pentyldibromoborane–dimethyl sulfide, prepared from 2-methyl-1-pentene and dibromoborane–dimethyl sulfide,[8] were added at 0 °C 2.5 mL of SMe_2 and 20 mL of Et_2O, followed by a slow addition of $LiAlH_4$ in Et_2O (6.25 mmol) with stirring. The reaction was allowed to proceed for 3 h at 0 °C, followed by 1 h at room temperature. The resulting alkylbromoborane was slowly transferred to the solution of 1-bromo-1-octyne (25 mmol) in Et_2O (5 mL) at 0 °C. After 1 h at room temperature, the reaction mixture was added to the solution of sodium methoxide (80 mmol) in methanol at 0 °C and stirred at room temperature for 1 h. Acetic acid (3 mL) was slowly added to neutralize any excess sodium methoxide. Solvents and volatile materials were removed under vacuum. Acetic acid (30 mL) was added and heated under reflux

(5) Kulkarni, S. U.; Basavaiah, D.; Zaidlewicz, M.; Brown, H. C. *Organometallics* **1982**, *1*, 212.

(6) In the present experiments, only 5–10% of 1-bromo-1-octyne remained unreacted corresponding to the amount of ether-cleaved product $R^1B(OEt)_2$ formed during the hydridation step (estimated by ^{11}B NMR spectrum of **1**), indicating that there is no dihydroboration (for experimental details, see ref 7).

(7) Brown, H. C.; Basavaiah, D.; Kulkarni, S. U. *J. Organometal. Chem.* **1982**, *225*, 63.

(8) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384.

for 3 h. The reaction mixture was cooled and the usual workup[9] afforded after distillation 3.44 g (70%) of 4-methyl-6-tridecene (**4D**), bp 74–76 °C (0.5 mm), n^{20}D 1.4370 [lit.[1] bp 88–90 °C (1 mm), n^{20}D 1.4365)]. GC analysis indicated 100% chemical purity. **4D**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.68–1.65 (m, 22 H), 1.78–2.34 (m, 4 H), 5.37 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.56, 13.84, 18.98, 19.90, 22.40, 28.63, 29.45, 31.60, 32.41, 32.72, 38.76, 39.92 (alkyl C), 128.34, 131.16 (C=C).

To a mixture containing 25 mmol of **2** (R^1 = 2-methyl-1-pentyl, R^2 = *n*-hexyl) was slowly added at 0 °C 26.6 mL of 3 N sodium hydroxide and stirred at room temperature for 1 h. The usual oxidation with hydrogen peroxide[9] afforded 3.9 g (75%) of 4-methyl-6-tridecanone (**5B**), bp 100–101 °C (0.5 mm), n^{20}_D 1.4361 [lit.[10] bp 136.5 °C (10 mm), n^{20}_D 1.4358]. GC analysis indicated 100% chemical purity. **5B**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.68–1.95 (m, 24 H), 2.0–2.44 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.61, 13.79, 19.43, 19.84, 22.40, 23.51, 28.50, 29.08, 31.62, 39.11, 42.72, 49.62 (alkyl C), 205.02 (C=O).

This procedure represents the first general one-pot synthesis of *B*-(*trans*-1-alkyl-1-alkenyl)boronate esters (**3**) which are not available by direct hydroboration. It is noteworthy that the hydroboration of internal alkynes provides the opposite isomer of this vinylborane. These vinylboron intermediates offer great promise in organic synthesis. They have been conveniently transformed into the corresponding trans alkenes or ketones, representing a simple synthesis of such functionalities without loss of any alkyl groups. We are presently exploring the possibilities of utilizing **3** for the stereodefined synthesis of trisubstituted alkenes.

Registry No. **1** (R^1 = *n*-C_6H_{13}; X = Br), 79357-05-4; **2** (R^1 = *n*-C_6H_{13}; R^2 = *n*-C_6H_{13}), 82752-58-7; **2** (R^1 = 2-methyl-1-pentyl; R^2 = *n*-hexyl), 82742-10-7; **3** (R^1, R^2 = *n*-C_6H_{13}), 82742-08-3; **4a**, 7206-16-8; **4b**, 41446-63-3; **4c**, 74392-31-7; **4d**, 80583-44-4; **5a**, 6064-27-3; **5b**, 80583-41-1; **5c**, 50395-66-9; **5d**, 82742-09-4; 1-hexene, 592-41-6; 1-octene, 111-66-0; 2-methyl-1-pentene, 763-29-1; cyclopentene, 142-29-0; *cis*-3-hexene, 7642-09-3; 1-bromo-1-hexyne, 1119-64-8; 1-bromo-1-octyne, 38761-67-0; 1-bromo-1-heptyne, 19821-84-2; 2-methyl-1-pentyldibromoborane-dimethyl sulfide, 72205-97-1; dibromoborane–dimethyl sulfide, 55671-55-1.

(9) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.
(10) Schlenk, W., Jr. *Leibigs Ann. Chem.* **1973**, 1195.
(11) Soják, L.; Hrivnák, J. *J. Chromatogr. Sci.* **1972**, *10*, 701.
(12) Rabilloud, G. *Bull. Soc. Chim. Fr.* **1966**, 634.
(13) In a mixture of isomers, the vinylic carbons of trans alkenes can be distinguished from the corresponding carbons of the cis alkenes. Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757.

(14) (a) Postdoctoral research associate on Grant GM-10937 from the National Institutes of Health. (b) Postdoctoral research associate, Purdue University.

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