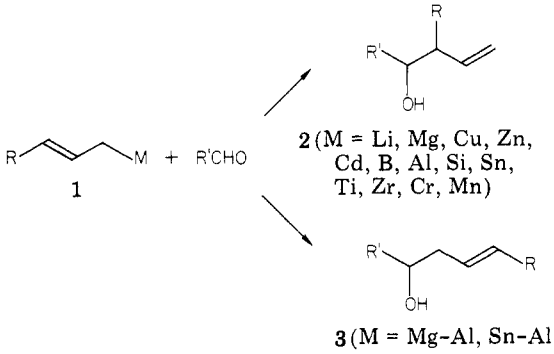
21378-21-2; 2-methyl-2-propen-1-ol, 513-42-8; 2-furanmethanol, 98-00-0; 2,4-dimethyl-1-hexen-3-ol, 88056-79-5.

George Büchi,* Dennis E. Vogel
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received August 25, 1983

Selective Synthesis of either Branched or Linear Homoallyl Alcohols via the Reaction of Aldehydes with the Allylic Borane–Selenium System

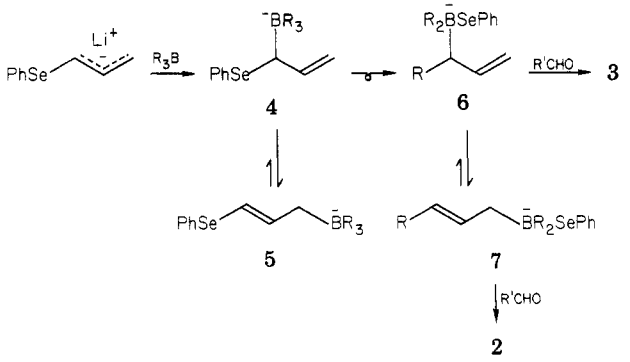
Summary: Either branched (**2**) or linear (**3**) homoallyl alcohols can be prepared independently by choosing the reaction conditions through the reaction of (phenylselenyl)allyl carbanion with trialkylboranes.

Sir: In general, γ-substituted allylic organometallic compounds **1** react with aldehydes to produce branched homoallyl alcohols **2**.[1] Quite recently, we have found that the



linear isomer **3** can be obtained through the combination of the certain allylic organometallics with aluminum derivatives.[2] The selective synthesis of either branched or linear homoallyl alcohols is becoming increasingly important for control of acyclic stereochemistry;[3] the former type of reaction is useful for a 1,2 asymmetric induction in acyclic systems, while the latter alcohols can be converted into the tetrahydrofuran derivatives with alkyl substituents at the 2,5 positions. We now report that either branched or linear alcohols can be prepared at will from the single starting material by merely choosing the reaction conditions.

The key of our procedure is based on the findings that the alkyl group of R_3B in complex **4** undergoes a facile migration from boron to the α carbon[4] and that the allylic rearrangement of the resulting boron–selenium complex **6** to **7** is slow in comparison with the usual allylic boranes.[5]



To a solution of 1.2 mmol of freshly prepared lithium diisopropylamide dissolved in 10 mL of THF was added allyl phenyl selenide (1 mmol, 0.13 mL) at −78 °C under nitrogen atmosphere, and the mixture was stirred for 30 min at this temperature: method A, R_3B (3 mmol) was added at −78 °C and the resulting mixture was kept at 0 °C for 1 h; method B, R_3B (3 mmol) was added at −78 °C and the resulting mixture was kept at room temperature for 12 h; method C, R_3B (1 mmol) was added at −78 °C and the resulting mixture was kept at room temperature for 12 h. After an appropriate operation among these three methods, the mixture was again cooled to −78 °C and an aldehyde (1 mmol) was added. The reaction was quenched at room temperature with H_2O. Excess boranes were oxidized with H_2O_2–NaOH as usual. The ratio of **3** to **2** was investigated at this stage.

The results are summarized in the Table I. Method A provides the linear adduct either predominantly or exclusively. The short rection period at lower temperature must suppress the allylic migration from **6** to **7**.[7] The prolonged reaction period at room temperature completes the migration, giving the branched adduct (method B). Interestingly, use of 2 equiv of R_3B with method B (at room temperature for 12 h) causes a decrease of **2** and an increase of **3**. For example, the ratio of **2**/**3** from benzaldehyde was 91:9 with 3 equiv of Et_3B, while the ratio

Table I. Selective Synthesis of Either Branched or Linear Homoallyl Alcohols[a]

aldehyde	R_3B	method	homoallyl alcohol,[b] % 3 (*E*:*Z*)	homoallyl alcohol,[b] % 2 (erythro:threo)	total yield,[c] %
C_6H_5CHO	Et_3B	A	94 (86:14)	6	88
	Et_3B	B	9	91 (24:76)	89
	n-Bu_3B	B		~100 (12:88)	92
	Et_3B	C	~100 (88:12)		45[d]
p-$CH_3C_6H_4CHO$	Et_3B	A	>99 (~100:0)	trace	90
	Et_3B	B		~100 (36:64)	92
p-$CH_3OC_6H_4CHO$	Et_3B	A	71 (*e*)	29 (*e*)	80
	Et_3B	B	8	92 (14:86)	81
p-$O_2NC_6H_4CHO$	Et_3B	C	77 (*e*)	23 (*e*)	65[d]
	Et_3B	B		~100 (18:82)	93
n-C_3H_7CHO	Et_3B	B		~100 (25:75)	85
n-$C_9H_{19}CHO$	Et_3B	B		~100 (39:61)	83

[a] All reactions were carried out on a 1-mmol scale as described in the text. [b] By ^1H NMR and GLPC analysis (PEG 6000, 5%, 2 m). [c] Isolated (combined) yield through a short column. When a mixture of 3 and 2 was obtained, separation was performed through silica gel chromatography using hexane–ether (20:1) as eluant. In some cases, the reduced product of the starting aldehyde was accompanied, presumably owing to the reduction with the ate complexes (**4**–**7**).[6] [d] The reaction was incomplete and the aldehyde was recovered. [e] Not determined.

0022-3263/83/1948-5408$01.50/0

changed to 40:60 with 2 equiv Et_3B. Further, use of 1 equiv of R_3B produces **3** either exclusively or predominantly (method C). Presumably, excess R_3B removes PhSeLi from **6** to afford $R_3BSePhLi$ and the corresponding allylic borane, and hence use of excess R_3B facilitates the allylic migration. The regioselectivity for the formation of **3** from aliphatic aldehydes is not so high at the present time. Various kinds of primary alkyl groups as R may be tolerated both in the linear and branched alcohols. This is especially important, since the preparation of the allylic organometallic compounds with a long alkyl chain, in turn the preparation of **2** and **3** with such a substituent,[3] is not so easy. Furthermore, combination between organoselenium chemistry[8] and the boron migration reaction,[9] nowadays rather old chemistry, may provide a new synthetic reaction. Further work along this line is now under active investigation.

Registry No. **2** (R = Et, R′ = Ph) (isomer 1), 87999-70-0; **2** (R = Et, R′ = Ph) (isomer 2), 87999-71-1; **2** (R = Bu, R′ = Ph) (isomer 1), 87999-72-2; **2** (R = Bu, R′ = Ph) (isomer 2), 87999-73-3; **2** (R = Et, R′ = p-$CH_3C_6H_4$) (2somer 1), 87999-74-4; **2** (R = Et, R′ = p-$CH_3C_6H_4$) (isomer 2), 87999-75-5; **2** (R = Et, R′ = p-$CH_3OC_6H_4$) (isomer 1), 87999-76-6; **2** (R = Et, R′ = p-$CH_3OC_6H_4$) (isomer 2), 87999-77-7; **2** (R = Et, R′ = p-$O_2NC_6H_4$) (isomer 1), 87999-78-8; **2** (R = Et, R′ = p-$O_2NC_6H_4$) (2somer 2), 87999-79-9; **2** (R = Et, R′ = Pr) (isomer 1), 87999-80-2; **2** (R = Et, R′ = Pr) (isomer 2), 87999-81-3; **2** (R = Et, R′ = n-C_9H_{19}) (isomer 1), 87999-82-4; **2** (R = Et, R′ = n-C_9H_{19}) (isomer 2), 87999-83-5; (*E*)-**3** (R = Et, R′ = Ph), 58927-86-9; (*Z*)-**3** (R = Et, R′ = Ph), 58927-85-8; (*E*)-**3** (R = Et, R′ = p-$CH_3C_6H_4$), 87999-84-6; **3** (R = Et, R′ = p-$CH_3OC_6H_4$), 87999-85-7; **3** (R = Et, R′ = p-$O_2NC_6H_4$), 87999-86-8; Et_3B, 97-94-9; Bu_3B, 122-56-5; C_6H_5CHO, 100-52-7; p-$CH_3C_6H_4CHO$, 104-87-0; p-$CH_3OC_6H_4CHO$, 123-11-5; p-$O_2NC_6H_4CHO$, 555-16-8; n-C_3H_7CHO, 123-72-8; n-$C_9H_{19}CHO$, 112-31-2; allyl phenyl selenide, 14370-82-2.

(1) "Compr. Org. Chem.," Vol 1, Barton, D. and Ollis, W. D. Eds. Pergamon, Oxford, 1979, p 605.
(2) Yamamoto, Y.; Maruyama, K. *J. Org. Chem.* **1983**, *48*, 1564. Yamamoto, Y.; Maeda, N.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1983**, 742.
(3) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 3. Yamamoto, Y.; Maruyama, K. *Heterocycles*, **1982**, *18*, 357. Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555.
(4) The migration reaction of α-heterosubstituted organoboranes and borates is well-known for the following heteroatoms: H, Cl, Br, I, O, S, N, and P. For a review article, see: Negishi, E. "Organometallics in Organic Synthesis"; Wiley: New York, 1980; Vol 1. For some key references, see: Zweifel, G.; Arzoumanian, H.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 3652. Lane, C. F.; Brown, H. C. *Ibid.* **1971**, *93*, 1025. Hooz, J.; Linke, S. *Ibid.* **1968**, *90*, 5963, 6819. Tufariello, J. J.; Lee, L. T. C.; Wojtokowski, P. *Ibid.* **1967**, *89*, 6804; Köster, R.; Rickborn, B. *Ibid.* **1967**, *89*, 2782. Brown, H. C.; Carlson, B. A.; Prager, R. H. *Ibid.* **1971**, *93*, 2070. Levy, A. B.; Schwartz, S. J. *Tetrahedron Lett.* **1967**, 2201. Yamamoto, Y.; Toi, H.; Murahashi, S.-I.; Moritani, I. *J. Am. Chem. Soc.* **1975**, *97*, 2558. The branched homoallyl alcohols are obtained through the migration reaction of the oxygen-substituted butenyl carbanion-R_3B complexes: Yamaguchi, M.; Mukaiyama, T. *Chem. Lett.* **1980**, 993.
(5) The formation of ate complexes suppresses such rearrangment. See: Mikhailov B. M. *Organomet. Chem. Rev., Sec. A.* **1972**, *8*, 1.
(6) Yamamoto, Y.; Toi, H.; Sonoda, A.; Murahashi, S.-I. *J. Am. Chem. Soc.* **1976**, *98*, 1965.
(7) R_3B may also coordinate to the γ position of phenylselenyl allylic carbanion to give 5: Yamamoto, Y.; Saito, Y.; Maruyama, K. *Tetrahedron Lett.* **1982**, *23*, 4597. However, it seems that this complex does not undergo any rearrangement.
(8) For review articles on organoselenium chemistry, see: Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. Krief, A. *Ibid.* **1980**, *36*, 2531.
(9) We also examined the reaction of alkylthio-substituted allylic carbanions with trialkylboranes, but the migration reaction did not occur. See also: Hara, S.; Imai, S.; Hara, T.; Suzuki, A. *Synth. Commun.* **1982**, *12*, 813.

Yoshinori Yamamoto,* Yoshikazu Saito
Kazuhiro Maruyama

Department of Chemistry, Faculty of Science
Kyoto University, Kyoto 606, Japan

Received August 9, 1983

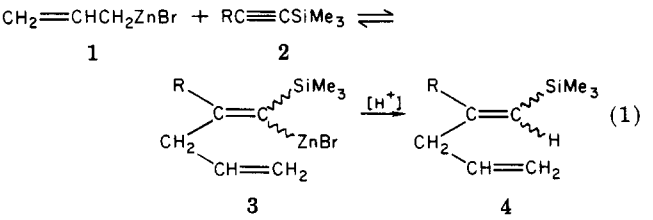
Allylmetalations. The Allylzincation of 1-(Trimethylsilyl)-1-alkynes

Summary: Allylzinc bromide (**1**) reacts with a variety of 1-(trimethylsilyl)-1-alkynes **2** to provide regio- and stereoselective carbometalated products **3**, the zinc atom being placed at the carbon bearing the silicon. Under the conditions of the reaction, the stereochemistry of the products is highly dependent on the structure of **2**.

Sir: Carbometalation reactions provide an extremely attractive method for the synthesis of organic molecules.[1] Certainly one of the greatest advantages in this approach is that at the same time a carbon–carbon bond has formed a new organometallic reagent is generated that can be carried on through further reactions. As a consequence, very rapid construction of organic molecules is feasible.

Although allylzincations of terminal alkynes[2] (presumably through the corresponding alkynylzinc halides) and alkynylmetallics[3] utilizing allylzinc halides are known, internal alkynes have been reported to be unreactive.[2a,e,g,3a] Thus the presence of electropositive atoms on the triple bond appears to be a prerequisite for efficient reaction.

We were intrigued by the possibility of utilizing **2** as substrates for the allylzincation reaction for several reasons. Silicon, being more electropositive than carbon, might be expected to facilitate the carbometalation and allow functionalization on what is formally an internally substituted alkyne. In addition to providing some insight on the stereochemical nature of the addition and the mechanism of the reaction,[2i] the products of such a reaction would provide useful synthons for further transformations. In analogy to reactions of **1** with other alkynylmetallics, we anticipated that the regiochemical outcome of the carbometalation reaction would be such as to place the zinc on the same carbon as the silicon. A regio- and stereoselective allylzincation would provide 1,1-dimetalloalkenes **3**[4] in which the two metals were *chemically differentiable* (eq 1). These reagents could be utilized to generate a



(1) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841.
(2) (a) Gaudemar, M. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1971**, *273*, 1669. (b) Courtois, G.; Mauze, B.; Miginiac, L. *Ibid.* **1972**, *274*, 658. (c) Bernadou, F.; Mauze, B.; Miginiac, L. *Ibid.* **1973**, *276*, 1645. (d) Frangin, Y.; Gaudemar, M. *Ibid.* **1974**, *278*, 885. (e) Courtois, G.; Mauze, B.; Miginiac, L. *J. Organomet. Chem.* **1974**, *72*, 309. (f) Bernadou, F.; Miginiac, L. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1975**, *280*, 1473. (g) Bernadou, F.; Miginiac, L. *Tetrahedron Lett.* **1976**, 3083. (h) Frangin, Y.; Gaudemar, M. *Bull. Soc. Chim. Fr.* **1976**, 1173. (i) Frangin, Y.; Gaudemar, M. *J. Organomet. Chem.* **1977**, *142*, 9.
(3) (a) Mauze, B. *J. Organomet. Chem.* **1977**, *131*, 321. (b) Bellassoued, M.; Frangin, Y.; Gaudemar, M. *Synthesis* **1977**, 205.

0022-3263/83/1948-5409$01.50/0